

The Effect of Carbon Concentration on the Amorphization and Properties of Mechanically Alloyed Cobalt-Carbon Alloys

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ABSTRACT

Magnetic alloys that are amorphous exhibit soft magnetic properties; hence they play an essential role in electronic and electrical systems and devices. They are used in applications that include electrical power generation and transmission, electronic motors, solenoids, relays, magnetic shielding, and electromagnets. This work was an attempt to investigate the solid-state formation of Co-C amorphous alloys, their thermal stability and magnetic properties. Amorphous Co-C alloys with compositions of 2 to 40 at.% C were successfully synthesized from elemental Co and C (graphite) using mechanical alloying, a solid-state powder processing technique. All alloy compositions were milled for up to 40 hours. After 20h of milling some of the alloys (≤ 20 at.% C) had partially amorphized, while the higher concentrations had completely amorphized. After 40h of milling, complete amorphization was observed in all alloys, except for the 2 and 5 at.% C alloys. The thermal analyses of the milled powders showed very interesting results. DSC results indicated that alloys with compositions through 20 at.% C crystallized in two steps; the lower temperature event precipitated metastable cobalt carbide from the amorphous phase, followed by the eventual transformation to fcc cobalt and graphite from both the remaining amorphous and the metastable carbide at the higher temperature. Two types of carbides were observed - Co_3C in the 2 and 5 at.% C alloys, and Co_2C in the higher carbon alloys through 20 at.% C. For compositions above 20 at.% C, only one step crystallization was observed, that of the decomposition of the amorphous phase to amorphous carbon and cobalt – primarily fcc phase. Activation energy calculations show that the low temperature carbide precipitation was controlled by carbon diffusion, while the high

temperature decomposition reaction forming cobalt and amorphous carbon was controlled by cobalt diffusion.

Room temperature magnetic measurements of the milled powders were made using vibrating sample magnetometer (VSM). High saturation magnetization (M_s) and very low coercivity (H_c) are desired for efficient performance of soft magnets. But in this study, M_s decreased with both carbon composition and milling time. It decreased from 195 Am²/kg for the un-milled pure Co to between 178 and 44 Am²/kg for the alloys, with the worst being the 40 at.% C sample milled for 40h. The M_s drop as function of composition made sense, as its related to the volume fraction of cobalt in the alloy. However, the M_s drop as a function of milling time is unclear. In the case of H_c , its value did drop from 12.7 kA/m for the un-milled pure Co to between 7.5 and 1.3 kA/m when the C content is less than 15 at.%. These gains are not significant enough to favor the use of these alloys as soft magnets.

Amorphous metal alloys tend to have strengths that are much higher than their crystalline counterparts, and they have hardness values comparable to those of particulate ceramic materials used to reinforce metal matrices. The Co-C amorphous alloy with 40 at.% C that had been milled for 40h (the most stable of all the samples) was used to reinforce cobalt matrix by powder processing methods that included spark plasma sintering (SPS) at temperatures below those of crystallization. Volume fraction ranged from 1 to 20 % reinforcement. The densities of these composites were between 81 and 85 % of theoretical values, hence there were substantial porosities. Despite this the matrix strengthening of the cobalt matrix, as assessed by Vickers microhardness tests, was significant. Hardness increased from 210 HV for unreinforced matrix to 537 HV for the 20 vol.% amorphous. The primary contributor to the strengthening appears to be boundary strengthening by the particles whose average size of about 4 microns is comparable to the grain size of the matrices of the composites. The hardness data fits the Hall Petch-like relationship based on particle spacing. Having a reinforcement particle with a chemistry similar to that of the matrix as is the case in this study, has the potential to improve interfacial bonding and also minimize the difference between the components' coefficient of thermal expansions, which are major issues with the use of ceramics to reinforce metal matrices. The microstructures of the composites indicated good bonding at their interfaces.

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GENERAL AUDIENCE ABSTRACT

Magnetic alloys that are amorphous (have no long-range atomic order) exhibit soft magnetic material properties (easily magnetized and demagnetized); hence they play an essential role in electronic and electrical applications. This work investigated the solid-state formation of Cobalt-Carbon (Co-C) amorphous alloys, their thermal stability and magnetic properties. Amorphous Co-C alloys with compositions of 2 to 40 atomic weight % of C were successfully synthesized from elemental Co and C (as graphite) using a mechanical alloying technique (high-energy milling to alloy materials by impact). All alloy compositions were milled for up to 40 hours. After 20h of milling some of the alloys (≤ 20 atomic weight % of C) had partially become amorphous, while the higher concentrations had completely become amorphous. After 40h of milling, complete amorphization was observed in all alloy compositions, except for the 2 and 5 atomic weight % of C alloys (2-5 atomic weight % of C).

Thermal analyses (Differential Scanning Calorimetry, DSC) of the milled powders showed that alloys with compositions through 20 atomic weight % of C crystallized via a low temperature precipitation of a metastable cobalt carbide from the amorphous phase, followed by a high temperature transformation to a face centered cubic (fcc) cobalt and graphite phase from both the remaining amorphous and the metastable carbide.

Activation energy calculations showed that the low temperature carbide precipitation was controlled by carbon diffusion, while the high temperature decomposition reaction forming cobalt and amorphous carbon was controlled by cobalt diffusion.

High saturation magnetization (M_s) and very low coercivity (H_c) are desired for efficient performance of soft magnets. Thus, room temperature magnetic measurements of the milled powders were made using vibrating sample magnetometer (VSM). But in this study, M_s decreased with both carbon composition and milling time. The M_s drop as function of composition made sense, as its related to the volume fraction of cobalt in the alloy. However, the M_s drop as a function of milling time is unclear. In the case of H_c , its value did drop from 12.7 kA/m for the un-milled pure Co to between 7.5 and 1.3 kA/m when the C content is less than 15 atomic weight %. These gains are not significant enough to favor the use of these alloys as soft magnets.

Amorphous metal alloys tend to have strengths that are much higher than their crystalline counterparts, and they have hardness values comparable to those of particulate ceramic materials used to reinforce metal matrices. The Co-C amorphous alloy with 40 atomic weight % of C that had been milled for 40h was used to reinforce cobalt matrix by powder processing methods (including spark plasma sintering (SPS) at temperatures below those of crystallization). The densities of these composites were between 81 and 85 % of theoretical values and hence there was substantial porosity. Despite this the matrix strengthening of the cobalt matrix, as assessed by Vickers microhardness tests, was significant. The primary contributor to the strengthening appeared to be boundary strengthening by the particles whose average size of about 4 microns was comparable to the grain size of the matrices of the composites. Having a reinforcement particle with a chemistry similar to that of the matrix has the potential to improve interfacial bonding and also minimize the difference between the components' coefficient of thermal expansions, which are major issues with the use of ceramics to reinforce metal matrices. The microstructures of the composites indicated good bonding at their interfaces.

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Table of Contents

1. Introduction.....	1
1.1 Preface.....	1
1.2 Objectives of this work	3
References.....	4
2. Background	6
2.1 Historical Review of Amorphous Metals Alloys.....	6
2.2 The Basic Concepts and Properties of Bulk Amorphous Metals Alloys	20
2.2.1 Thermodynamics of an Undercooled Liquid	21
2.2.2 Glass Forming Ability.....	25
2.2.3 Glass Transition	28
2.2.4 Crystallization.....	35
2.2.4.1 Polymorphic Crystallization	37
2.2.4.2 Eutectic Crystallization	38
2.2.4.3 Primary Crystallization	38
2.2.5 Properties of Bulk Amorphous Metals Alloys	40
2.3 Metal Matrix Composites	47
2.4 Magnetic Materials	59
2.4.1 Soft Magnetic Materials.....	64
2.4.2 Hard Magnetic Materials	71
2.5 Amorphization of Metals.....	72
2.5.1 Rapid Quenching	73
2.5.2 Metallic Mold Casting	73
2.5.3 Solid State Amorphization	76
2.6 Mechanical Alloying	79
2.6.1 Amorphization by Mechanical Alloying	86
2.6.2 Amorphization of Cobalt-Based Alloys by Mechanical Alloying	90
2.7 Metallic Amorphous Composites.....	95
2.8 Amorphous Magnetic Materials	99
2.8.1 Cobalt-Based Amorphous Soft Magnetic Materials.....	102
2.8.2 Mechanically Alloyed Cobalt-Based Amorphous Soft Magnetic Materials	105
References.....	108
3. Experimental Procedure	144

3.1 Material Selection	144
3.2 Powder Processing and Sample Preparation.....	146
3.2.1 Mechanical Alloying and Production of the Co-C Amorphous Powders.....	147
3.2.2 Production of the Composite Powder	148
3.2.3 Consolidation of the Composite Powders	149
3.3 Characterization	151
3.3.1 Differential Scanning Calorimetry (DSC)	151
3.3.2 X-Ray Diffraction (XRD)	152
3.3.3 Optical microscopy.....	152
3.3.4 Scanning Electron Microscopy (SEM).....	152
3.3.5 Transmission Electron Microscopy (TEM).....	153
3.3.6 Vibrating Sample Magnetometer (VSM).....	153
3.3.7 Density Measurements	153
3.3.8 Hardness Testing.....	154
3.3.9 Particle Size Analysis	154
References.....	155
4. Amorphization of Co-C Alloys by Mechanical Alloying	157
4.1 Introduction.....	157
4.2 Experimental procedure.....	159
4.3 Results and Data Analysis	160
4.3.1 X-ray Diffraction Analysis	160
4.3.2 Thermal behavior and Differential Scanning Calorimetry (DSC) Analysis.....	166
4.3.3 Transmission Electron Microscopy (TEM) Analysis.....	200
4.4 Discussion.....	207
4.5 Summary.....	210
4.6 Acknowledgements	211
References.....	212
5. Magnetic Properties of Amorphous Co-C Alloys Prepared by Mechanical Alloying	218
5.1 Introduction.....	218
5.2 Experimental procedure.....	220
5.3 Results and Data Analysis	221
5.3.1 X-ray Diffraction Analysis	221
5.3.2 Thermal behavior and Differential Scanning Calorimetry (DSC) Analysis.....	221

5.3.3 Transmission Electron Microscopy (TEM) Analysis.....	222
5.3.4 Particle Size Analysis	222
5.3.5 Magnetic Properties.....	226
5.4 Summary.....	237
5.5 Acknowledgements	238
References.....	239
6. Processing and Properties of Amorphous Co-C Reinforced Co Matrix Composite	243
6.1 Introduction.....	243
6.2. Experimental procedure.....	246
6.3. Results and Data Analysis	248
6.3.1 Selection and Analysis of Reinforcement Particles.....	248
6.3.1.1 X-Ray Diffraction (XRD)	248
6.3.1.2 Thermal Behavior and Differential Scanning Calorimetry (DSC) Analysis.....	249
6.3.1.3 Transmission Electron Microscopy (TEM) Analysis.....	250
6.3.1.4 Particle Size Analysis	251
6.3.2 Analysis of Composite Materials.....	252
6.3.2.1 X-Ray Diffraction (XRD)	252
6.3.2.2 Crystallite Size Analysis	254
6.3.2.3 Optical Microscopy	254
6.3.2.4 Density Measurement.....	269
6.3.2.5 Hardness Testing and Mechanical Properties.....	271
6.3.2.6 Magnetic Properties.....	275
6.4 Summary.....	282
6.5 Acknowledgements	283
References.....	285
7. Summary and Contributions	289
7.1 Summary.....	289
7.2 Contributions.....	291

List of Figures

Figure 2.1: Number of publications on amorphous materials published each year for the period 1960- 2010 [17].	8
Figure 2.2: Schematic illustration of the structural origin of certain features in the density function $\rho(r)$ for an amorphous solid [204].	21
Figure 2.3: Gibbs free energy for the solid and liquid as a function of temperature T at constant pressure P [206, 207].	22
Figure 2.4: Free energy ΔG as a function of the nucleus radius r at a temperature T below the melting temperature T_m [82, 206-212].	24
Figure 2.5: The relationship between the critical cooling rate v_c for glass formation and reduced glass transition temperature T_{rg} on the example of some selected alloy groups [217].	26
Figure 2.6: DSC curve of Zr-Ti-Ni-Cu-Be glassy alloy offers the transition temperature T_g and crystallization temperature T_x and shows the difference of $\Delta T_x = T_x - T_g$ that defines the thermal stability range [176].	27
Figure 2.7: Dependence of the specific heat c_p on the temperature T during the transfer of the supercooled melt into the glass state (upper curve) and the crystalline phase (lower curve) [219].	29
Figure 2.8: Dependence of the entropy S on the temperature T in the transfer of the supercooled melt into the glass state (upper curve) and crystallization (lower curve). The Kauzmann temperature T_K is defined by the extrapolation of the liquid to $\Delta S = S_{\text{liquid}} - S_{\text{crystalline}} = 0$ [221].	30
Figure 2.9: Volume V as a function of the temperature T in the range of the glass transition temperature T_g for a supercooled melt at different cooling rates v_1 and v_2 (upper curves) compared to the volume change in crystallization (lower curve) according to [202].	31
Figure 2.10: Schematic representation of the free energy G of unrelaxed (unstable) and relaxed (metastable) glass as well as a crystalline (stable) equilibrium phase [206].	32
Figure 2.11: The viscosity η of different liquids as a function of temperature T above the glass transition temperature T_g and normalized. The behavior of the strong glasses follows the Arrhenius function, and the fragile glasses can be described with a Vogel-Fulcher-Tamman function [227].	34
Figure 2.12: Schematic representation to the illustration of the phase formation for the continuous cooling and heating: (a) rapid cooling, leading to amorphous formation, (b) crystallization by slow heating of the amorphous [237].	36
Figure 2.13: Schematic representation of the possible phase transformation of glass as a function of the free energy G : (α : mixed crystal, β : intermetallic phase, and γ : metastable phase). The numbers 1 to 5 characterize the various transformation modes. The solid compound line marks the stable equilibrium, while the broken lines characterize metastable equilibria [237].	37
Figure 2.14: Schematic representation of the change in the free energy G as a result of demixing, and the phase separation due to the nucleation and growth taking place between c and c' instead, spinodal decomposition occurs between c_s and c'_s [208].	39
Figure 2.15: (a) Tensile strength and (b) Vickers hardness vs. Young's modulus for various crystalline and bulk amorphous metals [217].	41
Figure 2.16: Ashby diagram of the damage tolerance in form of yield strength versus fracture toughness (K_C or K_{JC}) of engineering materials [256].	42

Figure 2.17: The critical casting thickness for the glass formation as a function of the year the corresponding alloy has been discovered [11].	47
Figure 2.18: Schematic of composite strengthening as a function of reinforcement aspect ratio (s), size (d), and volume fraction (f). The Figure 18 (a) shows matrix dominated strengthening, with the reinforcement constituting too low a volume fraction to carry a significant proportion of the load. The Figure 18 (b) shows stiffening and strengthening gained from load transfer to high aspect ratio reinforcement, where it is too coarse to strengthen the matrix by affecting dislocation motion [332]......	54
Figure 2.19: A summary of the different types of magnetic behavior [383].	61
Figure 2.20: The magnetic behavior of each element of the periodic table at room temperature [383]......	62
Figure 2.21: Typical hysteresis loop for ferromagnetic materials.	63
Figure 2.22: Typical magnetic hysteresis loops of soft and hard ferromagnetic materials.	64
Figure 2.23: Typical magnetization and permeability curves [397].	66
Figure 2.24: A flow diagram showing the influence of the three empirical rules on the glass formability of alloys [217]......	75
Figure 2.25: Correlation in different glass-forming alloys between the critical cooling rates (R_c) reduced glass transition temperature (T_g/T_m) and thickness of glass (t_{max}) [217].	75
Figure 2.26: Illustration of a collision between two balls and trapped powder [544].	79
Figure 2.27: Particle microfracture evolution during mechanical alloying [557].	80
Figure 2.28: (a) SPEX 800 mill. (b) Vial and grinding media (Tungsten carbide).	80
Figure 2.29: (a) Fritsch Pulverisette P-5 four station ball mill. (b) Schematic depicting the ball motion inside the ball mill [544].	81
Figure 2.30: The Szegvari attritor mill.	82
Figure 2.31: Diagram of the components of the stationary tank of an attritor mill [544].	82
Figure 2.32: (a) Hypothetical binary phase diagram exhibiting limited solid solubility on both ends and also showing the presence of an intermetallic phase. (b) Gibb's Free energy vs solute composition at a temperature corresponding to T_r . Note that points 1, 2 and 3 represent the free energy values of the mixture of A and B, the amorphous phase, and the intermetallic phase, respectively [544].	87
Figure 2.33: Schematic representation of the basic principles of amorphization by solid state reaction [517, 593]......	88
Figure 2.34: XRD patterns of $Co_{87}B_{13}$ in at.% after various periods of milling: (a) as received powder. (b) Milled 20 min. (c) milled 70 min. (d) milled 3hr. (e) milled 70hr [609]......	91
Figure 2.35: X-ray diffraction patterns for the elemental powders of $Co_{87}Nb_{46}B_{15}$ in at.% milled for up to 200 hours [615].	93
Figure 2.36: X-ray diffraction patterns for the elemental powders of $Co_{50}C_{50}$ in at.% milled for up to 24 hours [619]......	94
Figure 2.37: X-ray diffraction patterns for the elemental powders of $Co_{50}C_{95}$ in at.% milled for up to 100 hours [620]......	95
Figure 2.38: The relationship between permeability and saturation flux density in several soft magnetic alloys [247, 669 and 670]......	100
Figure 2.39: The relationship between core losses and frequency for soft magnetic materials used for high frequency power transformers [671]......	101
Figure 2.40: Permeability versus frequency of different magnetic materials [677].	103
Figure 3.1: Phase diagram of the Co-C system [10].	145

Figure 3.2: The calculated heat of mixing for the Co-C system using Miedema's heat of mixing formulas.	145
Figure 3.3: SPEX 8000M Mixer/Mill® with a tungsten carbide vial set.	147
Figure 3.4: The Szegvari attritor mill that was used in this work.	149
Figure 3.5: Schematic of Spark Plasma Sintering setup [30].	150
Figure 3.6: Schematic of joule heating mechanism and coulomb discharge between powder particles upon applying pulsed current [30].	150
Figure 3.7: An example of DSC data analyzed for exothermic peak of mechanically alloyed $\text{Co}_{60}\text{C}_{40}$ powder milled 40h with heating rate of 10 °C/min using the Proteus software.....	151
Figure 4.1: X-ray diffraction patterns for $\text{Co}_{60}\text{C}_{40}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.	160
Figure 4.2: X-ray diffraction patterns for $\text{Co}_{70}\text{C}_{30}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.	161
Figure 4.3: X-ray diffraction patterns for $\text{Co}_{80}\text{C}_{20}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.	162
Figure 4.4: X-ray diffraction patterns for $\text{Co}_{85}\text{C}_{15}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.	162
Figure 4.5: X-ray diffraction patterns for $\text{Co}_{90}\text{C}_{10}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.	163
Figure 4.6: X-ray diffraction patterns for Co-C and alloyed for 40 hours, compared with the blended powder of Co-C.	163
Figure 4.7: X-ray diffraction patterns for Co_{95}C_5 in at.% milled for up to 40 hours, compared with the blended powder of Co-C.	164
Figure 4.8: X-ray diffraction patterns for Co_{98}C_2 in at.% milled for up to 40 hours, compared with the blended powder of Co-C.	164
Figure 4.9: The calculated heat of mixing for the Co-C system using Miedema's heat of mixing formulas.	165
Figure 4.10: Differential scanning calorimetry curves of $\text{Co}_{60}\text{C}_{40}$ in at.%, milled for up to 40 hours at a heating rate of 10 °C/min.	167
Figure 4.11: X-ray diffraction patterns for $\text{Co}_{60}\text{C}_{40}$ in at.% milled 20h and heated in different temperatures.	168
Figure 4.12: X-ray diffraction pattern and d-spacing values of the $\text{Co}_{60}\text{C}_{40}$ powder, milled 20h after heated up to 725°C.	169
Figure 4.13: X-ray diffraction pattern of the $\text{Co}_{60}\text{C}_{40}$ powder milled 20h after being heated up to 725°C, compared with the ICDD numbers of 00-015-0806 and 00-001-1278.	170
Figure 4.14: EDS spectra from the mechanically alloyed powder of $\text{Co}_{60}\text{C}_{40}$ (milled 20h and annealed at 725°C) shows intense cobalt peaks, a minor carbon peak and nothing else in more than a trace amount of oxygen.	171
Figure 4.15: Effect of the milling time on the crystallization temperature, T_x and the enthalpy of crystallization, ΔH_x of mechanically alloyed $\text{Co}_{60}\text{C}_{40}$ in at.%.	172
Figure 4.16: Differential scanning calorimetry curves of $\text{Co}_{70}\text{C}_{30}$ in at.%, milled for up to 40 hours at a heating rate of 10 °C/min.	173
Figure 4.17: Differential scanning calorimetry curves of $\text{Co}_{80}\text{C}_{20}$ in at.%, milled for up to 40 hours at a heating rate of 10 °C/min.	174

Figure 4.18: Kissinger's plots of the crystallization activation energy of the Co-at. % C, alloys milled up to 40h: (a) 2 at.%, (b) 5 at.%, (c) 10 at.%, (d) 15 at.%, (e) 20 at.%, (f) 30 at.% and (g) 40 at%.	177
Figure 4.19: Activation energy of crystallization E_a for Co-at.% C with different milling times, as a function of at.% C contents.	178
Figure 4.20: Differential scanning calorimetry curves of $\text{Co}_{85}\text{C}_{15}$ in at.%, milled for up to 40 hours at a heating rate of $10^\circ\text{C}/\text{min}$.	180
Figure 4.22: X-ray diffraction patterns for $\text{Co}_{90}\text{C}_{10}$ in at.%, milled for 40h and heated at different temperatures.	181
Figure 4.23: Differential scanning calorimetry curves of Co_{95}C_5 in at.%, milled for up to 40 hours at a heating rate of $10^\circ\text{C}/\text{min}$.	182
Figure 4.24: Differential scanning calorimetry traces of Co_{95}C_5 in at.% powder, mechanically alloyed for 20 hours, continuously heat-treated at a rate of $10^\circ\text{C}/\text{min}$, compared with the DSC baseline of the Co_{95}C_5 powder milled for 20h. The DSC traces appeared after heating the sample to 359°C , cooled to room temperature, then reheated to 497°C . Thereafter it was cooled to room temperature again, back and forth in the same way until 1100°C .	183
Figure 4.25: X-ray diffraction patterns for Co_{95}C_5 in at.%, milled for 20h and heated back and forth to different temperatures, compared with unmilled cobalt.	185
Figure 4.26: EDS spectra from the mechanically alloyed powder of Co_{95}C_5 , milled 20h and annealed at 770°C , shows intense cobalt peaks, a minor carbon peak and nothing else in more than a trace amount of oxygen.	188
Figure 4.27: Differential scanning calorimetry curves of Co_{98}C_2 in at.%, milled for up to 40 hours at a heating rate of $10^\circ\text{C}/\text{min}$.	190
Figure 4.28: X-ray diffraction patterns for pure cobalt powders milled for up to 40 hours, compared with unmilled cobalt powder.	191
Figure 4.29: Differential scanning calorimetry curves of pure cobalt, milled for up to 40 hours at a heating rate of $10^\circ\text{C}/\text{min}$.	192
Figure 4.30: X-ray diffraction patterns for pure cobalt milled for 40h and annealed at 650°C .	193
Figure 4.31: Effect of the carbon content (at.%) on the reaction temperature of the cobalt carbides, $T_{\text{cobalt carbide formation}}$ and the enthalpy of the reaction, $\Delta H_{\text{cobalt carbide formation}}$ of mechanically alloyed Co-C system.	195
Figure 4.32: Comparison of enthalpy of crystallization, $\Delta H_{\text{cobalt carbide formation}}$ produced by different carbon contents on three different milling times.	195
Figure 4.33: Effect of the milling time (h) on the enthalpy of the reaction, $\Delta H_{\text{cobalt carbide formation}}$ of mechanically alloyed Co-C system.	196
Figure 4.34: Effect of the milling time (h) on the reaction temperature of the Co_2C , $T_{\text{cobalt carbide formation}}$ of mechanically alloyed Co-C system.	197
Figure 4.35: A typical bright filed micrograph of mechanically alloyed powder of Co- 40 at.% C, milled for 40h: (a) $\text{Co}_{60}\text{C}_{40}$ amorphous particles, (b) selecting amorphous particle for the SAED pattern analysis.	200
Figure 4.36: TEM characterization of mechanically alloyed powder of Co- 40 at.% C, milled for 40h: (a) Bright filed micrograph, (b) SAED pattern. The bright filed micrograph shows an amorphous microstructure. While in the SAED pattern, the feature of concentric rings in the pattern disappears and a halo is left around the bright center spot, which confirms that the structure is a completely amorphous phase.	201

Figure 4.37: EDS spectra and EDS mapping analysis from the mechanically alloyed powder of Co ₆₀ C ₄₀ that was milled 40h: (a) EDS spectra of the elements analysis, (b) bright filed micrograph, (c) EDS mapping of the C and a combination of morphology with its distribution, (d) EDS mapping of element the O, (e) EDS mapping of the Co and a combination of morphology with its distribution. The EDS spectra and EDS mapping analysis shows intense cobalt peaks, a minor carbon peak, but nothing else except a trace of oxygen.	202
Figure 4.38: TEM characterization of mechanically alloyed powder of Co- 10 at.% C, milled for 40h: (a) EDS spectra of the element analysis, (b) a SAED pattern. However, in the SAED pattern, the feature of concentric rings disappears and a halo is left around the bright center spot, which confirms that the structure is a completely amorphous phase.....	203
Figure 4.39: TEM characterization of mechanically alloyed powder of Co- 5 at.% C, milled for 40h: (a) EDS spectra of the element analysis, (b) bright filed micrograph shows the selected areas.	204
Figure 4.40: TEM characterization of mechanically alloyed powder of Co- 5 at.% C, milled for 40h: (a) SAED pattern 1, (b) SAED pattern 2. A halo from this analysis as well as diffracted spotty rings, indicates that this region is composed of nanocrystals embedded in an amorphous matrix.....	205
Figure 4.41: TEM characterization of mechanically alloyed powder of Co- 2 at.% C, milled for 40h: (a) EDS spectra of the elements analysis, (b) bright filed micrograph shows the selected area.....	206
Figure 4.42: TEM characterization of mechanically alloyed powder of Co- 2 at.% C, milled for 40h, shows the SAED pattern. A halo as well as diffracted spotty rings, indicates that this region is composed of nanocrystals embedded in an amorphous matrix.	207
Figure 4.43: Schematic diagram summarizing calorimetric results of the mechanically alloyed Co-C alloys (up to 40 at% C) milled for up to 40h.	208
Figure 5.1: The effect of milling time on the particle size of the pure cobalt and Co-C mechanically alloyed powders for various carbon contents.	223
Figure 5.2: The effect of carbon content on the particle size of the pure cobalt and Co-C mechanically alloyed powders for various milling times.....	225
Figure 5.3: Morphology of the Co-C mechanically alloyed powder particles milled for 40h: (a) Co- 5 at.% C, (b) Co- 10 at.% C. The micrographs present typical individual agglomerated particles for the lower carbon concentrations.....	225
Figure 5.4: The hysteresis loops of the Co- at% C alloys milled up to 40h: (a) pure Co, (b) 2 at.%, (c) 5 at.%, (d) 10 at.%, (e) 15 at.%, (f) 20 at.%, (g) 30 at.% and (h) 40 at%.	228
Figure 5.5: Plot of saturation magnetization, M _s , of Co-C mechanically alloyed powders for various milling times at room temperature against carbon content.....	229
Figure 5.6: The effect of milling time on the saturation magnetization, M _s , of the pure cobalt and Co-C mechanically alloyed powders for various carbon contents at room temperature.	230
Figure 5.7: Variations of the room temperature coercivity, H _c , with carbon content for the pure cobalt and the Co-C mechanically alloyed powders for various milling times.....	232
Figure 5.8: The effect of milling time on the coercivity, H _c , of the pure cobalt and Co-C mechanically alloyed powders for various carbon contents at room temperature.	233
Figure 5.9: Variations of the room temperature remanent magnetization, M _r , with carbon content for the pure cobalt and the Co-C mechanically alloyed powders for various milling times.	235

Figure 5.10: The effect of milling time on the remanent magnetization, M_r , of the pure cobalt and Co-C mechanically alloyed powders for various carbon contents at room temperature.....	235
Figure 5.11: The effect of carbon content on the remanent-to-saturation ratio, M_r/M_s	236
Figure 5.12: The remanent-to-saturation ratio M_r/M_s , as a function of milling time.	237
Figure 6.1: X-ray diffraction patterns for Co- 40at. % C milled for 40 hours, compared with the blended powder of unmilled Co-C.	249
Figure 6.2: Differential scanning calorimetry curves of the unmilled Co and Co- 40 at.% C, milled for 40 hours at a heating rate of 10 °C/min.	250
Figure 6.3: A SAED pattern of mechanically alloyed powder of Co- 40 at.% C, milled for 40h. However, in the SAED pattern, the feature of concentric rings disappears and a halo is left around the bright center spot, which confirms that the structure is a completely amorphous phase.	251
Figure 6.4: Co- 40 at.% C milled 40h particle size distribution.	252
Figure 6.5: XRD patterns of 1, 2, 5, 10 and 20 vol.% reinforcement composites powders compared with unmilled Co powder as well as amorphous particles (Co- 40 at.% C milled 40h).....	253
Figure 6.6: XRD patterns of 1, 2, 5, 10 and 20 vol.% $\text{Co}_{60}\text{C}_{40}$ milled 40h reinforcement composites bulks compared with unmilled Co powder.....	254
Figure 6.7: Optical micrograph of a composite of Co with 1 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 50X.	255
Figure 6.8: Optical micrograph of a composite of Co with 1vol. % $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.	256
Figure 6.9: Optical micrograph of a composite of Co with 2 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 50X.	257
Figure 6.10: Optical micrograph of a composite of Co with 2 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.	258
Figure 6.11: Optical micrograph of a composite of Co with 2 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.	258
Figure 6.12: Optical micrograph of a composite of Co with 5 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Photomicrograph is shown at 5X, which provides a scan with low magnification for a good overview of the sample, essentially a “scan” of the sample.	259
Figure 6.13: Optical micrograph of a composite of Co with 5 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 50X.	260

Figure 6.14: Optical micrograph of a composite of Co with 5 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	261
Figure 6.15: Optical micrograph of a composite of Co with 5 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	261
Figure 6.16: Optical micrograph of a composite of Co with 5 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	262
Figure 6.17: Optical micrograph of a composite of Co with 10 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 20X.	264
Figure 6.18: Optical micrograph of a composite of Co with 10 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 50X.	264
Figure 6.19: Optical micrograph of a composite of Co with 10 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	265
Figure 6.20: Optical micrograph of a composite of Co with 10 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	265
Figure 6.21: Optical micrograph of a composite of Co with 10 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	266
Figure 6.22: Optical micrograph of a composite of Co with 10 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	266
Figure 6.23: Optical micrograph of a composite of Co with 20 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 20X.	267
Figure 6.24: Optical micrograph of a composite of Co with 20 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 50X.	267
Figure 6.25: Optical micrograph of a composite of Co with 20 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite	

of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	268
Figure 6.26: Optical micrograph of a composite of Co with 20 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	268
Figure 6.27: Optical micrograph of a composite of Co with 20 vol.% Co ₆₀ C ₄₀ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and Co ₆₀ C ₄₀ particles while black areas are pores. Photomicrograph is shown at 100X.	269
Figure 6.28: Density measurements as a percentage of the theoretical and experimental values plotted with respect to volume percent reinforcement amorphous particles (Co ₆₀ C ₄₀).....	270
Figure 6.29: Vickers microhardness of Co/Co ₆₀ C ₄₀ composites versus volume fraction of the reinforcement amorphous particles (Co ₆₀ C ₄₀) content as well as compared with the pure cobalt Vickers microhardness. The plot showing average composite Vickers microhardness increase with higher volume fraction of reinforcement.....	272
Figure 6.30: Plot of Vickers microhardness as a function of the inverse square root the edge-to-edge interparticle spacing λ_{e-e}	275
Figure 6.31: The hysteresis loops of the SPS bulk Co/Co ₆₀ C ₄₀ composites (a) pure Co compared with 1, 2 and 5 vol.% Co ₆₀ C ₄₀ , (b) pure Co compared with 10 and 20 vol.% Co ₆₀ C ₄₀	276
Figure 6.32: Variation of the room temperature saturation magnetization, M_s , with the volume fraction of the reinforcement amorphous particles (Co ₆₀ C ₄₀) content for the pure cobalt, amorphous particles (Co ₆₀ C ₄₀) and the SPS bulk Co/Co ₆₀ C ₄₀ composite material.	277
Figure 6.33: Variation of the room temperature coercivity, H_c , and magnetocrystalline anisotropy constant, K_1 , values plotted with respect to volume percent reinforcement amorphous particles (Co ₆₀ C ₄₀).	279
Figure 6.34: Variation of the room temperature remanent magnetization, M_r , and Remanent-to-Saturation ratio (M_r/M_s) values plotted with respect to volume percent reinforcement amorphous particles (Co ₆₀ C ₄₀).....	281

List of Tables

Table 2.1: Typical amorphous bulk metallic glass alloys systems reported up to date and the calendar years when their first papers and patents were published.	18
Table 2.2: Typical iron-based and cobalt-based bulk metallic amorphous alloys systems and their magnetic properties [450-466].....	69
Table 2.3: Typical examples of cobalt-based bulk metallic amorphous alloys and their magnetic properties [683, 684].....	104
Table 3.1: The mechanical alloying experimental design. The check (x) indicates to the experiments that were performed.	148
Table 3.2: Five composite blends with differing reinforcement volumes.	148
Table 3.3: Theoretical density of the Co/Co ₆₀ C ₄₀ composites.....	154
Table 5.1: The mean particle size of the Co- at.% C of the mechanically alloyed powders (μ).	223
Table 6.1: Five composite blends with differing reinforcement volumes.	247
Table 6.3: Density measurement values for all composites.....	270
Table 6.4: Averages of Vickers microhardness measurements on composite sample.	271
Table 6.5: Calculated reinforcement particle spacing values in μm.	274
Table 6.6: Magnetic parameters of the composite samples at at 300K: saturation magnetization (M _s), coercivity (H _c), remanent magnetization (M _r) and Remanent-to-Saturation ratio.	276

Chapter 1

1. Introduction

1.1 Preface

Amorphous metals have been widely used in engineering applications in the last four decades, however, reports on amorphous metallic materials began in the early 1930s. The first published studies of amorphous metals date back to the 1934 during the use of vapor deposition technology to produce superconducting materials [1-4]. In general, amorphous metallic materials are systems or metal alloys that lack a long-range periodic ordering of their atoms. However, amorphous metallic materials are structurally non-crystalline, with a high degree of disorder or entropy, as in liquids, but in this case they are solids, so in these materials there is no concept of a primitive cell or spatial group of symmetry. Due to this atomic disorder and low internal stress fields, amorphous metals exhibit unique mechanical, electrical, and magnetic properties, compared to crystalline metals. Thus, amorphous metallic materials have received increasing interest from researchers for their fundamental scientific importance and engineering application potential [5-8] and thence several groups of academia and industry from different countries have conducted research to expand their applications in the market. According to several premier scholarly journals, research and development in amorphous metallic materials has been on-going since the early 1960s [9-13]. For 60 years, scientists have focused on understanding the concepts of synthesizing the amorphous metallic materials including the ability to engineer their structure and properties for use in different applications [6, 7, 12 and 14]. For example, in the U.S.A. much work on amorphous metallic materials has been conducted by the government and findings have been introduced into practical applications for decades. While, in Japan the government has funded researches on amorphous metallic materials for more than 30 years [15]. Thus, amorphous metallic materials have had a large share in the world's research and on different applications, including the aerospace and automotive industries, electronic systems, electric transformers, medical products and magnetic appliances [14-18].

Since the first synthesis of an amorphous metallic alloy by the rapid quenching from the liquid state of the Au-25 at.% Si system by Duwez and his coworkers at Caltech in 1960 [19], amorphous metallic alloys have continued to attract the attention of researchers. Therefore, the metallurgists and researchers have tried in many different ways to produce amorphous alloys in commercial

quantities, using less energy and expense, so that they could be used in different applications. In the 1980's, methods used to synthesize amorphous metals expanded to include techniques such as: mechanical alloying [20], irradiation [21], diffusion induced amorphization in multilayers [22], and hydrogen absorption [23]. However, these techniques are limited to the production of wires, powders, and foils. In contrast, bulk amorphous metals (BMGs), are solid amorphous metals with dimensions greater than a few millimeters. They are formed by casting an alloy of three or more elements which makes it possible to achieve dimensions of 5mm or greater at a reduced cooling rate of $<10^3$ K/s [10, 24]. Consequently, binary alloys have been unable to form bulk metallic glass with much success.

On the other hand, mechanical alloying techniques can produce a larger amount of amorphous metal powders, which can be compacted and sintered in the desired sizes, shapes and dimensions for practical applications, using a rapid sintering technique such as spark plasma sintering (SPS) [25]. However, the mechanical alloying amorphization is a solid state amorphization reaction, which is capable of amorphizing materials below their crystallization temperature, using interdiffusion mechanisms [26- 28]. Moreover, amorphization by mechanical alloying has a wider glass forming composition range in many binary alloy systems; therefore equiatomic compositions are most favorable for amorphization by mechanical alloying [29, 30]. On the other hand, with a rapid quenching technique, amorphization is restricted to the compositions near the eutectic, due to kinetic restraints [29]. This unique capability of mechanical alloying is reason for choosing mechanical alloying as a processing technique for this work.

Amorphization by Mechanical Alloying (MA) is a method that pursues a solid state amorphization reactions (SSAR) approach. In general, the mechanical alloying (MA) is a high energy ball milling process by which constituent powders are repeatedly deformed, fractured and welded by grinding media to form a homogeneous alloyed microstructure or uniformly dispersed particulates in a matrix [31]. According to Schwarz and Johnson [32], who reported on the mechanism of amorphous phase formation by mechanical alloying, the results of amorphous phases that are formed by the mechanical alloying processes were rationalized on the basis that amorphization occurs under a chemical solid state reaction by the formation of a multilayer structure during milling, wherein the asymmetric interdiffusion couple and the negative heat of mixing, were considered to be the driving force for diffusion. Moreover, the defects created by the

mechanical process in the ball mill play a major role in the amorphization process [33]. However, deformation is well known to create defects, such as vacancies, dislocations, atomic site defects, antiphase boundaries or grain boundaries. In the meantime, these defects will increase the free energy of the crystalline phase, which is considered responsible for amorphization during mechanical alloying/milling [33]. Indeed, the role of these defects in this process is similar to the role of those defects in the ion and electron irradiation technique.

Therefore, this work focuses on the amorphization of the binary system of Co-C by mechanical alloying SPEX mill technique, in view of an understanding of the amorphous phase transformation development and how the chemical composition and mechanical alloying parameters affect the resulting microstructure and properties. This work also in one of its aspects studies the metallic amorphous composites, and explains the benefits of using metallic amorphous alloys as a reinforcement material in metal matrix composites.

1.2 Objectives of this work

The purpose of this study is to investigate the solid state interaction between the elemental powders of Co and C during high-energy ball milling in order to understand their chemical composition influence on the amorphization process of Co-C alloys. In summary, the itemized objectives of this study are to:

- Prepare metallic amorphous $\text{Co}_{100-x}\text{C}_x$ ($0 \leq x \leq 40$ at.%) binary alloy powders over a wide range of composition using the SPEX mill system for mechanical alloying under different milling condition to understand the evolution of amorphous phase transformation and investigate the effect of the milling time and carbon content on the thermal properties of the mechanically alloyed Co-C powders.
- Understand the correlation between the magnetic properties of the mechanically alloyed Co-C powders and chemical composition, as well as the mechanical alloying milling time.
- Produce bulk metallic amorphous composites using different volume percentage of amorphous $\text{Co}_{60}\text{C}_{40}$ alloys as a reinforcement material in Co matrix composites, and studying the microstructures, porosity and mechanical properties of these composites.

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Chapter 2

2. Background

2.1 Historical Review of Amorphous Metals Alloys

Amorphous metals have been widely used in engineering applications in the last four decades, however reports on amorphous metallic materials began in the early 1930s. The first published studies of amorphous metals date back to the 1934, when Kramer [1, 2], Brenner [3] and Buckel [4] used a vapor deposition technique to deposit metallic films. In general, amorphous metallic materials are structurally non-crystalline, with a high degree of disorder or entropy, as in liquids, but in this case they are solids. In other words, amorphous metallic materials are systems or metal alloys that lack a long-range periodic ordering of their atoms. In these materials there is no concept of a primitive cell or spatial group of symmetry. Due to this atomic disorder and low internal stress fields, amorphous metals show unique mechanical, electrical, and magnetic properties, compared with crystalline metals. Thus, amorphous metallic materials have attracted increasing attention of researchers for their fundamental scientific importance and engineering application potential [5-8]. According to several leading journals, research and development in amorphous metallic materials has been on-going since the early 1960s [9-13]. For 60 years, scientists have focused on understanding the concepts of synthesizing the amorphous metallic materials including the ability to form, structure, properties and develop them to use in different applications [6, 7, 12 and 14]. For example, in the U.S.A. much work on amorphous metallic materials have been conducted by the government and have been applying their findings for decades; while in Japan the government has funded researches on amorphous metallic materials for more than 30 years [15]. Thus, amorphous metallic materials has had a large share in the world's research and on different applications, including the aerospace and automotive industries, electronic systems, electric transformers, medical products and magnetic appliances [14- 18].

Amorphous metallic materials have appeared as byproducts of vapor deposition and electrodeposition in the process of producing superconducting materials, but were ignored for a long time. The years from 1952 to 1958, saw many developments in the synthesis of amorphous metals by Hilsch's group [4, 19-22] and many others on deposited metals such as Bi and Ga on a much cooled substrate to produce superconducting materials. The presence of very high cooling rates during deposition subdued the formation of the typical crystalline structure in the long range

periodic order in the metals or metal alloys, while the short range atomic order of the super cooled molten materials appeared. This state or phase with a high degree of disorder is called the “amorphous phase.”

In 1960, the same basic principles led Pol Duwez and his coworkers at Caltech to design the first successful rapid quenching experiment to produce amorphous metals by quenching a thin layer of a molten alloy onto a copper substrate [23]. In this experiment, Pol Duwez’s group observed that by directly quenching Au-25 at.% Si alloy from molten (liquid) state to solid state, at very high cooling rates of 10^6 to 10^8 K/S, it solidified as a metallic glass structure, also called amorphous metallic or non-crystalline material. To put it another way, during the rapid solidification process from a molten material, the atoms do not have enough time to rearrange themselves to form crystalline nuclei; in this case the liquid reached a temperature below the glass transition temperature, and it solidified as a metallic glass structure. However the process of nucleation and growth of the crystalline phase, could kinetically rise during the solidification process, yielding a frozen liquid configuration. An important result of obtaining extremely high cooling rates was the amorphous metals or metallic glasses could only be produced as ribbons, foils, or wires with thicknesses of less than 50 μm , so that the heat could be extracted quickly enough to achieve the necessary cooling rate [9, 17and 24]. Because of this work, Duwez’s group achieved a controlled composition of an amorphous alloy which was stable at room temperature. A year after Duwez’s work on Au-25 at.% Si was reported. Cohen and Turnbull discovered strongly amorphous formations on Au-31 at.% Si alloy [25]. The alloy composition that Cohen had used was close to the eutectic point in the equilibrium phase diagram of Au-Si, which meant that it had a very low melting point; this turned out to be a favorable situation for the formation of an amorphous structure in metals. Significantly, this simple term provided a very powerful guide in the search for alloy systems susceptible of being quenched in an amorphous structure. Duwez’s work later became the backbone work on amorphous metals or metallic glasses, which received a lot of attention in the decades to come as seen in Figure 1 [17and 26-28].

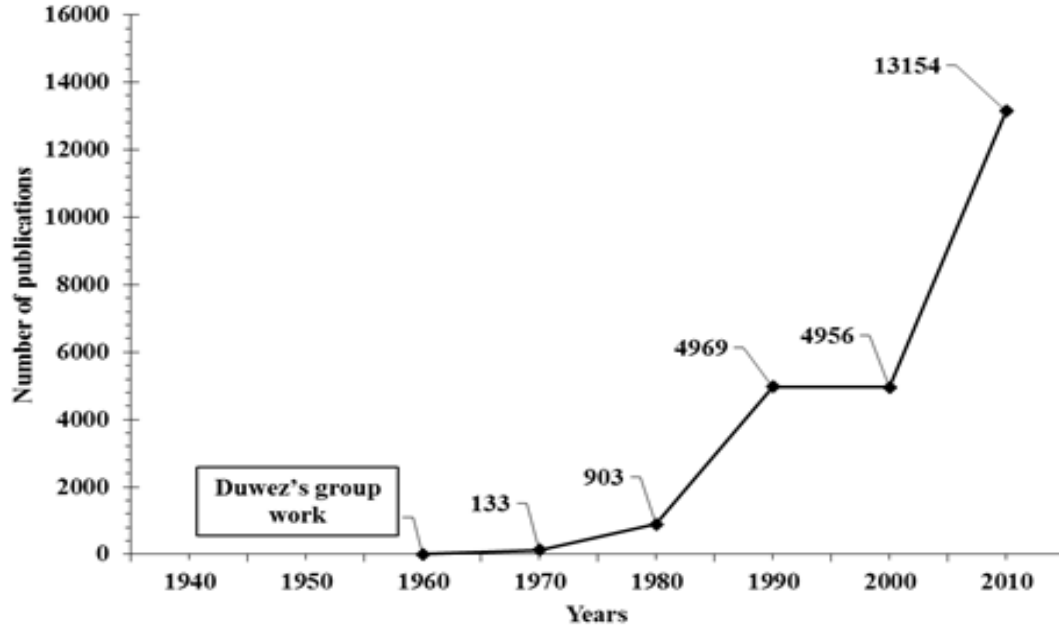


Figure 2.1: Number of publications on amorphous materials published each year for the period 1960- 2010 [17].

In 1965, Duwez and his coworkers developed a new amorphous alloy which was found to have more thermal stability, by substituting the Au in the Au-Si alloy with a metal having a higher melting point [29]. In this work Duwez used Pd-20 at.% Si in order to avoid the thermal instability that was observed in the Au-Si amorphous alloys. Also in 1965, Mader and Nowick [30] produced the first ferromagnetic amorphous alloy. A vapor deposited thin films of Co-25 to 60 at.% Au alloys, which demonstrated that ferromagnetism can exist even without lattice periodicity, as predicted by Gubanov [31]. In 1966 Tsuei and Duwez tried to produce a ferromagnetic amorphous alloy by replacing some atoms of Pd in the Pd-Si system with other atoms of a magnetic element, so as to obtain magnetic properties [32]. According to Tsuei's report [32] the alloys of $\text{Pd}_{75}\text{Fe}_5\text{Si}_{20}$, $\text{Pd}_{68}\text{Co}_{12}\text{Si}_{20}$ and $\text{Pd}_{65}\text{Ni}_{15}\text{Si}_{20}$ in at.% remained amorphous, but they were relatively weak ferromagnets because of the low concentration of magnetic atoms. From 1967 to 1969, Duwez and Lin [33-35] reported on the first strongly magnetic amorphous alloy; they observed that the $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ in at.% alloy had soft magnetic properties with a coercivity of about 3 Oe. On the other hand, Ruhl et al. reported that amorphous alloys were not limited to a metal-metalloid system, but also could be obtained from metal-metal system [36]. Through their experiments in 1967, they presented the possibility of using Nb-33 to 78 at.% Ni alloys and Ta-55 to 67 at.% Ni alloys to

produce amorphous materials and the extent of the metal-metal system implementation and the potential of such a system.

In 1968, Chen and Turnbull [37] in studying for $\text{Au}_{77}\text{Ge}_{13.6}\text{Si}_{9.4}$ in at.% alloy, announced the existence of the glass transition temperature in Au-Ge-Si liquid-quenched amorphous alloys. A year later, Chen and Turnbull [38] studied the formation, stability and structure of Pd-Si based alloy glasses. In these two important articles, Chen and Turnbull demonstrated that the existence of a glass transition temperature provided convincing proof that the liquid-quenched amorphous alloys were indeed glassy and thus the term “metallic glasses” was completely justified.

By the end of the 1960s as seen in Figure 1, there were many studies on amorphous metallics [39]. These studies addressed different approaches to the rapid quenching of molten alloys and amorphous alloys, such as quenching methods [40-48], process mechanisms [49-54], microstructure [55-71], and forming amorphous [72-84], annealing behavior [85-95], electrical and magnetic properties [96-110], mechanical properties [111-121] and practical applications [122-128].

In the early 1970s the production of amorphous metallic materials picked up more momentum and focused on the resulting discovery of technically interesting properties such as high strength, soft magnetic behavior and excellent corrosion resistance. For example, in 1970 Chen and Wang reviewed such mechanical properties, as Young's modulus, plastic deformation, and the ultimate strength of metallic glasses of Pd-Si-based alloys produced mainly by quenching from the melt [129]. In 1971, Masumoto and Maddin also studied the mechanical properties of Pd-20 at.% Si metallic amorphous alloy [130]. In contrast, Leamy et al. in 1972 studied the tensile flow and fracture behavior of Pd-Si-based metallic amorphous alloys ($\text{Pd}_{82}\text{Si}_{18}$, $\text{Pd}_{79.5}\text{Au}_4\text{Si}_{16.5}$ and $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ in at%), using the rapid quenching technique [131]. In the same year Giessen and Wagner clarified the structure morphology and mechanical, electronic, and thermal properties of amorphous alloys produced by rapid quenching [132]. In 1973, Jones published a long paper dealing with the developments in the splat cooling and metastable phases [133]. Jones discussed in details the methods that were available for quenching from the melt on that time, the structural features obtained in both metastable crystalline and amorphous phases, the response of the asquenched structures to annealing (relaxation), and the properties and applications of splat cooled alloys. A year later, Chen and Polk reported the preliminary observations that they found in the

mechanical properties of roller-quenched glassy metal Ni-Fe based alloys (Fe-P-C, Ni-P-B and Ni-Fe-P-B alloys) in various quenching conditions [134].

During the same period there were some other researchers who focused on the magnetic properties of amorphous alloys. For example, in 1974 Fujimori et al. studied the magnetization process in an amorphous alloy of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ in at.% [135]. In 1975, Egami et al. addressed a study showing that the amorphous Fe-Ni-based alloys ($\text{Fe}_{80}\text{P}_{16}\text{B}_1\text{C}_3$, $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, $\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ and $\text{Fe}_{29}\text{Ni}_{49}\text{P}_{14}\text{B}_6\text{Si}_2$ in at.%) work as soft magnetic materials[136]. Sherwood et al. also in 1975 studied the magnetic properties of roller quenched ribbons of metallic glasses in the system $(\text{Fe-Co-Ni})_{75}(\text{P-B-Al})_{25}$ [137]. In contrast, Naka in 1974 studied the corrosion resistivity on the amorphous Fe-Cr alloys [138]. Meanwhile, Masumoto in 1975 reviewed the structural stability and mechanical properties of amorphous metals [139]. Other work done in 1976 by Naka et al. [140] was also on the amorphous alloy corrosion resistivity, by studying chromium-bearing amorphous iron alloys in neutral and acidic solutions that contained chloride. With these primary results and observations, amorphous metallic drew further attention from the labs and scientific communities and became the focus of intense the technological and fundamental studies that time [141-144].

By 1975 the importance of the amorphous metallic alloys had increased practically after all the interesting properties of crystalline alloys had been obtained in amorphous metals. Since then the amorphous metallic alloys have become more commercially used in engineering applications, which has led to increasing efforts to understand and improve the whole field. In 1976, a new method of manufacturing thin ribbons of amorphous metal on a supercooled fast-spinning wheel was developed by Liebermann and Graham [145] based on the concept of the melt spinner developed by Pond and Maddin in 1969 [48]. Liebermann used the new method to produce an amorphous metal alloy of composition $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ in at.%. This alloy became commercialized in early 1980s and it was known as Metglas and used for low-loss power distribution transformers (Amorphous metal transformer).

In contrast, Takayama in 1976 reviewed and clarified very well the formation and stability of amorphous structures [146]. Güntherodt in his work in 1977 also reviewed the preparation, characterization, structure, formation and the electronic, magnetic, and mechanical properties of amorphous metallic [147]. In the same year Waseda et al. [148] discussed the structure and

crystallization of amorphous metallics experimentally and theoretically. A brief review of amorphous metals from fundamentals to practical prospects was presented by Gilman in 1980 [149]. In contrast, Chen in the same year published a complete review about the structure, transport and transformation kinetics, mechanical properties, magnetic properties, electrical properties and corrosion resistance of the amorphous metals [150]. Also Luborsky in 1980 published studies and general reviews about the magnetic properties of amorphous metals such as a brief summary within the context of applying amorphous metals as soft magnetic alloys [151], a study about the possibility of using the localized band model to describe the behavior of the curie temperature of binary metal-metalloid amorphous alloys [152] and a comprehensive review on amorphous ferromagnets [153]. By the end of 1980, many other studies and reviews in improved amorphous metals synthesis and their application were been published extensively.

In the early 1980s there was a dramatic extension in the thickness of the amorphous metallic alloys from 1 mm into 1 cm by using new a rapid series of inventions and incremental innovations in the amorphous metals synthesizing technique. For example, Lee et al. [154, 155] in 1981 produced spherules of the amorphous metal alloy of $\text{Au}_{55}\text{Pb}_{22.5}\text{Sb}_{22.5}$ in at.%, ranging in size up to 1.5 mm in diameter. Lee's procedure was to melt the alloy of Au-Pb-Sb in a stainless-steel vessel and force it through a fine orifice and quench the drops as they come out in either liquid N_2 or in methanol chilled to -98°C . The next major development was Turnbull's group development to produce amorphous ingots of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ in at.%, with a diameter of 5 mm which took place in the 1982 [156]. Turnbull's group was using a surface etching followed with heating-cooling cycles. Using boron oxide flux, the achievable thickness was increased to a centimeter. A further development in 1984, also was by Turnbull's group [157]. In this work they succeeded to increase the casting thickness in the previous work of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ in at.%, to 1 cm, which became the first bulk metallic glass. In a further development, the amorphous multicomponent alloys, was produced at the Tohoku University in Sendai, Japan in the late 1980's. In this work Inoue et al. discovered the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy [158] and $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10}$ alloy in at.% [159] were highly amorphous forming. Inoue's group used a water-cooled Cu mold to cast the alloys. The La-Al-Ni amorphous alloy up to 5 mm thick and La-Al-Ni-Cu amorphous alloy was casted up to 9 mm thick.

Further development in the amorphous metals synthesizing led in the early 1980s to the solid-state amorphization reaction techniques. In 1982 Yeh et al. [160] found that charging a crystalline

intermetallic of Zr_3Rh with hydrogen gas at sufficiently low temperatures ($\leq 200\text{ }^\circ\text{C}$) leads to the formation of amorphous $\text{Zr}_3\text{RhH}_{5.5}$. In this work, Yeh et al. observed that the amorphous phase was formed in the grain boundaries regions and then grew into the grains interiors of the Zr_3Rh as the overall concentration of dissolved hydrogen increased. Based on that, Yeh et al. showed that the features of this reaction of hydrogen-induced transformation to some extent resemble those of the melting transition. Yeh's work was the first example of what has since become known as glass formation by solid-state diffusion reaction, or reaction amorphization, or most recently as solid state amorphization reaction (SSAR).

In 1983 another work done using solid-state amorphization reaction was reported by Herd et al. [161]. In this work Herd also obtained an amorphous Rh-Si alloy by annealing a bilayer of amorphous Si and crystalline Rh thin films well below the crystallization temperature. In contrast, Schwarz and Johnson in 1983 [162] produced an amorphous alloy from pure polycrystalline metals, using a solid-state reaction. Schwarz and Johnson heated thin multilayered Au-La films (individual layers between 100-600 Å thick) below the crystallization temperature. At temperatures of 50-90 $^\circ\text{C}$, it was found that an amorphous phase started to grow at the interlayer boundaries during an interdiffusion at 90 $^\circ\text{C}$ and that further annealing led to an almost complete amorphization of the whole stack of films. Schwarz and Johnson concluded that the abnormal fast diffusion of Au in La, which led to the transformation reaction at low temperatures was driven by the large negative heat of mixing in the amorphous alloy. With this achievement Schwarz and Johnson demonstrated the potential for producing an amorphous alloy from pure polycrystalline metallics using a solid-state reaction.

Soon after that discovery by Schwarz and Johnson, there were many studies using the solid-state interdiffusion reaction of pure polycrystalline metals to produce amorphous alloys. For instance, in 1984 Schwarz et al. [163] have used the approach to form of amorphous alloy Au-Y, Clemens et al. [164] did so for Ni-Zr and Van Rossum et al. [165] did so for Hf-Ni. Furthermore, Schröder et al. [166] in 1985 formed the amorphous alloy Zr-Co by using solid-state reactions. Other works in 1986 were successfully accomplished by Clemens [167] on Ni-Zr and Ni-Ti, while Lin and Spaepen [168] used SSAR to form of amorphous alloy Ni-Nb.

Therefore, the idea that the amorphous state corresponds to a frozen-in liquid which crystallizes when there is diffusion of its constituents is no longer correct. Notably, the crystal-amorphous

transformation occurs with a large diffusivity of one of the components in the alloy with other components in the presence of a simultaneous impediment of the crystallization into a new crystalline structure. In this case we can say, the solid state amorphization process depends on the large mobility of one component in the growing amorphous phase. Since this process takes place at a fixed temperature, there is no need for a thin sample and, in principle, bulk amorphous alloys can be made.

Parallel to the SSAR researches during the early 1980s, experimented with ball milling or mechanical alloying (MA) as a way to produce amorphous alloys and an alternative way of imparting heavy deformation by co-deformation of two elemental metals to form a filamentary or lamellar composite with a large cross-sectional reduction ratio, thus bringing about amorphization without the need for annealing. However, the idea of this process consisted of combining the grinding balls, usually made of hard material such as stainless steel or tungsten carbide, with a small amount of powder, either a mixture of metallic elements or a powder of a prealloyed intermetallic compound. The container could be rotated or vibrated or subjected to a combined form of motion. The milled or alloyed powder were found to be sensitive to the particular form of grinding motion that was used during the milling process.

Generally speaking, both mixed elements and prealloyed powders often behave in the same way with respect to amorphization. The preparation of amorphous powder by means of mechanical alloying can also lead to the production of bulk amorphous materials after consolidation of that powder. The first work to produce the amorphous alloy by using the mechanical alloying was established by Yermakov et al. [169] in 1981. They reported that the amorphous alloy of Co-Y was produced when the elemental mixture powder of Co-Y was mechanically alloyed in a high energy ball mill. Soon after the findings of Yermakov et al., Koch et al. [170] in 1983 prepared Ni-40 at.% Nb amorphous alloy by using ball milling technique. Koch's work was later considered as the first work in which the mechanical alloying technique was specific enough to produce other amorphous alloys. In 1984 Atzmon et al. [171] also succeeded in forming amorphous alloys of Ni-Zr and Cu-Zr from crystalline elemental powders using mechanical alloying. Other works in 1985 succeeded in using mechanical alloying to form amorphous alloys: Schwarz et al. [172] produced Ni-Ti, Hellstern and Schultz [173] produced Ni-Zr, Co-Zr, Fe-Zr and Cu-Zr.

In addition, Politis and Johnson [174] in 1986 were able to form an amorphous alloy from Ti-Cu crystalline elemental powders by using mechanical alloying. Subsequently many amorphous binary metal alloys have been successfully synthesized by mechanical alloying of the elemental powders. All these systems have large negative enthalpies of mixing; the driving force for amorphization in the mechanical alloying is essentially the same as in solid state interdiffusion reactions [162]. The accumulated evidence suggests that mechanically aided amorphization and mechanically induced amorphization are variants of a single process. However, mechanical alloying provides a homogeneous mixture of elemental components, and severe plastic deformation introduces defects and vacancies which may assist and facilitate the diffusion process. In this case the free energy of the amorphous alloy is lower than that of the mixture of the crystalline elements. For this reason, the mechanical alloying is considered as one of the forms of solid-state amorphization reaction. More details on this process of mechanically induced amorphization will be presented later in this work. The solid-state amorphization reaction and mechanical alloying are crucial to the development of modern materials science and specifically amorphous metals alloys. The metallic amorphization theory and research have focused on the formation ability for the amorphous alloys and increased their bulk size and thermal stability. The mechanical alloying mechanism to produce amorphous metallic alloys and the bulk size of the producer are among the reasons that led to the choice of mechanical alloying as an amorphization technique, known as “SPEX” and which will be introduced later, in this work. Moreover, during the last three decades many exciting experiments have been carried out successfully by using mechanical alloying, demonstrating many equilibrium and/or non-equilibrium phases in a number of alloy systems including amorphous alloys, nanocrystalline materials, quasicrystals, rare-earth magnets and intermetallics [175].

In the 1990’s, the successful formation of amorphous metals at cooling rates as low as 1K/s was a great breakthrough in the research on amorphous metals. These low cooling rates were achieved by simple casting into metallic molds. The thickness of these bulk amorphous alloys could be up to several centimeters while retaining an amorphous structure and the maximum thickness mostly depended on the alloy. The alloys based on zirconium and palladium were found to be the best amorphous-forming alloys, but those based on iron, titanium, copper, magnesium, and other metals were also known. Many of these amorphous alloys were formed by using the “confusion effect” phenomenon. Such alloys contained so many different elements that upon

cooling at sufficiently fast rates, the constituent atoms simply could not coordinate themselves into the equilibrium crystalline state before their mobility was stopped. In this way, the random disordered state of the atoms was locked in, yielding a “frozen liquid” configuration. Thus in the early of 1990s, bulk metallic amorphous alloys with extraordinary amorphous-forming abilities were discovered, such as Vitreloy 1 and 4 [176, 177]. In 1993 Peker and Johnson [176] at Caltech, in collaboration with researchers from the U.S.A Department of Energy and NASA developed the first commercial amorphous alloy, Vitreloy 1 (Vit1) with a composition of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ in at.%, with a critical casting thickness of up to 10 cm, using silica containers. Two years later, also at Caltech Bakke et al. [177] discovered Vit4 with a composition of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ in at.%. Then in 1997 Lin et al. [178] designed an empirical alloy for Vit105 with a composition of $\text{Zr}_{52.5}\text{Ti}_5\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}$ in at.%, which showed that it was one of the best amorphous-forming alloys. In contrast, the Inoue group at the Tohoku University in Sendai, Japan reworked the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ in at.% alloy by replacing the 40% Ni with the 10% Ni and 30% Cu to become $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ in at.% [179]. The Inoue group thus developed an alloy with a critical casting thickness of 7.2 cm. Furthermore, the Pd-Cu-Ni-P family was considered as one of the metallic systems that had the highest amorphous-forming ability known in the amorphous metallic alloys.

Further significant developments in amorphous metal alloys synthesizing techniques came in the early 2000s. For example Yi et al. in 2000 [180] developed a new Ni-based bulk amorphous alloys in the alloy system Ni-Ti-Zr-(Si,Sn). The Inoue group in 2001 [181] formed a new Cu-based bulk glassy alloys in the Cu-Zr-Ti and Cu-Hf-Ti systems by the copper mold casting method. In contrast, Kündig at ETH Zürich [182] successfully investigated Zr-Ti-Cu-Ni-Al alloys, focusing on those similar alloys to Vit105. Subsequently, in 2002 Amiya and Inoue [183] produced the calcium-based bulk glassy alloys in Ca-Mg-Ag and Ca-Mg-Ag-Cu systems by a metallic mold casting method. Another major development was introduced by Lu et al. in 2004, with an improvement of the Fe-based bulk glassy alloys (nonferromagnetic amorphous steel alloys) by adding Yttrium to an earlier developed of Fe-Cr-Mo-Mn-C-B-based bulk glassy alloys [184] with a typical composition of $(\text{Fe}_{67.1-a-b-c}\text{Cr}_a\text{Co}_b\text{Mo}_c\text{Mn}_{11.2}\text{C}_{15.8}\text{B}_{5.9})_{98.5}\text{Y}_{1.5}$ in at.% [185], where in $4 \leq a \leq 10$; $b \leq 6$; and $12.5 \leq c \leq 14$. These new steel products showed interesting physical, magnetic, and mechanical properties, along with high thermal stability. Ponnambalam et al., also in 2004, [186] reported that Fe-Mn-Cr-Mo-(Y, Ln)-C-B (Ln = Lanthanides) bulk metallic glasses alloys

were formable amorphous steel alloys and that Fe-Mn-Cr-Mo-(Y, Ln)-C-B (Ln = Lanthanides) alloys exhibited a plastic behavior and high mechanical strengths. These results suggest that the present Fe-based bulk metallic glasses can potentially be developed as formable non-ferromagnetic amorphous steel alloys.

By the end of 2010, many technologically important amorphous metallic alloys were discovered. For example in 2005, Bian and Inoue discovered the Ce-Cu-Fe-Al-Si bulk metallic glass alloys [187]. Qin et al., also in 2005 [188], synthesized Ni-Nb (-Ta)-Ti-Zr bulk amorphous alloys with a high thermal stability and high corrosion resistance properties. In contrast, Schroers, et al. [189] worked on Au-Ag-Pd-Cu-Si bulk amorphous alloys and reported that the combination of properties made the Au-Ag-Pd-Cu-Si alloys attractive for many applications including electronic, medicine, dentistry, surface coating, and jewelry. Another major development in 2005, introduced by Wada et al. [190], was improvement in the plasticity by forming porous Pd-Pt-Cu-P bulk glassy alloys. More works had been done in 2007, and in example of that, work done by Yuqiao et al. [191] to develop the Ni-Pd-P-B alloy by adding B into the $\text{Ni}_{60}\text{Pd}_{20}\text{P}_{20}$ alloy in at.% with a typical composition of $\text{Ni}_{60}\text{Pd}_{20}\text{P}_{17}\text{B}_3$ in at.%. In this work Yuqiao reported that the alloy with 3 at.% of B showed a distinctively improved glass-forming ability; this was the first time a Ni-based bulk glassy alloy was prepared with a diameter over 1 cm. In contrast, Zhu et al. [192] reported on synthesizing new Ti-based bulk glassy alloys with a typical composition of $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{40-x}\text{Pd}_{10+x}$ in at.%, where in ($x = 0, 2, 4, 6, 8$ and 10). Zhu et al. expected that the Ti-Zr-Cu-Pd alloy could be applied as biomaterials because of the absence of toxic elements such as Ni, Al and Be. In 2008 Zhu et al. [193] synthesized the Ti-Zr-Cu-Pd-Sn bulk glassy alloys with a critical casting thickness of 1 cm by means of copper mold casting. Another famous work in 2010 was by Matsumoto et al. [194]. They discovered novel glassy alloys with a typical composition of $\text{Fe}_{(97-x-y)}\text{P}_x\text{B}_y\text{Nb}_2\text{Cr}_1$ in at.%, where in ($x = 5-13, y = 7-15$), considered the forerunner of high magnetization and low loss characteristics for inductor core materials, through carrying out experiments involving the induction melting of the mixture of pre-melted Fe-P, Fe-B, Fe-Nb, Fe-Cr and pure metal of Fe in an argon atmosphere. In this work the single roller melt-spinning method in an argon atmosphere were used to produce a ribbon of $\text{Fe}_{(97-x-y)}\text{P}_x\text{B}_y\text{Nb}_2\text{Cr}_1$ glassy alloy with a width of about 1 mm and thickness of about 25-150 μm .

During the last 10 years the bulk amorphous alloys have increased in span and breadth as a result of the research works and engineering applications being conducted. Based on this breadth and the importance of the bulk amorphous alloys, many researchers are testing new alloy compositions and investigating the mechanical, structural, thermophysical, and magnetic properties of these alloys. As an example of this recent work, Demetriou et al. in 2011 [195], dealt with developing palladium based bulk amorphous alloys with a typical composition of $\text{Pd}_{79}\text{Ag}_{3.5}\text{P}_6\text{Si}_{9.5}\text{Ge}_2$ in at.%. Demetriou et al. observed that the damage tolerance (the combination of strength and toughness) to the $\text{Pd}_{79}\text{Ag}_{3.5}\text{P}_6\text{Si}_{9.5}\text{Ge}_2$ alloy is higher than any known and studied material, and the superior damage tolerance capacity of this palladium alloy can be thought of as a superior alternative to conventional palladium dental alloys.

Also another work done in 2011 by Lou et al. [196] addressed the development of bulk glassy alloy of $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ in at.%, which was cast into amorphous rods in 73 mm diameter using copper mold casting. In 2012 Nishiyama et al. [197] reported the production of the world's biggest size of amorphous bulk glassy alloy with a diameter of 80 mm and a length of 85 mm, using the water-quenching method to quench molten $\text{Pd}_{42.5}\text{Cu}_{30}\text{Ni}_{7.5}\text{P}_{20}$ alloy in at.%. Moreover, Mann et al. in 2013 [198] synthesized a new CoFe-based bulk metallic glasses alloy with high thermoplastic forming ability. They used $(\text{Co}_{0.5}\text{Fe}_{0.5})_{62}\text{Nb}_6\text{M}_2\text{B}_{30}$ glassy alloys in at.%, where in (M = Er, Tb, Y, Dy). Mann et al. reported that the new CoFe-based bulk metallic glasses alloy had a large supercooled liquid region, strong thermoplastic forming, high fracture strength and good soft magnetic properties. Thus Mann et al. concluded that because of the good properties that the new CoFe-based bulk metallic glass alloy have, they are promising candidates for engineering applications as structural and functional materials. In 2014 Yang et al. [199] reported on their production of a new Fe-based bulk metallic glasses with unprecedented compressive plasticity (>20%) at room temperature without any final fracture, using the water quenching and copper mold casting methods, respectively to quench a molten from of $\text{Fe}_{50}\text{Ni}_{30}\text{P}_{13}\text{C}_7$ alloy in at.%. A more recent study in 2015 on the effect of high-order multicomponent on the formation and properties of Zr-based bulk glassy alloys was reported by Inoue et al. [200]. In this study, the glass formation of $\text{Zr}_{55}\text{Al}_{10}\text{Fe}_6\text{Co}_6\text{Ni}_6\text{Cu}_6\text{Pd}_6\text{Ag}_5$ alloy in at.% was carried out in the melt spinning technique on a single copper roller with a tangential wheel.

Very recently, in the beginning of 2017 Geng et al. [201] carried out a study on the mechanical and magnetic properties for a new (Fe,Co,Ni)-B-Si-Ta bulk glassy alloy, in comparison with numerous data on mechanical and magnetic properties for Fe-based amorphous alloys. The research Geng et al. deals with developing a Fe-based bulk amorphous alloys with a typical composition of $\text{Fe}_{60-x}\text{Co}_x\text{Ni}_{10}\text{B}_{16.7}\text{Si}_{8.3}\text{Ta}_5$ in at.%, where in ($x = 10, 20$ and 30). This work used copper mold casting technique to form amorphous structure with critical diameters up to 1.5 mm, and the results have showed that the bulk glassy alloys exhibit good soft magnetic properties with high saturation magnetization and low coercive force.

To date, a number of processing methods and many of designing alloys based on amorphous bulk metallic glass alloys have been developed, as reviewed earlier, starting from the early of 1930s to the present, focusing on the big major research work during the period of the development of amorphous bulk metallic glass alloys.

Table 1 summarizes the typical amorphous bulk metallic glass alloys systems that have been reported to date, together with the calendar year when the first paper or patent for each alloy system was published. Additionally, it is expected that the fields of application will be significantly extended in the near future on the basis of the useful and unique engineering properties of amorphous bulk metallic glass alloys resulting from the simultaneous achievements of novel atomic configurations, unique multi component alloy compositions, various bulk forms, slow solidification process, Newtonian flow deformability and net-shape casting formability.

Table 2.1: Typical amorphous bulk metallic glass alloys systems reported up to date and the calendar years when their first papers and patents were published.

Amorphous bulk metallic glass alloy systems	Year	Amorphous bulk metallic glass alloy systems	Year
Au-Si	1960	Fe-Mn-Mo-Cr-C-B	2002
Pd-Si	1965	Ca-Mg-Cu	2002
Co-Au	1965	Ni-Nb-(Sn-Ti)	2003
Pd-Fe-Si	1966	Pr(Nd)-(Cu, Ni)-Al	2003
Pd-Co-Si	1966	Nd-Fe-Al	2004
Pd-Ni-Si	1966	Ni-Zr-Nb-Al	2004
Fe-P-C	1967	Al-Co-Zr	2004
Nb-Ni	1967	Ca-Mg-Zn	2004
Ta-Ni	1967	Ca-Mg-Zn-Cu	2004
Au-Ge-Si	1968	Co-Fe-Ta-B	2004

Pd-Au-Si	1972	Fe-Co-Nd-Dy-B	2004
Pd-Cu-Si	1972	Cu-Zr	2004
Ni-P-B	1974	Fe-Co-Zr-Mo-W-B	2004
Ni-Fe-P-B	1974	Mg-Cu-Y-Gd	2004
Pt-Ni-P	1975	La-Cu-Ni-Al	2004
Co-Y	1981	Mg-Cu-Tb	2004
Au-Pd-Sb	1981	Nd-Al-Cu-Ni-Fe	2004
Pd-Ni-P	1982	Pt-Cu-Ni-P	2004
Zr-Rh-H	1982	Mm-Ni-Cu-Al-C	2005
Rh-Si	1983	Mg-Ni-Pr	2005
Au-La	1983	Cu-Hf-Ti-Ag-Ta	2005
Cu-Zr	1984	Gd-Cu-Ni-Al	2005
Au-Y	1984	Cu-Zr-Ti-Hf	2005
Ni-Zr	1984	Al-Y-Fe	2005
Hf-Ni	1984	Ce-Al-Ni-Cu	2005
Nd-Fe-B	1984	Pr-Al-Ni-Cu	2005
Zr-Co	1985	d-Y-Al-Co	2005
Zr-Fe	1985	Tb-Y-Al-Co	2005
Ti-Ni	1986	Dy-Y-Al-Co-Fe	2005
Ti-Cu	1986	Er-Y-Al-Co	2005
Mg-Ln-Cu (Ln- Lanthanide)	1988	Sc-Y-Al-Co	2005
La-Al-Ni	1989	Au-Ag-Pd-Cu-Si	2005
La-Al-Cu	1989	Ce-La-Pr-Nd-Co-Al	2006
Ln-Al-TM (TM- Transition Metal)	1989	Cu-Hf	2006
Zr-Ti-Al-TM	1990	Cu-Zr	2006
Ti-Zr-TM	1993	Ni-Nb	2006
Zr-Ti-Cu-Ni-Be	1993	Cu-Hf-Al	2006
Nd(Pr)-Al-Fe-Co	1994	Cu-Zr-Al-Gd	2006
Zr-(Nb, Pd)-Al-TM	1995	Fe-Nb-B-Si-Y	2006
Cu-Zr-Ni-Ti	1995	Co-Cr-Mo-C-B	2007
Fe-(Nb, Mo)-(Al, Ga)-(P, C, B, Si, Ge)	1995	Mg-Cu-Gd	2007
Pd-Cu(Fe)-Ni-P	1996	Mg-Cu-Ag-Gd-Ni	2007
Co-(Al, Ga)-(P, B, Si)	1996	Fe-B-Y-Nb	2007
Fe-(Zr, Hf, Nb)-B	1996	Fe-B-Y-Mo	2007
Co-Fe-(Zr, Hf, Nb)-B	1996	Ti-Zr-Cu-Pd-Sn	2008
Ni-(Zr, Hf, Nb)-(Cr, Mo)-B	1996	Fe-P-B-Nb-Cr	2010
Ti-Ni-Cu-Sn	1998	Pd-Ag-P-Si-Ge	2011
La-Al-Ni-Cu-Co	1998	Zr-Cu-Ag-Al-Be	2011
Ni-Nb	1999	Pd-Cu-Ni-P	2012
Ni-(Nb, Cr, Mo)-(P, B)	1999	Co-Fe-Nb-M-B (M= Er, Tb, Y, Dy)	2013

Zr-based glassy composites	1999	Fe-Ni-P-C	2014
Zr-Nb-Cu-Fe-Be	2000	Zr-Al-Fe-Co-Ni-Cu-Pd-Ag	2015
Cu-Zr-Ti	2001	Fe-Co-Ni-B-Si-Ta	2017
Cu-Hf-Ti	2001		

2.2 The Basic Concepts and Properties of Bulk Amorphous Metals Alloys

The amorphous state in metals is essentially identified by two outstanding features. Firstly, there is a glass transition, which has shown no typically discontinuous change in thermodynamic properties, such as volume V , entropy S and specific heat C_p . The second feature is the lack of a long-range periodic atomic order e.g, no a crystalline structure [202]. In general, amorphous metallic alloys are found to have “preferred neighborhood relationships” between the atoms, as well as their number, distances and angular relationships, also called topological or physical short-range order. In this case, the short-range order typically reaches the direct neighbors of a central atom or molecule, i.e., the first coordination sphere (sometimes the second coordination sphere) [203]. However, the schematic diagram in Figure 2 shows the atomic structure and the corresponding density distribution function $\rho(r)$ which reflects this short-range order. In the immediate vicinity of a certain atom, for instance, in the range of one to two atomic shells, an ordered atomic configuration is present, which is completely lost at a greater distance from the reference atom. As mentioned above, the amorphous metallic alloys can be produced by a number of different processes and techniques, such as the cooling of molten metal by rapid quenching or casting, vapor deposition and electrodeposition and solid state amorphous reactions by mechanical alloying. Therefore, the formation of a metallic glass amorphous substance, in case of rapid quenching happens by cooling the molten metal, using a high cooling rate to avoid crystallization. Knowing the thermodynamic and kinetic aspects of crystallization is therefore essential for understanding the formation of amorphous materials.

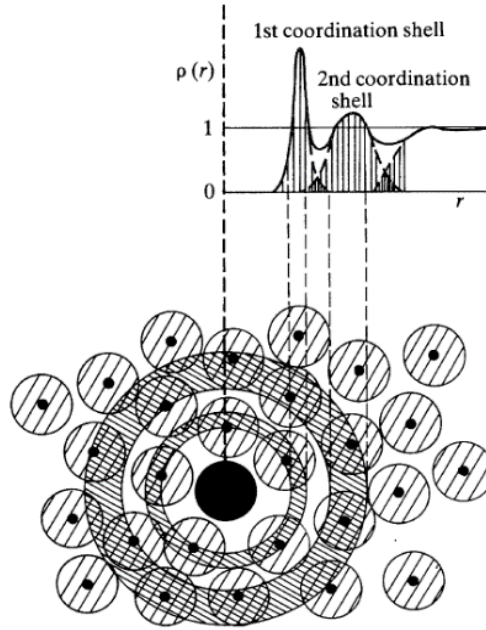


Figure 2.2: Schematic illustration of the structural origin of certain features in the density function $\rho(r)$ for an amorphous solid [204].

2.2.1 Thermodynamics of an Undercooled Liquid

The transition of the metal from the liquid state to the solid state is usually due to the conventional crystallization processes, through the nucleation and crystal growth [205]. In the case of amorphous or glassy phase, the transition from the liquid to the solid state there is a sufficiently high cooling rate to solidify the melt, so that the nucleation and crystal growth are suppressed, and consequently the melt freezes in its disordered configuration of the atoms which is a characteristic of liquids. The crystallization process can be described thermodynamically aspects can by means of the Gibbs free energy G of the solid and liquid phase, which defined by enthalpy H , entropy S and temperature T as:

$$G = H - T S \quad \text{Eq. 1 [206, 207]}$$

Figure 3 shows the Gibbs free energy of the liquid and solid phases as a function of the temperature T (at a constant pressure P) for any given material. First, at high temperature, the $T S$ term dominates and therefore the high entropy of the liquid causes it to have the lowest G . In contrast, at low temperatures, the ordered stable crystalline structure reduces the enthalpy, H , thus reducing the Gibbs free energy, G . Second, at the melting temperature T_m (the intersection of the curves) is

characterized in that both phases have the same value of free energy, which means that they are in thermodynamic equilibrium:

$$\Delta G (T_m) = G_{Liquid} - G_{Solid} = 0 \quad \text{Eq. 2 [206, 207]}$$

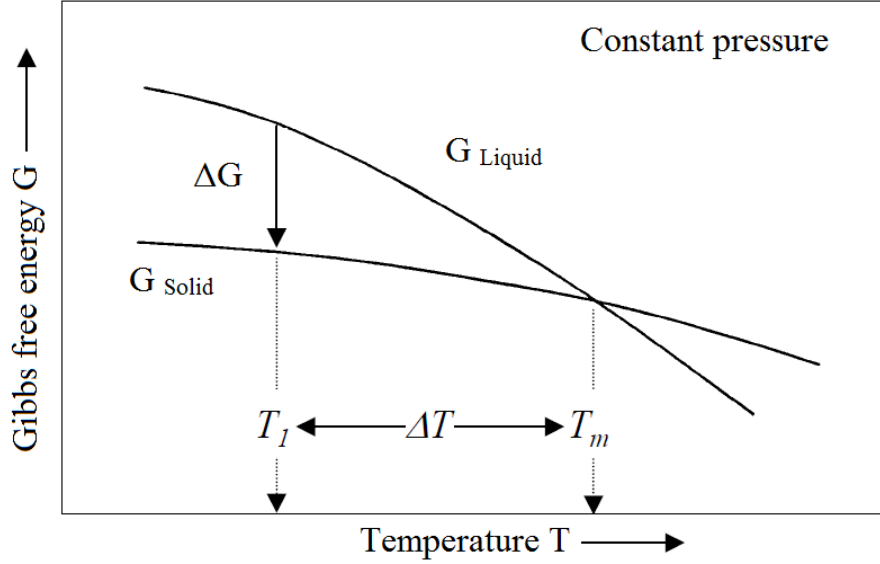


Figure 2.3: Gibbs free energy for the solid and liquid as a function of temperature T at constant pressure P [206, 207].

The formation of viable nuclei is possible only when the thermodynamic equilibrium temperature is undercut by a certain amount of ΔT (supercooling):

$$\Delta T = T_m - T \quad \text{Eq. 3 [206, 207]}$$

This increases the free energy of the system by the amount of ΔG :

$$\Delta G (T < T_m) = G_{Liquid} - G_{Solid} > 0 \quad \text{Eq. 4 [206, 207]}$$

And so this free energy ΔG is available for the nucleation. This means that with the increase in the supercooling ΔT , the difference between the free energy of the melt G_{Liquid} and the crystalline G_{Solid} will increase, and consequently the driving force for the crystallization will increase too. The question of the possible supercooling of metallic melts without crystallization can thus not be explained solely by thermodynamic influences; obviously, Kinetics aspects, such as low mobility of the atoms and delayed diffusion processes, decisively contribute to suppress the nucleation and crystal growth.

The nucleation in metallic melts can be on homogeneous or heterogeneous nucleation. While homogeneous nucleation is facilitated by supercooling the melt in the free melt volume, heterogeneous nucleation takes place on existing surfaces, e.g., on impurities or on the surface of the melt crucible [208]. The energy barrier for the formation of a growth-capable nucleus, is reduced, provided that the nucleus wets the surface [209]. Nevertheless, regardless of whether homogeneous or heterogeneous nucleation is considered in a system, the free energy of the system changes by the formation of the nuclei. This change in the free energy ΔG is determined by two opposing components, the energy contribution $-\Delta G_v$, which is proportional to the volume of the nucleus, and the energy contribution $+\Delta G_G$ to be applied, which is required to form the liquid-solid boundary interface of the nucleus [207]:

$$\Delta G = -G_v + G_G \quad \text{Eq. 5 [206, 207]}$$

Due to the proportionality of the energies to the volume or to the surface, the nuclei with the radius r are assumed to have a spherical shape [82, 206-212]:

$$\Delta G(r) = -\frac{4}{3}\pi r^3 \Delta g_v + 4\pi r^2 \gamma \quad \text{Eq. 6 [82, 206-212]}$$

Where Δg_v is the Gibbs free energy difference between unit volume of crystal and liquid, and γ is interfacial energy per unit area of the solid/liquid interface. It can be seen from Figure 4 that the free energy ΔG is a function of the radius of the nucleus, which shows that the energy contribution, which is proportional to the surface area of the nucleus in the case of a small radius ($r < r^*$), is predominant compared with the volume-proportional energy contribution. This leads to positive ΔG values and does not allow thermodynamically stable nuclei. The function $\Delta G(r)$ passes through a maximum only when the critical nucleus radius r^* is reached, that is, the surface/volume ratio of the nucleus changes in favor of the volume. ΔG of the system decreases, resulting in stable, growth-capable nuclei. The critical radius r^* required for the crystallization can be calculated by determining the maximum from Equation 6 [82, 206-212] and to be:

$$r^* = \frac{2\gamma(T)}{\Delta g_v(T)} \quad \text{Eq. 7 [82, 206-212]}$$

Thus, the activation energy ΔG^* , which must be applied to the homogeneous nucleation [206-208]:

$$\Delta G^*(r^*) = \frac{16}{3} \pi \frac{\gamma^3}{(\Delta g_v)^2} = \frac{1}{3} F^* \gamma \quad \text{Eq. 8 [82, 206-212]}$$

Where F^* corresponds to the surface of the critical nucleus. This results in the fact that the critical work required for nucleation is $1/3$ of the total surface energy of the nucleus.

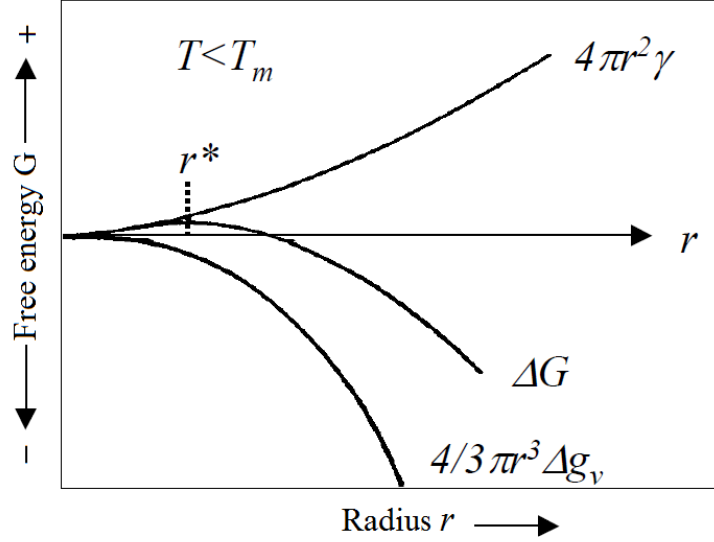


Figure 2.4: Free energy ΔG as a function of the nucleus radius r at a temperature T below the melting temperature T_m [82, 206-212].

For the heterogeneous nucleation an activation energy is defined as $\Delta G^*_{het}(T)$, which corresponds to the nucleation process of the homogeneous nucleation and reduced by the factor $f(\theta)$, which takes into account the wetting angle θ and assumes values between 0 and 1 [213] :

$$\Delta G^*_{het}(T) = \Delta G^*_{hom} f(\theta) \quad \text{Eq. 9 [213]}$$

As a rule, the wetting angle between the nucleus and the surface to be moistened is less than 180° [214], as indicated by:

$$f(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \quad \text{Eq. 10 [213]}$$

Consequently, the heterogeneous nucleation is energetically preferred as the factor $f(\theta)$ less than 1 , compared to the homogeneous nucleation. Therefore, it is a practical type of crystallization to begin with. In the case of metallic glasses production, the impurities of the melt, such as oxides inclusions, must be largely avoided.

On the other hand, the homogeneous nucleation that occurs by means of the supercooling of the melt can only be circumvented by a correspondingly high cooling rate, and thus the

correspondingly high amount of supercooling, since the diffusion processes required for the formation of the crystalline lattice are made difficult at low temperatures. The classical nucleation theory [82] calculates the homogeneous nucleation rate $I(T)$ as:

$$I(T) \propto \frac{K}{\eta(T)} \exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad \text{Eq. 11 [82]}$$

ΔG^* is the activation barrier and it is necessary for the formation of a critical nucleus which is defined by the interfacial tension γ and the difference between the free energy between liquid and solid phase Δg_v as in Equation 8. Furthermore, the proportionality constant K , the viscosity η , as well as the Boltzmann constant k_B , are taken into account. The viscosity η is given by the Stokes-Einstein relation [214] as:

$$D \sim \frac{RT}{\eta} \quad \text{Eq. 12 [214]}$$

As a measure of the mobility of the atoms, and is inversely proportional to the diffusion constant D .

A common consideration of the thermodynamic and kinetic conditions which have a lasting effect on the subcoolability of a melt reveals these temperature-dependent influencing variables:

- The difference between the Gibbs free energy of liquid and solid phase Δg_v ;
- The interfacial tension γ between the nucleus and the supercooled melt; and
- The viscosity η of the supercooled melt determine decisively the glass forming ability of an alloy.

2.2.2 Glass Forming Ability

Glass forming ability (GFA) of an alloy or material is the freedom of the alloy for vitrification, which is related to the physical nature of the alloy and indicates whether the alloy can be produced in a vitreous state formed by the transition from the molten to the glass phase. However, to transit the alloy from molten to the glassy state requires a certain stability of the supercooled melt in opposition to the crystallization. That means the glass forming ability has a decisive criterion, which is the cooling rate of the molten metal, v_c , and knowing it is required for to avoid the crystallization. A high glass forming ability is thus obtained when the critical cooling rates have been reached, leading to amorphization of the material. In the case of metal alloys, the critical

cooling rates are in the range of about 10^8 to 10^{-2} K/S [215], i.e. the glass forming ability of metallic alloys varies significantly.

According to Turnbull [82], a decisive criterion for the glass forming ability is the ratio between the liquidus temperature T_m (liquid) and the glass transition temperature T_g , which is defined by the reduced glass transition temperature T_{rg} :

$$T_{rg} = \frac{T_g}{T_{m(liquid)}} \quad \text{Eq. 13 [82]}$$

A high reduced glass transition temperature T_{rg} is a good indicative for the glass forming ability. This high value of T_{rg} is essentially achieved by lowering the liquidus temperature. Since T_g usually depends only weakly on the composition [216], while T_m (liquid) can be lowered very much, especially in eutectic alloy systems by targeted adjustment of the eutectic composition. A highly reduced glass transition temperature is advantageous for glass formation for two reasons. First, a reduced temperature interval T_m (liquid) – T_g leaves less time for nucleation and growth (assuming the same cooling rates). On the other hand, a low liquidus temperature is the result of high thermodynamic stability of the melt compared to crystallization [208]. This process can lead to higher supercooling. Figure 5 shows a schematic of the critical cooling rate that is required for glass formation on the reduced glass transition temperature for some typical alloying groups [217].

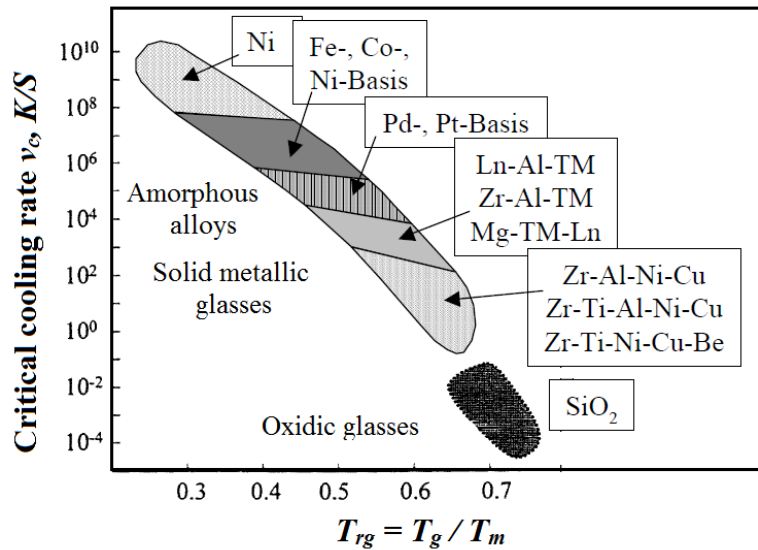


Figure 2.5: The relationship between the critical cooling rate v_c for glass formation and reduced glass transition temperature T_{rg} on the example of some selected alloy groups [217].

In addition to the reduced glass transition temperature T_{rg} , the range of the supercooled melt ΔT_x is also given by Inoue as a criterion for the glass forming ability [217] calculated as:

$$\Delta T_x = T_x - T_g \quad \text{Eq. 14 [217]}$$

Thus the temperature difference between the onset crystallization temperature T_x and the glass transition temperature T_g as seen in Figure 6, indicates the extent of the supercooled liquid region and the possibility of measuring the thermal stability of the supercooled melt against crystallization. Usually, the larger the difference in temperatures (ΔT_x), the better the GFA. However, the linear dependence is only detected for $\Delta T_x \leq 70 \text{ K}$ for the alloys groups that have been studied and as shown in Figure 5. On the other hand, given the high values of the ΔT_x , this correlation does not necessarily apply, and this happens when the supercooled melt is separated into two phase regions which have different chemical compositions [218].

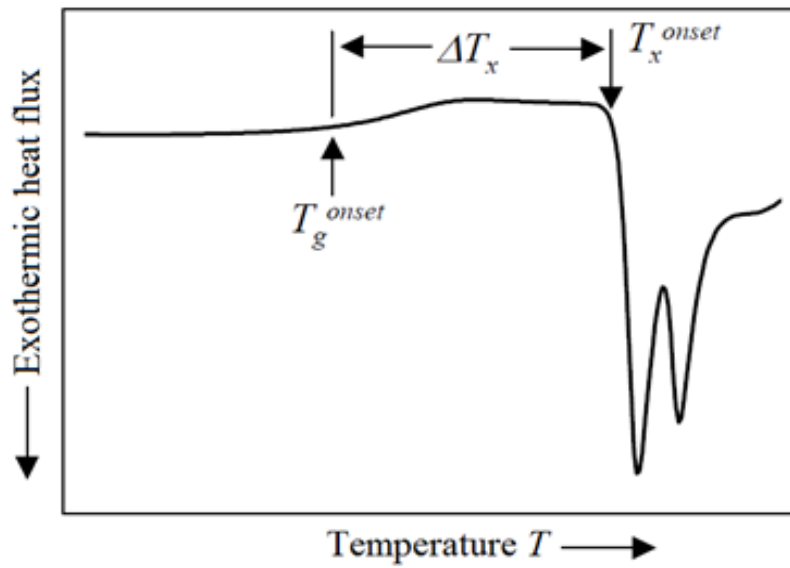


Figure 2.6: DSC curve of Zr-Ti-Ni-Cu-Be glassy alloy offers the transition temperature T_g and crystallization temperature T_x and shows the difference of $\Delta T_x = T_x - T_g$ that defines the thermal stability range [176].

An empirical rule developed by Inoue states that to get a high glass forming ability of a metallic alloy, it has to comply with the following three prerequisites:

1. The alloy should contain at least 4 elements.

2. These elements should have diametrically different atomic diameters ($\geq 12\%$) and
3. The 3 main elements of the alloy should have a high negative heat of mixing.

Therefore, this rule confirms the presence of the thermodynamic and kinetic influences on the glass forming ability that was mentioned in the beginning. The three conditions that have been specified by Inoue satisfy an alloy whose molten state is characterized by a tightly packed atomic structure of local, short range atomic configurations. These therefore differ from the atomic order of the crystalline equilibrium phases. Due to the high entropy S of the liquid phase, the driving force for the crystallization ΔG in Equation 1 goes down. Furthermore, in Equation 12 the high packing density of the atoms results in a high viscosity η of the supercooled melt, which, in turn, impedes the diffusion processes. Due to the strongly divergent atomic configurations of the liquid and the crystalline phases, long range atomic arrangements are necessary for the structure of the crystalline lattice. Consequently, an increase in the thermal stability of the liquid phase against crystallization is to be expected. A second consequence of the different atomic configurations of liquid and crystalline phase (n) is a high interfacial energy between the two phases, which hinders the nucleation of a crystalline phase, as seen in Equation 5. Therefore the previously mentioned thermodynamic and kinetic influences partly increase the glass transition temperature T_g and or lower the melting temperature T_m of the alloy. Both lead to an increase in the reduced glass transition temperature T_{rg} thus improving the glass forming ability.

2.2.3 Glass Transition

One of the features of the metallic glass alloys is the existence of a glass transition. The glass transition occurs during the heating of the metallic glass alloy as well as during the cooling of the melt, provided that the cooling rate is high enough to prevent crystallization. Moreover, the glass transition temperature T_g is not an exactly definable temperature, but a temperature range that is characterized by the continuous transition of the supercooled melt into the solid glass state. However, the T_g is dependent on the cooling or heating rate and on the respective thermal history of the alloy. Furthermore, at the glass transition, there are extensive thermodynamic state variables, such as volume V , enthalpy H and entropy S , as well as state variables derived therefrom, such as the coefficient of thermal expansion α and the specific heat c_p .

While the sudden decrease of these state variables occurs during the crystallization of the liquid phase at the melting point T_m , the change in the state variables volume, enthalpy and entropy

proceeds steadily at the glass transition. Therefore this change in the state variables is characterized by a continuous reduction in the slope of the curves with decreasing temperatures. On the other hand, the specific heat has a discontinuous behavior at T_g . The course of c_p at the glass transition temperature T_g is shown schematically in Figure 7. When the amorphous alloy is heated, there is hardly any difference between c_p of the amorphous state and c_p of the crystalline state, yet an abrupt increase of the former becomes apparent only at T_g , due to the configurational degrees of freedom obtained in the transition to the liquid phase.

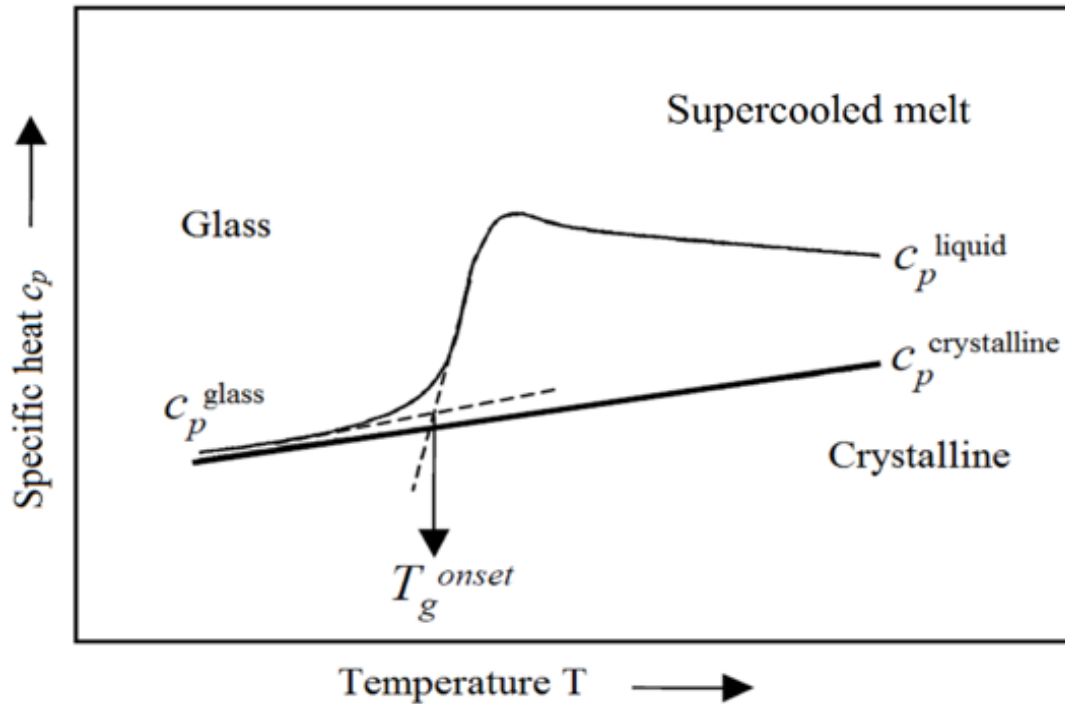


Figure 2.7: Dependence of the specific heat c_p on the temperature T during the transfer of the supercooled melt into the glass state (upper curve) and the crystalline phase (lower curve) [219].

On the other hand, Figure 8 shows the continuous change in the entropy S at the glass transition as a function of the temperature. The difference of the entropy between liquid and crystalline phases $\Delta S = S_{\text{liquid}} - S_{\text{crystalline}}$ becomes lower with increasing supercooling [220].

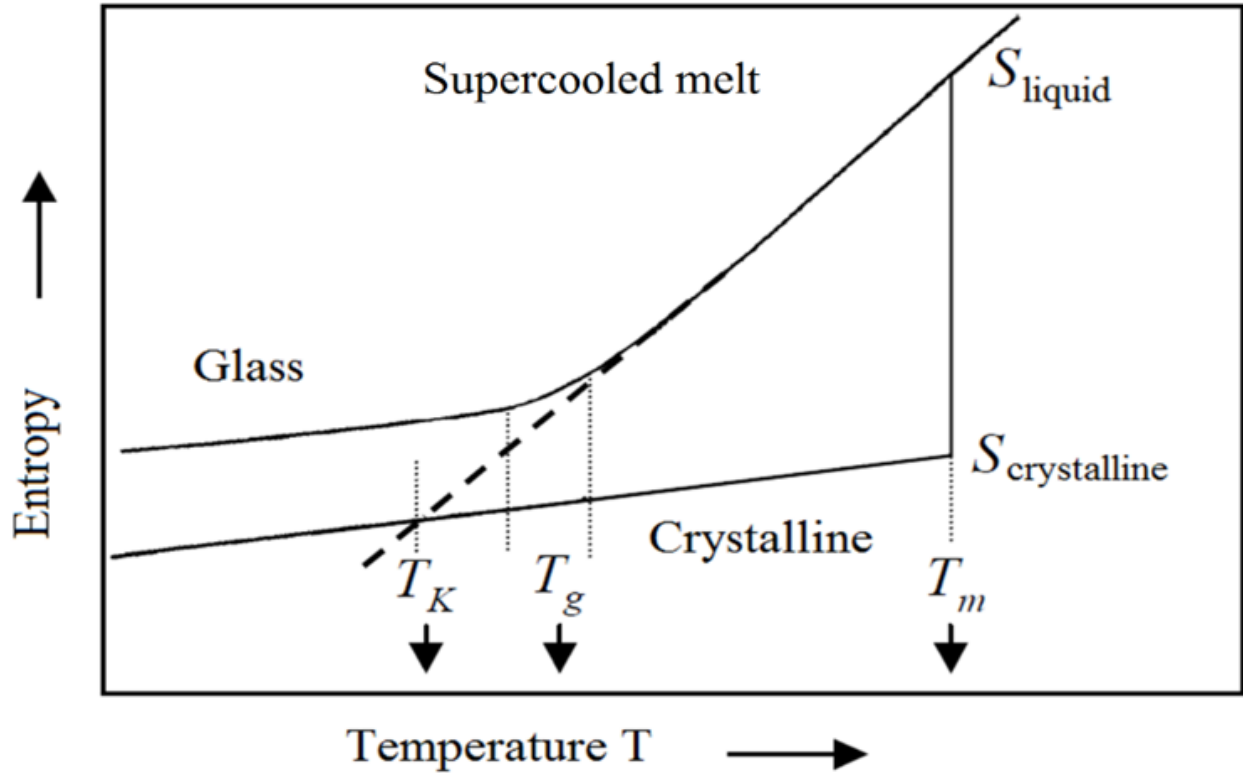


Figure 2.8: Dependence of the entropy S on the temperature T in the transfer of the supercooled melt into the glass state (upper curve) and crystallization (lower curve). The Kauzmann temperature T_K is defined by the extrapolation of the liquid to $\Delta S = S_{\text{liquid}} - S_{\text{crystalline}} = 0$ [221].

For a very slow and continuous cooling to the supercooled melt (dashed line in Figure 8), the entropy of the supercooled melt would reach the same value at the Kauzmann temperature T_K ($\Delta S = S_{\text{liquid}} - S_{\text{crystalline}} = 0$) as the entropy of the crystalline phase at $T < T_K$ even assume negative values [222]. Since the liquid always has a lower order than the crystal, the supercooled melt solidifies at the latest point at T_K as the glass [223]. Thus, with the Kauzmann temperature, the theoretically achievable lower limit for the supercoolability of a melt is given. Therefore, T_K is also regarded as an "ideal glass transition temperature." On account of the high cooling rates necessary for glass formation of metallic alloys, the glass transition temperatures actually occurring are considerably higher than T_K .

As already mentioned, the volume V changes in the same characteristic manner at the glass transition as well as the entropy S . Figure 9 shows schematically the relationship between the cooling rate v of the supercooled melt and the resulting change in the glass transition temperature

T_g as well as the volume V . Thus the higher cooling rate ($v_2 > v_1$) of the supercooled melt leads to a higher glass transition temperature ($T_{g2} > T_{g1}$) and to a larger volume of the glass ($V_2 > V_1$). This larger volume due to the faster cooling can be explained by a higher proportion of free volume in the glass which is always present in the melt by the greater mobility of the atoms in liquids compared to solids and with increasing rate of solidification of the supercooled melt in this state is frozen since the system does not have time to rearrange the atoms into energetically more favorable positions [220]. At the same time, the Gibbs free energy G of the system is larger at a higher cooling rate; the glass is increasingly thermodynamically more unstable. If these unstable glasses are heated to a temperature T' (Figure 9), the volume V' will be adjusted after a time t . This is associated with a reduction in the glass transition temperature. If the system gives sufficient time for the free volume to be released, the minimum free energy G of the supercooled melt, shown in Figure 10, is reached; this means the glass goes from an unstable into a metastable state. This process is called “structural relaxation” of a glass. In the case of slow cooling and crystallization, the free energy G of the system is abruptly lowered. However, with sufficiently slow cooling, the crystalline equilibrium phases of the alloy form, and the energetically stable state of the system is adjusted.

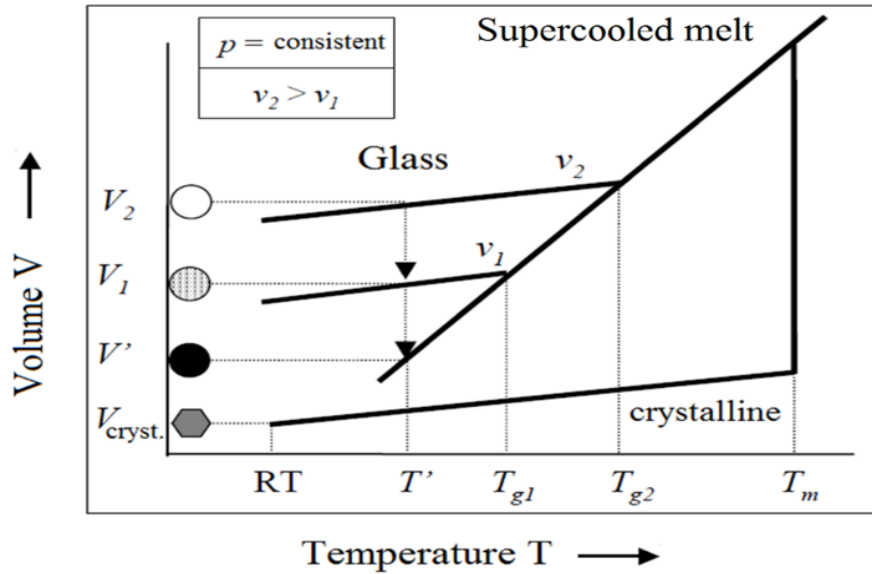


Figure 2.9: Volume V as a function of the temperature T in the range of the glass transition temperature T_g for a supercooled melt at different cooling rates v_1 and v_2 (upper curves) compared to the volume change in crystallization (lower curve) according to [202].

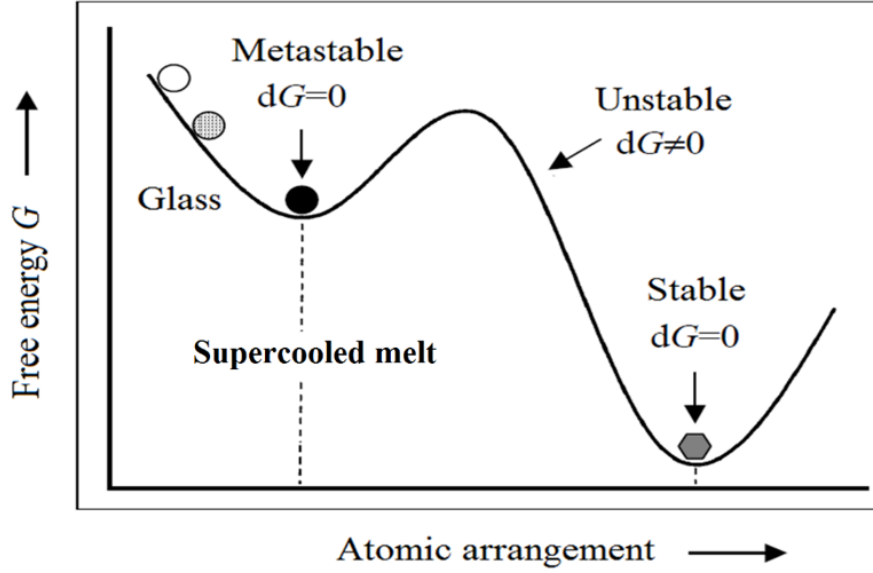


Figure 2.10: Schematic representation of the free energy G of unrelaxed (unstable) and relaxed (metastable) glass as well as a crystalline (stable) equilibrium phase [206].

The viscosity η also varies with the T_g in the typical manner. First, it increases strongly with the decreasing of the supercooled melt temperature and reaches the value of T_g which is up to 10^{15} times higher compared to the viscosity of the melt [215]. By definition, the temperature at which the viscosity η of the supercooled melt reaches the value of 10^{13} poise ($=10^{12} \text{ Pa}\cdot\text{s}$) is determined for T_g [224]. At T_g , the amorphous substances show a very different temperature dependence on the viscosity, depending on their composition [225]. In the case of amorphous materials with a very high glass forming ability such as SiO_2 , the viscosity changes only slightly with the temperature [226]. This behavior can be caused by an Arrhenius function:

$$\eta(T) = A \exp\left(\frac{B}{k_B T}\right) \quad \text{Eq. 15 [226]}$$

Where A and B are temperature independent constants and k_B is the Boltzmann constant. The glasses that have a low glass forming ability, for example, orthoterphenyl, show a marked drop in the viscosity above T_g [226]. This behavior largely follows a Vogel-Fulcher-Tamman equation:

$$\eta(T) = A \exp\left(\frac{B}{T - T_0}\right) \quad \text{Eq. 16 [226]}$$

Where T_0 is an extrapolated temperature at which the viscosity would diverge, usually called the Vogel-Fulcher temperature. If the viscosity η is logarithmically over the normalized glass

transition temperature (T_g / T), the glasses can be classified into strong (high glass formation) and fragile (low glass formation) glasses according to Angell model, as seen in Figure 11 [227]. With the degree of curvature of the viscosity curves, characterized by D_f , the ‘fragility’ parameter is determined by the following:

$$D_f = \frac{B}{T_0} \quad \text{Eq. 17 [228]}$$

The Vogel-Fulcher-Tammann equation, as well as the slope of the curves at T_g , is calculated by:

$$m_f = \left. \frac{d(\log \eta)}{d\left(\frac{T_g}{T}\right)} \right|_{T=T_g} \quad \text{Eq. 18 [228]}$$

These formulas characterize a certain glass forming ability. Therefore they are designated as fragility parameters D_f , or the fragility index m_f [229]. By introducing the minimum fragility index $m_{f \min}$ which obviously corresponds to Arrhenius behavior, D_f and m_f are given by the equation:

$$m_f = m_{f \min} + m_{f \min}^2 \cdot \ln(10) / D_f \quad \text{Eq. 19 [230]}$$

Based on this equation, the strong glasses are distinguished by the small increase in the viscosity curve, which means a high D_f value and smaller m_f value. On the other hand, the fragile glasses are correspondingly characterized by a small D_f and high m_f values. For example, one of the strongest metallic glasses alloys, the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloy, has a fragility parameter of $D_f = 22.7$ [215], and it compares quite well with the Angell plot Figure 11. At the same time, this comparison shows that glasses are often placed between both extreme proceedings of the Arrhenius and Vogel-Fulcher-Tamman behavior.

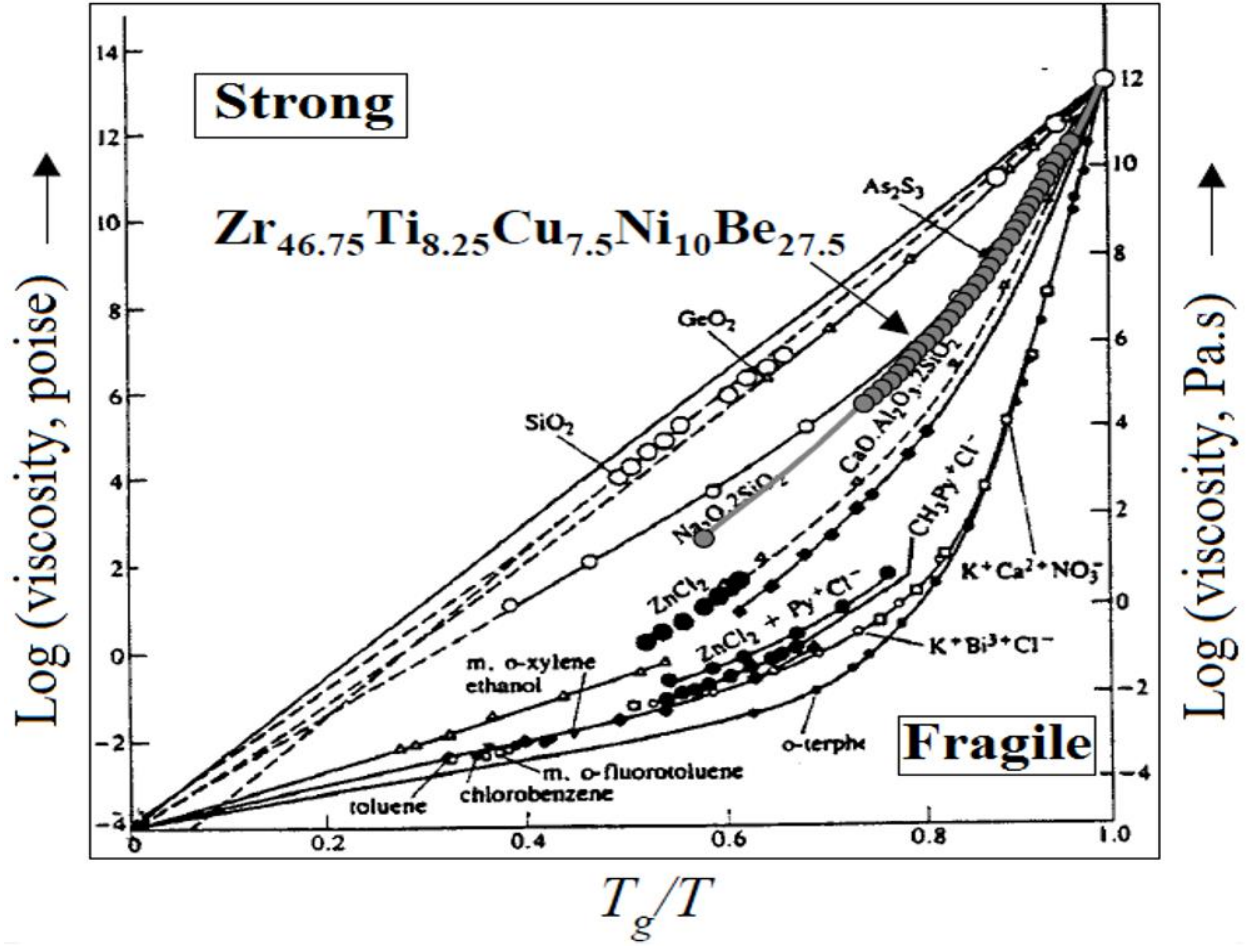


Figure 2.11: The viscosity η of different liquids as a function of temperature T above the glass transition temperature T_g and normalized. The behavior of the strong glasses follows the Arrhenius function, and the fragile glasses can be described with a Vogel-Fulcher-Tamman function [227].

The different behavior of the viscosity at T_g is generally attributed to the different kinds of the atomic bonds, because of the degrees of freedom or possibilities of the rearrangement of structural building units. Thus the stability against the crystallization depends on the bonding type between the atoms. The strong glasses are usually network formers such as SiO_2 , which means that they have strong covalent bonds. As a result, the structural changes are made more difficult. In contrast, fragile glasses have weaker atomic bonds, due to the low localization of the electrons such as the metallic bonds or van der Waals bonds [208]. However, the metallic glasses with a higher thermal stability against the crystallization are stronger glasses formers because of the high packing density of the atoms, owing to a strong restricted atomic mobility. This process leads to the formation of locally preferred structures (clusters) which have high strength interatomic bonds [231].

To date, the glass transition in its entirety (thermodynamic and kinetic aspects) has not been fully understood and is controversially discussed in the literature. The most important models for the description of the glass transition are the free volume theory, cooperative relaxation theory, and mode-coupling theory. However, the free volume theory describes the supercooled melt by a 3-dimensional system of hard spheres, with each sphere being assigned a mass center which has a certain space of free volume V_f [232]. Diffusion can only take place if at least as much free volume V_f^* is present in the vicinity of a molecule as is required for the diffusion step. By distinguishing between the liquid-like regions ($V_f > V_f^*$) and solid-like regions ($V_f < V_f^*$), a critical free volume corresponding to the glass transition is concluded. Moreover, the free volume theory leads to the Vogel-Fulcher-Tamman equation by assuming a temperature dependence of the free volume as in Equation 16. Furthermore, the free volume theory describes the glass transition as a first-order phase transition. In contrast, the cooperative relaxation theory sees the glass transition as second-order phase transformation, due to the cooperative configuration transformations of molecules (derived for polymers) as a function of entropy [233]. This is based on the assumption that the molecules in the material with a high packing density can only move when other molecules move along ("cooperativity" within a range of molecules). While the mode-coupling theory is based on the system of oscillating molecules, which can be described as damped harmonic oscillators [234-236]. An additional memory term describes the effect of the previous history on the density fluctuations and thus the local oscillatory capacity of the system. The property changes of the glass when approaching a critical temperature T_c are explained in this theory by changes of the temporal (an increase of the influence of the attenuation leads to increasing relaxation times).

2.2.4 Crystallization

Upon heating the amorphous phase, crystallization is based on the same physical principles as crystallization upon cooling a melt, which means that the driving force for crystallization is the difference between the free energy of the amorphous phase and crystalline phase [237], based on Equation 1. On the other hand, the nucleation and crystal growth processes, including homogeneous and heterogeneous nucleation, are also based on the same mechanisms in both cases. Thus, the difference between crystallization by cooling a melt or by heating the amorphous phase is mainly due to the different temperatures at which the phase transformations take place. Since the crystallization of the supercooled melt takes place at significantly lower temperatures during the heating process than the crystallization during the cooling of the melt, the viscosity of the two

liquids and the diffusion speed are very different, based on Equation 12. In addition, the crystallization of the amorphous phase differs from the crystallization of the melt by the occurrence of stress terms.

On a count of that criteria, Figure 12 schematically shows a temperature-time conversion (Time-Temperature-Transformation) diagram for continuous cooling, or heating process. Furthermore, it provides information about the phase formation of a system at different cooling and heating rates [207]. The amorphous state is achieved by a sufficiently high cooling rate and referred to as a line **(a)**, as seen in Figure 12, so that the "nose-like" course, which marks the beginning of α -crystallization, must not be crossed. The crystallization of the material, represented by line **(b)**, and takes place by heating the amorphous phase up to the crystallization temperature T_x , with a defined heating rate v . As shown in Figure 12, the amorphous phase first transforms into the thermally unstable crystalline β phase, while, the equilibrium phase α is reached only in a second crystallization step (at a higher temperature). The crystallization of the amorphous phase can also be affected by isothermal heat treatment at a temperature $T < T_x$ and a time t_x dependent thereon.

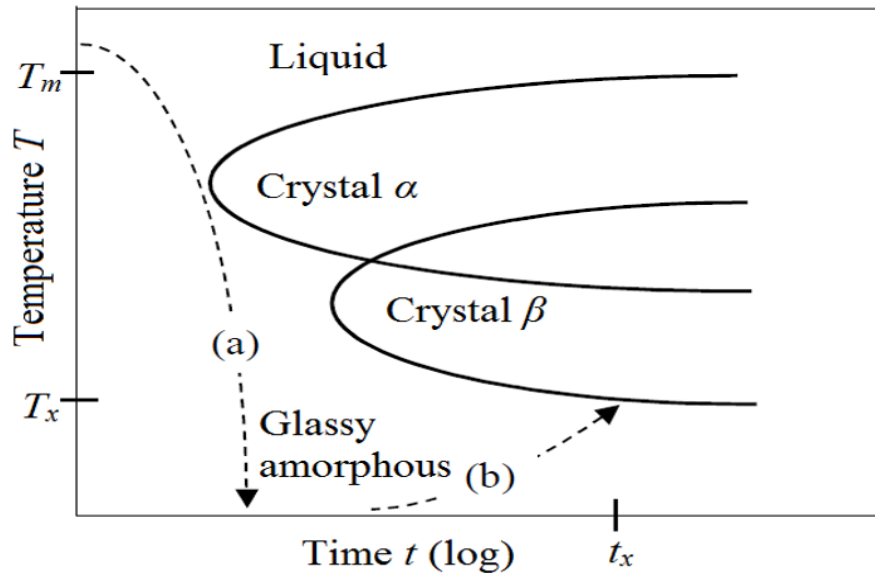


Figure 2.12: Schematic representation to the illustration of the phase formation for the continuous cooling and heating: (a) rapid cooling, leading to amorphous formation, (b) crystallization by slow heating of the amorphous [237].

As mentioned, the crystallization of metallic glasses depends on various mechanisms, depending on the thermodynamic and kinetic aspects. Therefore, the distinction is made between polymorphic transformation, eutectic crystallization and primary crystallization, and frequently a combination of the mechanisms is also found. However, on the basis of the schematic diagram shown in Figure 13, the various possibilities of the transformations as a function of the free energy G of the respective phases are described below [237].

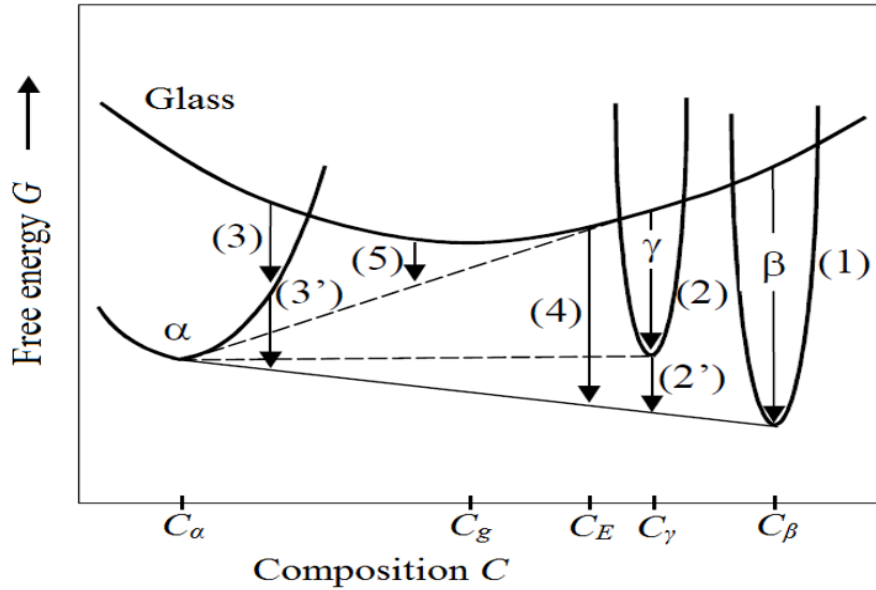


Figure 2.13: Schematic representation of the possible phase transformation of glass as a function of the free energy G : (α : mixed crystal, β : intermetallic phase, and γ : metastable phase). The numbers **1** to **5** characterize the various transformation modes. The solid compound line marks the stable equilibrium, while the broken lines characterize metastable equilibria [237].

2.2.4.1 Polymorphic Crystallization

Polymorphic crystallization is a phase transformation in which the resulting crystalline phase has the same composition as the amorphous starting phase. However, referring to Figure 13, this resulting crystalline phase can be a stable β with reference to **(1)**, or metastable γ with reference to **(2)**, the intermetallic phase in Figure 13. However, it could also be a highly supersaturated mixed crystal α with reference to **(3)**. Since neither the metastable γ phase nor the supersaturated α -mixed crystal reaches the stable equilibrium of the system in the first step of the transformation, these

two phases can be mixed with $c_\alpha + c_\beta$ in a second step of the conversion into the two equilibrium phases (reactions **2'** and **3'**).

In the alloy systems of low glass forming ability, which are mostly confined to the eutectic composition, the polymorphic transformation towards an equilibrium phase has not yet been observed. This is particularly due to the compositions in the stability range of an intermetallic phase, in the contrast to those in eutectic compositions. Consequently, they are characterized by a high driving force for crystallization, whereas no long range diffusion is required for the formation of a critical nucleus [238].

2.2.4.2 Eutectic Crystallization

Meanwhile the eutectic transformation is based on the diffusion controlled demixing of the glass phase [208]. Also, with reference to Figure 13, at the eutectic temperature T_E and a specific composition (the eutectic concentration) c_E , the two crystalline equilibrium phases of different concentrations (c_α and c_β) are formed simultaneously. However, the formation and growth of the equilibrium phases α and β result in a lowering of the free energy of the system up to the tangent which connects α and β (reaction **(4)**), as seen in Figure 13.

2.2.4.3 Primary Crystallization

The primary crystallization by precipitation of an intermetallic-phase, a quasicrystalline phase or a supersaturated mixed crystal of the concentration c_{al} (**with** $c_{al} \neq c_\alpha \neq c_\beta$) is shown in Figure 13 based on reaction (5). As a result of the precipitation (e.g. of the mixed crystal), the concentration of the glass phase changes by depletion of certain elements, and, at the same time, the concentration of the remaining constituents increases. This process continues until the glass phase, either the eutectic composition or the composition of another intermetallic compound is reached, so that the conversion is continued according to one of these mechanisms. Moreover, the morphology of the primary crystals is very different and obviously strongly dependent on the composition of the crystal. For example, in the alloy of $Zr_{55}Cu_{30}Al_{10}Ni_5$, a spherical lenticular shape and dendritic crystallites are found on the basis of primary crystallization [239], which differ only slightly in their composition. The reason for the different shape of the primary crystals is seen above all in the interfacial energy of the growing seed, such that a high interfacial energy results

in spherical primary crystals, while a low interfacial energy is associated with amorphous/crystalline instabilities and leads to dendritic growth [237].

Regardless of the type of crystallization occurring, some of the alloys already show a demixing of the supercooled melt below T_x into two amorphous phases (phase separation) of different compositions [218, 240 and 241]. This phase separation can, on the one hand, be based on the nucleation processes which originate in thermal fluctuations of the matrix [242]. In this case, the composition of the nuclei is strongly deviated from the concentration of the matrix phase. Thus the demixing takes place between c and c' of the $G(c)$ curve, as shown in Figure 14. Subsequent nuclei growth occurs by "normal" diffusion, which means that the diffusion proceeds in the direction of lowering the concentration ("downhill diffusion"). On the other hand, the demixing without nucleation can occur, if the composition of the matrix phase between the turning points ($d^2G/dc^2 \leq 0$) take place on the free energy curve, i.e., between c_s and c'_s of $G(c)$ curve, such as c_{AB} as shown in Figure 14 [208].

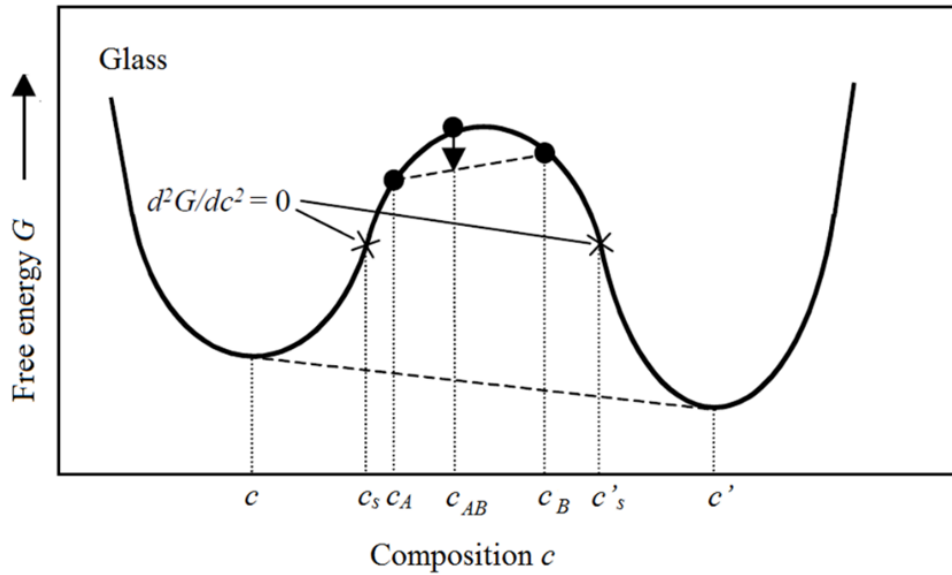


Figure 2.14: Schematic representation of the change in the free energy G as a result of demixing, and the phase separation due to the nucleation and growth taking place between c and c' instead, spinodal decomposition occurs between c_s and c'_s [208].

In the case of spinodal decomposition, the separation is also spinodal (spontaneous). The free energy of the system is reduced by the demixing (see tangent between c_A and c_B in Figure 14). The progressive of the separation is associated with an increase in concentration fluctuations and

continues until the equilibrium take place, which is the minimum point of the free energy. In the case of the spinodal decomposition, the diffusion occurring at the spinodal demixing runs opposite to the concentration gradient ("peak diffusion").

In addition to the formation of crystalline phases, the formation of a metastable quasi-crystalline phase in the first step of the transformation towards the equilibrium state is frequently observed in the glasses [243-246], which means the quasi-crystalline state of these alloys is characterized by free energy, which is located between the glass and the crystalline state.

2.2.5 Properties of Bulk Amorphous Metals Alloys

Since the discovery of the first metal amorphous alloy in the 1960s as seen in the historical review of the amorphous metals alloys section, metallurgists and researchers have tried in many different ways to produce amorphous alloys in huge quantities, using less energy and expense, so that they could be used in different applications. Metallurgists and researchers had pushed for the production of huge quantities of such amorphous metallic alloys precisely because they exhibited promising attributes in their microscopic properties in mechanical, magnetic, physical, and other properties. In contrast to crystalline metals, amorphous metals contain no crystal defects such as grain boundaries, dislocations, excretions of other phases, etc., in contrast to the properties of conventional metallic alloys [8].

Amorphous metals, as well as crystalline alloys, have metallic strength and, to a certain extent, metallic ductility. However, as already mentioned, the amorphous structure and the absence of crystal building blocks always present in crystalline solid bodies often require particularly favorable property combinations. For example, the very high yield strength that bulk metallic amorphous alloys show, compared with the crystalline pure metals and alloys, is one of the direct results of the unique microstructure of bulk metallic amorphous alloys [217]. Figure 15 shows a comparison between the yield strength (σ_y) and the Vickers hardness (H_v) as a function of Young's modulus (E) for the bulk metallic amorphous alloys and crystalline metallic alloys [217]. It is clear from Figure 15 that the strength and hardness of the bulk metallic amorphous alloys are several times higher than that of traditional engineering metals such as steel. This upturn in the mechanical properties of bulk metallic amorphous alloys that is shown in Figure 15 is due to the fact that with the random distribution of atoms, there are not groups of atoms that can easily move because they are gridlocked in the amorphous structure [247]. In other words, the lack of slip systems in the

metallic amorphous substances is beyond the high tensile strength in amorphous metals, which is the main cause of the plastic deformation [13, 248 and 249]. To give an illustration of what the slip systems and plastic deformation mean, let's look at the case of conventional grained metals, dislocation slipping in individual grain, and they cannot cross the grain boundary: this is slip band or slip systems [250-252]. However, in amorphous metals, plastic deformation is always induced by the shear deformation bands, without the influence of crystalline orientation or grain boundary. These bands are shear bands and they are highly plastic regions that form in amorphous metals during high uniaxial tensile stresses [10, 139]. These shear bands form characteristic voids and vein patterns which flow rapidly through amorphous metals due to the lack of grain structure leading to catastrophic failure [10, 139 and 253]. Moreover, metallic glasses have a very high mechanical resistance at room temperature with interesting toughness. However, most metallic glasses have a catastrophic failure without significant plastic deformation [254, 255]. Figure 16 shows a diagram based on the Ashby diagram and represents the relationship between the mechanical resistance and toughness for different materials at room temperature [256].

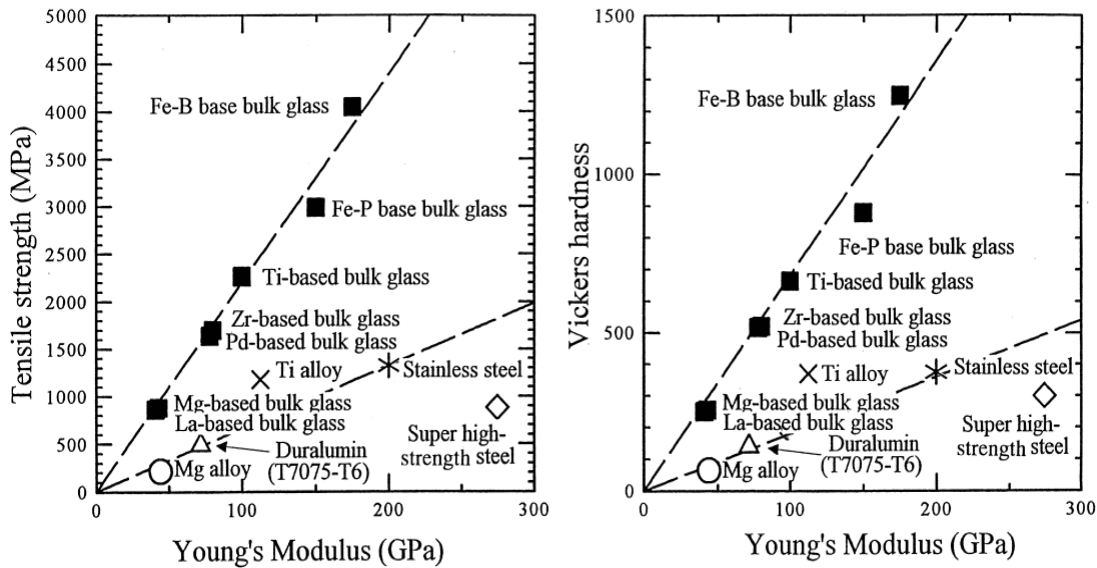


Figure 2.15: (a) Tensile strength and (b) Vickers hardness vs. Young's modulus for various crystalline and bulk amorphous metals [217].

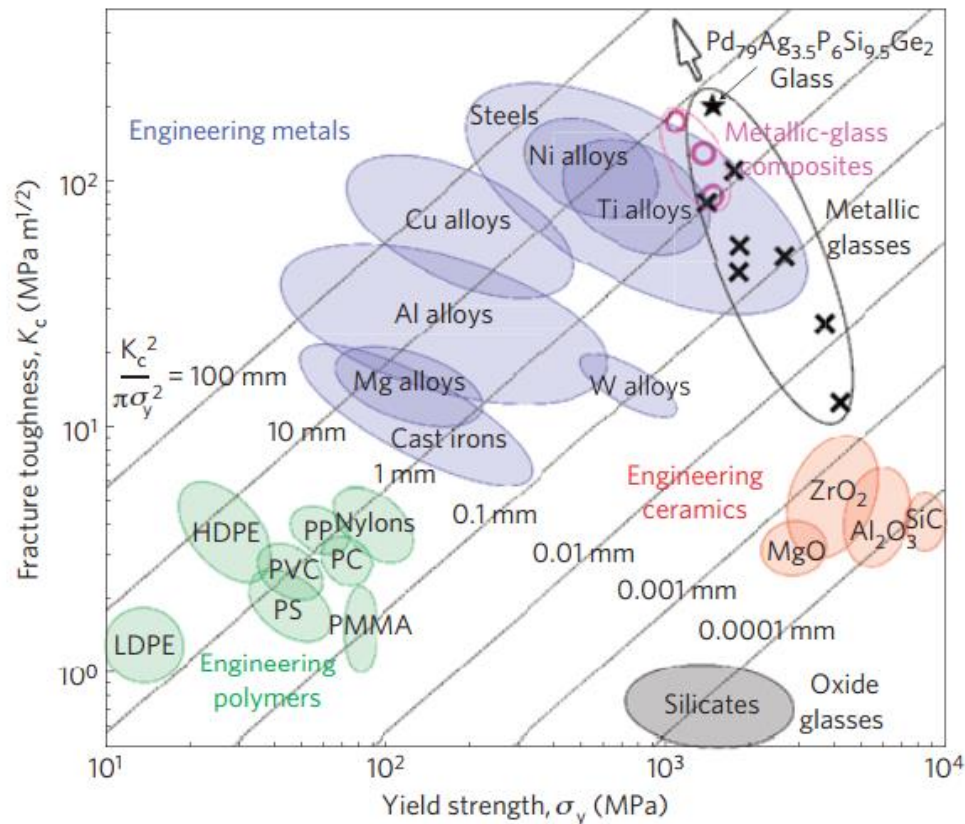


Figure 2.16: Ashby diagram of the damage tolerance in form of yield strength versus fracture toughness (K_C or K_{IC}) of engineering materials [256].

As shown in the toughness vs. strength diagram, the present metallic amorphous alloys appear outside and higher than the domain that was made by the strongest and toughest steels. In summary, the present results demonstrate that the combination of toughness and strength (i.e., the level of damage tolerance) potentially accessible to amorphous materials extends beyond the traditional limiting ranges towards levels previously inaccessible to any material. In addition, regarding corrosion resistance, most of the bulk metals amorphous alloys exhibit good corrosion resistivity [10, 13, 248 and 249]. The excellent corrosion resistance of the metallic amorphous alloys is mainly attributed to the homogeneous single amorphous phase [257-258]. In general, the lack of crystallographic defects such as grain boundaries, dislocations, and other defects where corrosion can occur preferentially are expected to lower the local corrosion susceptibility of amorphous metals, compare with the crystalline metals. However, this chemical homogeneity in the metallic amorphous alloys is obtained through the rapid cooling rates that have been used during the

amorphization process, so to produce a full amorphous structure, especially since not enough time is available for solid-state diffusion, the second phases, precipitation, or segregations are impossible to form. On other hand, the homogeneity in chemical composition and microstructure enhances amorphous oxide formation on the surface, which impedes ionic transport. Thus, the effect of the amorphous structure, chemical and structural homogeneity, and the possibility of forming a unique chemical composition, which is not typical of near-equilibrium crystalline alloys, are mostly considered as factors that can affect the corrosion properties of the metallic amorphous alloys. In addition to corrosion resistance, the metallic amorphous alloys have high wear resistance [260-263], which makes using the metallic amorphous alloys promising in applications where the erosion–corrosion resistance is important. In conclusion, bulk metallic amorphous alloys are among the materials that have good mechanical properties with exceptionally high yield and fracture strength, high fatigue strength, high fracture toughness, large elastic elongation, high hardness, high corrosion resistance and wear, high glass-forming ability, good castability, and good machinability.

The bulk metallic amorphous composites are another key thing that invites attention. In recent years, much work have been done to introduce the metallic amorphous to the composite microstructures to suppress the fracture while preserving the high strength, which typically combine a strong metallic amorphous with a ductile crystalline matrix reinforcements, or vice versa, to increase the strength, hardness and wear resistance of the ductile crystalline matrix [264-276]. Traditionally metal matrix composites (MMCs) are produced from metal matrices reinforced by the ceramics particles or fibers such as Al_2O_3 or SiC to enhance their mechanical properties [277-282]. But in this case and with the significant differences in the thermal coefficients expansion, chemical and physical properties between the metals and ceramics, typically induce poor bonding, where detrimental interfacial reactions often occur [283-287]. However, ceramics come with low wettability by the metal matrix, which generates particle agglomeration and porosity as well [288-291]. With respect to the good bonding between the metallic matrices and the reinforcements and good mechanical properties, many researches these days are using the metallic amorphous as reinforcements to the metallic matrices, and vice versa, where the metallic nature of the reinforcing phase plays an important role in achieving a good bonding between the matrices and the reinforcements, by creating a suitable thermal coefficient of expansion, and compatible chemical and physical properties [264, 265, 269, 272, 281and 283].

With regard to the production, development and application of the metallic amorphous composites, much research work has been conducted and more is still underway to date, designed to improve the metallic amorphous composites in terms of structure and application as well.

Another interesting attribute in the bulk metallic amorphous alloys is their electrical resistivity. The bulk metallic amorphous alloys are indeed metallic in their electrical conduction, but they can have very high resistivity because of inelastic scattering [292-296]. Due to their intrinsic disordered structure, metallic amorphous glasses exhibit a relatively high electrical resistivity compared with their metallic crystalline counterparts [292, 297]. However, the electrical transport properties of metallic amorphous alloys differ considerably from the electrical transport properties of ordinary crystalline metals. They are typically characterized by high resistance, 100 – 200 $\mu\Omega\text{cm}$ at room temperature [292]. The ordinary crystalline metals have a positive temperature coefficient of resistance (TCR) ($\alpha = (1 / \rho)d\rho / dT$, where ρ is the resistivity at temperature T), and their resistance is increased by an increase in temperature [297].

On the other hand, metallic amorphous alloys have a negative temperature coefficient of resistance (in range of $\pm 10^{-4}\text{K}^{-1}$) [292]. The relative change in resistance with temperature is very small in metal amorphous glass and is only a few percent in the temperature range of 20-300K [292]. Obviously, the difference in the behavior of the electrical resistance of ordinary crystalline metals and metal amorphous glasses is due to the difference in structure. However, the random atomic arrangement structure and temperature independent in the metal amorphous glasses accelerates the increase in the scattering of conduction electrons which leads up to high electrical resistivity [292, 297]. In ordinary crystalline metals, the resistance is well described by Drude's model [298, 299] or Boltzmann's model [297, 300], based on the assumption that the mean free path of the electron is much greater than the wavelength of the electron. Such assumptions, in the case of metal glass, are no longer satisfactory because of the random atomic arrangement and the effects of interference due to the wave nature of the electrons generated. On account of that, Mooij [301] has reported that the amorphous transition metals have a larger residual resistivity (ρ_0) than that of the crystalline phase, arising from a high disorder in the structure, and are comparable to the corresponding liquid alloys. Generally, Mooij has summarized the situation as follows: If $\rho_0 < 150 \mu\Omega\text{-cm}$, the temperature coefficient of resistance is small and positive, but it is negative when $\rho_0 > 150 \mu\Omega\text{-cm}$. Thus, it can be concluded that the connection between the high resistance

and the negative temperature coefficient of resistance comes from the interference effects resulting from a reduced electron free pathway. Therefore, because of their insensitivity to temperature variations, metallic glasses are suitable for applications in electronic circuits for which this property is an essential requirement [292].

The other important and interesting property to the bulk metallic amorphous alloys is their soft magnetic properties. However, this soft magnetic property is characterized by a low coercivity, resulting from the absence of any crystalline structure and no magnetocrystalline anisotropy; it is also due to the lack of the dislocations and grain boundaries, which, for crystalline materials, hinder domain wall motion [302]. Therefore, the bulk of metallic amorphous alloys with these magnetic properties has undoubtedly played a central role in the process of rapid technological innovation and evolution during the last 50 years.

Since 1967, when Duwez and Lin published their first report [33] about the good ferromagnetic properties that they obtained from the melt-spun ribbons of an Fe-P-C system, a large number of studies and a great deal of effort has been spent on investigating the magnetic properties of bulk metallic amorphous alloys [99,101,105,107,109,110, 135-137, 147, 150, 151, 153, 185, 198 and 201]. Looking at these significant efforts, the constant preoccupation of the researchers was to look for advanced bulk metallic amorphous alloys with high glass forming ability, super high strength and excellent magnetic properties. These properties were difficult to obtain simultaneously because complexity due to the necessity of high cooling rates. The most significant achievement after Duwez and Lin's work was done in 1995 by Inoue and Gook, who announced the possibility of producing bulk metallic amorphous alloys from the systems of the $\text{Fe}_{72}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_6\text{B}_4$ [303] and $\text{Fe}_{72}\text{Al}_5\text{Ge}_2\text{P}_{11}\text{C}_6\text{B}_4$ [304], possessing a high quality soft magnetic properties. Since then, using the three component empirical rules a variety of Fe-based, Co-based and Ni-based bulk metallic amorphous alloys have been produced, and as expected they have demonstrated unique properties compared to the crystalline counterparts. [217].

On the other hand, the bulk metallic amorphous alloys also have showed hard magnetic properties in addition to the soft magnetic properties [305-311]. Croat in 1981 [312] reported that the amorphous of a Pr-Fe alloys system, prepared by spin melting showed a high coercivity at 20K and that can make these alloys to be as hard magnetic materials. Also in another work, Nagayama et al. [313] observed that the coercivity of the amorphous Nd-Fe alloys system, quenched onto a

rotating copper roll, increased by increasing the Nd content. Additionally, Inoue et al. in another work on a Nd-Fe-Al system in 1996 reported that a hard magnetic amorphous alloy was created by using a copper mold casting method [314], and from the results Inoue concluded that the homogeneous dispersion of the Nd-Fe-Al clusters with the large random magnetic anisotropy could be responsible for the high coercivity and hard magnetic properties. Nevertheless, the work that has been done on the hard magnetic properties of the bulk metallic amorphous alloys is still very little compared to the work done on the soft magnetic properties. Since then, the magnetic bulk metallic amorphous alloys have been widely investigated and used in many different applications. In terms of the low coercive force and high magnetic permeability applications, the soft magnetic bulk metallic amorphous alloys has been exploited in different fields of applications such as cores, transformers, cantilevers, sensors and others [215, 315 and 316]. As an example of that, the bulk metallic amorphous alloys of the Licalloy TM [317], based on Fe-Cr-(P, Si)-(B, C), and SENNTIX [318], based on Fe-Cr-Nb- (P, Si)-B are used for induction cores. On the other hand, the hard magnetic bulk metallic amorphous alloys such as Nd-Fe-Al [319], Pr-Fe-Al [320] and Sm-Fe-Al [321] were used in the applications of the recording disks, actuators, and permanent magnetic motors, etc. [319]. Lastly, efforts are still being spent on research to improve the performance of the magnetic bulk metallic amorphous alloys so that they can be used in commercial microdevices.

On order to produce metallic amorphous alloys and also from the onset of the research in this field, a big challenge that scientists and metallurgists have been facing during the last 60 years has been producing bulk metallic amorphous alloys in large sizes, so that they can be used in several different applications. Thus, several theories and methods with different strategic and systematic approaches have been aimed at increasing the thickness and diameter of amorphous metallic alloys, but it has been a difficult and complicated task. In view of that, it is clear from Loeffler's overview about the critical casting thickness of the amorphous metallic alloys and the date of the discovery that the efforts at extending the amorphous metallic alloys bulk size has been difficult and progressing slowly, as shown in Figure 17 [11]. To that end, a mechanical alloying process has been used as one of these methods and approaches to solve this issue [10, 28 and 322]. However, the mechanical alloying technique can produce a large amount of amorphous metal powders, which can be compacted and sintered in the desired sizes, shapes and dimensions for practical applications, using a rapid sintering technique such as spark plasma sintering (SPS) [323].

Essentially, the SPS technique is based on direct current (DC) pulses which apply simultaneously with the pressure on the powder compact to realize a rapid sintering within a short sintering time in order to suppress or limit the crystallization events [324-326]. However, the metallic amorphous alloys that are produced by the mechanical alloying technique have wider compositional ranges of the amorphous phases compared with the rapid solidification technique. To give an illustration, the mechanical alloying technique generally produces amorphous phases around the equiatomic composition, while the rapid solidification technique is usually around deep eutectic compositions [322]. This unique capability of mechanical alloying is a good reason for choosing mechanical alloying as a processing technique for this work.

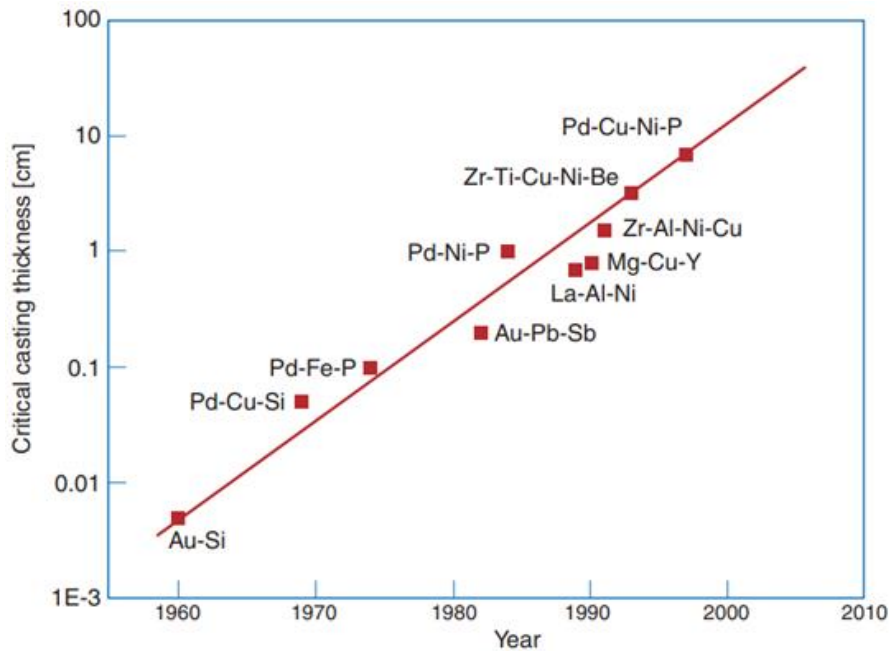


Figure 2.17: The critical casting thickness for the glass formation as a function of the year the corresponding alloy has been discovered [11].

2.3 Metal Matrix Composites

Metal matrix composites (MMCs) have been widely used in engineering applications in the last five decades, but humans have known composite materials since ancient times. For example, one of the earliest uses to the composites dates back to the 1500s B.C., when early Egyptians used a mixture of mud and straw to create strong and durable buildings [327]. In general, composites are materials that are combinations of two or more organic or inorganic components. One material serves as a "matrix," which is the material that holds everything together, while the other material

serves as reinforcement, in the form of fibers, particles or phases embedded in the matrix. The matrix holds the reinforcement to form the desired shape, while the reinforcement improves the overall mechanical properties of the matrix. When designed properly, the new combined material exhibits better strength than would each material separately [328- 330]. The concept of composites is not a human invention. For example, wood is a natural composite material consisting of one species of polymer-cellulose fibers with good strength and stiffness in a resinous matrix of another polymer, polysaccharide lignin [328]. According to a study in 1973, around 80% of the research and development in composite materials has been done since the early 1960s [331]. For almost 60 years, scientists have focused on trying to understand the concepts of composite materials made up of a reinforcement such as fibers, particles, flakes, phases, and/or fillers embedded in matrixes of the polymers, metals, or ceramics, and develop these composites to use in different applications [329, 332]. Metal matrix composites (MMCs) had a large share in this research on different applications, including the aerospace and automotive industries, electronic systems, medical products, civil construction, chemical industries, and consumer appliances [332-334].

The MMCs are defined as a class of artificial materials, consisting of continuous or discontinuous reinforcements including fibers, whiskers, particles, or phases dispersed in a metal (e.g., aluminum, copper, titanium etc.), or metallic alloy matrix. MMCs can be synthesized by many different methods such as powder metallurgy, diffusion bonding, infiltration, and stir casting processes. As a result of this new structure, the MMCs exhibit not only a high specific modulus, high specific strength, good thermal conductivity, good electrical conductivity, controllable thermal expansion coefficient, and excellent high temperature performance, but also designability and machinability. Therefore, they are an important class of advanced engineered materials in different applications and especially in the aerospace.

The concepts of metal matrix composites can be dated back to the 7000s B.C. where human beings in that time used copper awls made from a layered structure of copper reinforced by oxide inclusions [332]. They used the forging, hammering and welding processes on copper to create strong and durable awls. Characterization of those copper awls has showed a copper matrix enhanced by oxide inclusions, and structurally they are composites resulting from manufacturing processes; in this case they considered as copper matrix composite materials.

Another example of a metal matrix composite is ductile iron that was invented by Keith Millis and his coworkers at International Nickel Company Research Laboratory in the early 1940s [335]. By looking into the ductile iron microstructure, normally a composite microstructure will be found, consisting of spherical graphite particles embedded in an iron matrix [336, 337]. In general, the ductile iron is made by adding magnesium to the molten iron where magnesium changes the surface tension mechanism of the molten iron and precipitates the carbon out as small spherical particles, instead of flakes, thus making the iron casting more ductile [335]. However, it became clear that graphite takes a place on spherical shape by adding magnesium, or in some cases rare earth elements such as cerium and lanthanum to the base liquid metal, which gives rise to a melt with a low content of sulfur and oxygen [338]. As an outcome of this structure, ductile iron has shown a combination of relatively high tensile strength and significant ductility, compared with a gray iron with comparable strength [339]. This improvement in ductility in iron is due to the spherical shape of the graphite, which has a lower stress concentration factor than the sharper angular boundaries of flake graphite [339]. Notably, the ductile iron provides a good example of metal matrix composite involving the use of metal ferrous matrix, which typically contains ferrite, pearlite or a combination of these two phases into a so called “ferritic-pearlitic” matrix. While ferrite has low strength but high ductility, pearlite is strong and brittle, and, by combining it as composite, leads to a new material with better mechanical properties. Consequently, the ductile iron is, after all, an ancient example of an *in situ* composite produced directly from the melt, so it can be considered one of the first composite materials that was developed by a modern industry. Thus, in view of these rules of interpretations that define the ductile iron as an *in situ* metal matrix composite, there are many other materials that can be handled from the same point of view, and expounded by the same concept to the ductile iron matrix composite. For example, the aluminum silicon eutectic alloy is another example of an *in situ* composite which is composed of silicon needles embedded in the aluminum matrix [340]. Also, pearlite represents a lamellar composite structure which could be classified as metal matrix composite material too, because it is an intimate mixture of lamellar cementite in a matrix of ferrite.

Another example is dual-phase steels where a hard martensitic phase is embedded in a soft ferrite matrix [341]. On the other hand, the ultrahigh carbon steel after appropriate heat treatment can be considered as another example of the metal matrix composite material, with a composite structure consisting of hard cementite particles reinforcing a ferritic matrix [342]. Thus, after the

matrix metal composite has exhibited good mechanical properties compared with metals, much work has been done to improve the service performance of the metals by reinforcing their matrices and so to enhance their strength and stiffness and satisfy the requirements of the engineering applications, especially the space technology development.

As was seen in the historical background of the metal matrix composites, the ideas and methods of the metal matrix composites go back thousands of years. However, let's look at the metal matrix composites more closely. From the definition of a metal matrix composite as previously stated, it is a material in which a continuous metallic phase (the matrix) is combined with another phase (the reinforcement) to strengthen the metal in its mechanical properties and improve the physical properties, so long as metal matrix composite systems consist of two phases or more. They may be confused with the alloys. However, the second phase or the reinforcement in the metal matrix composite forms as a particulate, eutectic or eutectoid reaction, etc. and commonly the metal matrix composite starts as separate components, i.e., the metal matrix and the reinforcement. According to the shape of reinforcements, the metal matrix composites can be classified to dispersion strengthened, particle reinforced and fiber reinforced. However, dispersion strengthened is a composite microstructure consisting of an elemental matrix within which fine particles are uniformly dispersed with a diameter ranging from about 0.01 to 0.1 μm , and a volume fraction of particles ranging from 1 to 15% [343, 344]. In contrast, the particle reinforced composite also consists of dispersed particles, but in this case the particles have diameters greater than 1.0 μm and volume fraction of 5 to 40% [343, 344]. As a complete contrast, the fiber size in the reinforced metal matrix composites have a wide range of diameters typically in the range of 0.1 to 250 μm in length to continuous fibers, and in volume, from a few percentage points to greater than 70% [316]. Under these three main categories of the metal matrix composites and other subdivisions, researches began to focus on metal matrix composites in the early 1950s, but the space race and the aerospace industry in the late 1960s greatly boosted the growth of the metal matrix composites. The end result was an exponential increase in research projects on the metal matrix composites in the academic and industrial communities from that time until today.

The dispersion strengthened alloys are considered the as the first modern metal matrix composites which were developed based on Schmidt's patent in 1924 [345]. However, Schmidt in this work reported that mixtures of aluminum and oxide powders after consolidation exhibited

much higher hardness values than those of cast aluminum. Schmidt's work during that time didn't initiate further research until the space race began in the 1950s and 1960s, where extensive research projects were developed [346]. During that time, scientists began looking for high strength materials to use in aerospace applications, and the dispersion strengthened alloys were one of those materials that met the aerospace industry requirements. The principles of the strengthening mechanisms in the dispersion and precipitation hardening processes were working through impeding the dislocation motion with particles. However, small hard particles less than $1\mu\text{m}$ in diameter and non-shearable precipitates were embedded in a matrix to provide a non-coherent interface in order to impede the dislocations movement, leading to the strengthening of the matrix through the Orowan looping strengthening mechanism [347]. This mechanism can be described mathematically based on the circumvention of a moving dislocation around a dispersoid. In consequence, the dispersoid size plays an important role; in this case, the primary objective is to minimize the space between the particles [332]. However, increasing the interparticle spacing makes the dislocations freer to move which leads to less strengthening, while a low volume fraction calls for better ductility performance. In contrast, up to 15% volume is used for high temperature and higher creep resistance applications. However, in this case dislocations should climb over the dispersoids by diffusive processes. Therefore as the dispersoid size increases, the creep rates decreases and a higher creep resistance is achieved [332].

By the early 1960s, the continuous fiber reinforcement technology in metal matrix composites had begun, where researchers focused mainly on aluminum and copper matrix composites reinforced with tungsten, boron and other fibers to meet the needs of the aerospace industry [348]. However, producing lightweight materials combining different properties such as high strength and stiffness, high temperature resistance, low co-efficient of thermal expansion and high thermal fatigue was big challenge in that time. Therefore, the principal target in these studies was to produce materials that could be used in the aerospace applications. As an example of that, the boom/waveguide in the Hubble space telescope in 1967 was made of a metal matrix reinforced with fibers used in space applications, made from an aluminum alloy and carbon fibers [332].

To get back to the historical development of the continuous fiber reinforcements technology, the initial results of the researches on the fiber-reinforced metal composites were very promising. For example, Whitehurst et al.'s work in 1958 [349] was one of the earliest examples of reinforcing

metals, by using fiberglass to reinforce the aluminum matrix. Jech et al. also did work on the fiber reinforced composite which was represented in the reinforcement of titanium matrix with molybdenum fibers [350]. McDanel's work in 1960 [351] was another example of the earliest work on the reinforced metals. In this work, the copper matrix was reinforced with tungsten fibers, and the main goal of this study was to explore the fundamentals involved in reinforcing materials. According to the results, the copper matrix composite showed excellent reinforcement at room temperature. Meanwhile, Dean worked on reinforcing the nickel-base superalloys obtained by conventional casting with tungsten wires [352]. Subsequently, many research projects were launched in which the goal was to combine metals matrices and fiber reinforcements in different ways, provided their high chemical inertness, high shear strength and high resistance at elevated temperatures were retained. Thus, researchers experimented with different types of matrices including iron, chromium, nickel, zirconium, aluminum, etc., while they used fibers such as tungsten, aluminum oxide, silicon carbide, boron and glass as reinforcements.

In the continuous fiber reinforcement systems, the strengthening mechanism was based on transferring the load from the matrix to the fibers. However, the aim of embedding the high strength fibers in the matrix was to carry the load that the material could be exposed in the work site. On the other hand, the matrices were used in order to hold the fibers together and distribute the loads among them. Therefore, the new product properties (of composite materials) were determined by the properties of the fibers that had been used, while the matrices were chosen according for their density or corrosion resistance or some other property. In the continuous fiber reinforcement systems usually used reinforcing fibers with diameters ranging between 5 μ m to 150 μ m and with volume fractions of up to 80%, the composites were characterized by the excellent axial performance [332]. However, the fibers provided a maximum strength along their direction of alignment, while they were considerably weaker along the other directions and were therefore highly anisotropic. Inasmuch as the continuously reinforced composites exhibited excellent axial performance during that time, the amount of research was diminished during the 1970s, largely for reasons of high costs and production limitations such as machinability making these materials unsuitable for many potential applications [332, 353 and 354]. Yet, the continuing need for the lightweight materials to have high strength and stiffness, high temperature resistance and low coefficient of thermal expansion as well as high thermal fatigue required a new technology to meet this purpose. This need led scientists and researchers to develop discontinuous fiber composite

technology instead of the continuous fiber reinforced composites, leading to the development and better use of more effective material composites [332, 353 and 355].

During the 1980s, the discontinuous fiber reinforced composite technology achieved a rapid, and widely successful set of accomplishments in areas of both research and industry [332]. Indeed, the low cost, high workability, and better mechanical performance were factors in the renaissance of the discontinuous reinforcements, making them the most commercially attractive systems for many applications. Consequently, the discontinuous reinforcements such as short fibers, whiskers, and particulates were extensively studied and subsequently promoted to use as reinforcements in metal matrices. In particular, the aluminum, magnesium, copper, and titanium matrix composites entered the practical development stage with by end of 1980s [332]. Regarding that, several investigations on discontinuous reinforced metal matrix composites were done, with attention focusing on their strengthening mechanisms. A strengthening mechanism in discontinuously reinforced composites is an intermediate phase between a dispersion strengthened mechanism and a fiber strengthened mechanism; however, the strength of a discontinuous composite depends on many other factors in addition to the load transfer to the reinforcements [356]. Therefore, the other factors responsible for strengthening in the discontinuous composites are the finer grain size, finer subgrain size, increased dislocation density, increased kinetics to precipitate hardening, and some degree of Orowan strengthening, but mainly it is dependent on the aspect ratio of the reinforcement [332, 357-359]. However, if the aspect ratio of the reinforcement is high, the shear load transfer dominates, and in this case, the discontinuously reinforced composites behave as fiber reinforced composites. On the other hand, when the aspect ratio of the reinforcement is low, the matrix strengthening dominates, and in this case, the discontinuously reinforced composites behave as dispersion strengthened alloys. The relationship between reinforcement size and aspect ratio and their influences on the strengthening mechanisms of metal matrix composites are shown in the schematic illustration in Figure 18.

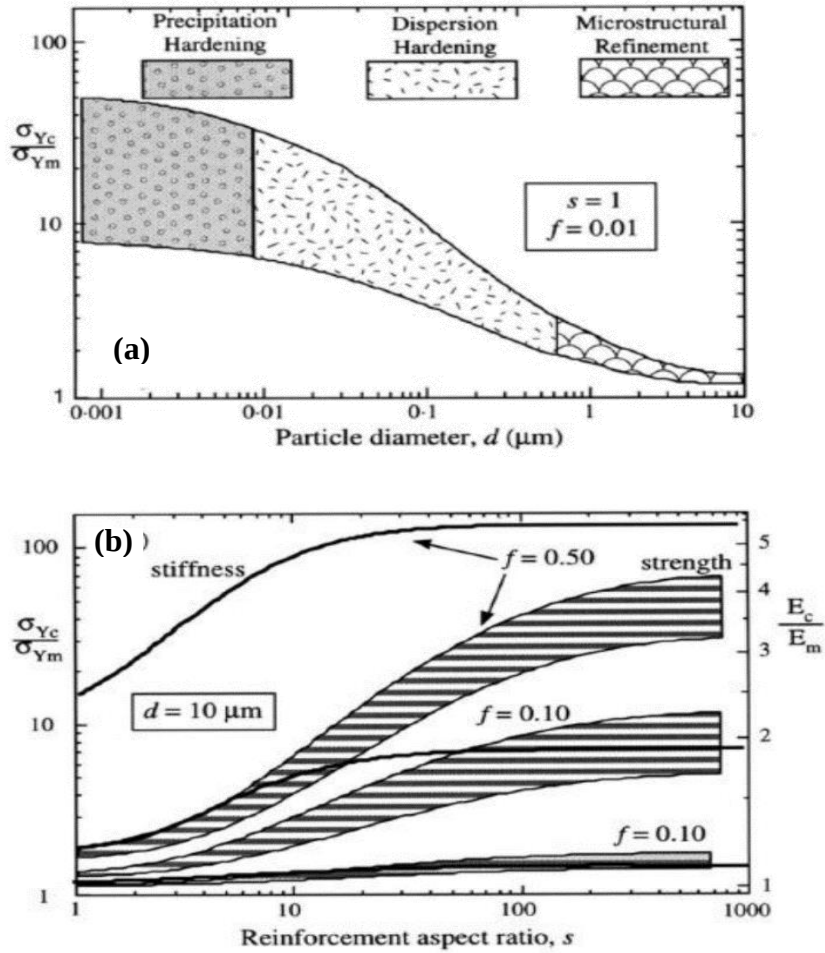


Figure 2.18: Schematic of composite strengthening as a function of reinforcement aspect ratio (s), size (d), and volume fraction (f). The Figure 18 (a) shows matrix dominated strengthening, with the reinforcement constituting too low a volume fraction to carry a significant proportion of the load. The Figure 18 (b) shows stiffening and strengthening gained from load transfer to high aspect ratio reinforcement, where it is too coarse to strengthen the matrix by affecting dislocation motion [332].

Over the past decades the majority of the discontinuous reinforced metal matrix composite processing and research have focused on the particulate reinforced composites, consisting of dispersed particulates or platelets with low aspect ratios. In general, the strongest particulate reinforced metal matrix composite would consist of large volume fractions of closely spaced, small diameter, high aspect ratio, high strength particles strongly bonded to and well distributed in a strong, work hardening matrix. However, these particulate reinforced composites usually have

particles ranging in size from 1-100 μ m and 5-40% volume fractions [332]. Due to the low aspect ratio to the reinforcement as mentioned, the strengthening mechanism does not rely on shear load transfer, but more based on dislocation strengthening in dispersion reinforcement. Therefore, the strengthening in this case occurs, initially when the dispersed particles are restricted to the matrix deformation by a mechanical restraint, which is a function of the interparticle spacing to diameter ratio and the elastic properties of the constituents [360]. The behavior of the particulate reinforced composite materials, beyond the elastic range, relies on whether or not the particles undergo plastic deformation before fracture. During loading, the softer matrix is restrained from the deformation by the rigid interfaces of the hard reinforcement particles to which it is attached [361]. With an increase in the load, a hydrostatic state of stress is developed which is identical to that in the elastic range, but this situation occurs at higher stress levels. If the loading keeps increasing, the hydrostatic stress also keeps increasing, following the increase of the load, until the unconstrained matrix yield strength reaches about 3 to 3.5 times. Then particulate fracture occurs instead of further increases in the hydrostatic constraint [361].

On the other hand, if a stress in the particles of 3 to 3.5 times the unconstrained matrix flow stress is insufficient to deform them, then a fracture initiated by particle cracking occurs throughout the matrix [361]. Such deformation behavior also shows up in the cemented carbide and cermet material [362]. However, when the hard dispersion particles cannot deform under the loading as in the carbide particles or cermet, the composite yield strength is proportional to the inverse square root of the interparticle spacing [363]. Therefore, if the interparticle spacing is reduced to about 0.5 μ m in dispersed particle composites, a crack nucleation will take place around the particle-particle boundaries as the weaker spots in the material, thereby leading to a significant drop in the strength of the particulate reinforced composite [364]. In fact, the matrix material is considered as a primary load bearing element in the particulate reinforced composite system. However, if the matrix of the composite is a soft material and known as a large plastic deformation material, the stronger reinforcing particles block any dislocation motion or slip, which, in turn, limits the plastic deformation [365]. On the other hand, if the matrix is a brittle material and any fracture occurs by crack propagation from existing cracks, in this case the stiffer reinforced particles limit the size of the initial cracks in the brittle matrix material, thereby controlling the strength [365]. Therefore, to create a strong particulate reinforced composite system, there must be a sufficient bonding between the reinforcing particles and the matrix. In both cases, the ductile and the brittle matrices compose

a strong body which behaves as a structural unit [360]. An example of that is cemented carbides that are produced by powder metallurgy techniques [366]. These composites are composed of carbide particles and a metallic matrix which often uses a cobalt matrix [366, 367].

In general these cemented carbides are characterized as very hard and wear-resistant materials. In the same way, in this work cobalt amorphous particles were used to enhance a cobalt matrix to obtain structural unity of the composite by improving the interface bonding between the matrix and the reinforcement, using the metallic matrix and metallic fillers such as cobalt amorphous particles and cobalt matrices in this work.

The strengthening and structural units in the composites in general and, in particular, the particulate reinforced composite is due to the effective bonding at the interface of the matrix and reinforcement, which is either a mechanical bonding or chemical bonding [368]. From the scientific and the practical points of view, the expression “bonding at the interface in composite materials” refers to a bounding surface between the reinforcement and the matrix which is an interfacial region with a finite thickness [368]. However, the interface is the zone where the different materials (reinforcement and matrix) in a composite coincide, and, due to the differences in the chemical and physical properties such as the crystal structure, atomic registry, elastic modulus, density, coefficient of thermal expansion and thermodynamic properties (including chemical potential), the interface between the reinforcements and matrices in the composites is very important and critical region [368, 369]. Therefore, the compatibility in the chemical and physical properties in the reinforcements and matrices help to create a strong interface bonding. In order to create a successful applicable composite, it must form an interface that is strong and favorable towards maximum compatibility between the reinforcement and the matrix. In view of that, and specifically in the particulate reinforced composites, the interface has a very significant effect on the strengthening, stiffening and toughness [370]. However, due to the difference of the properties of the composite phase components as mentioned earlier, the interface or interphase between the particles and matrices, a complex stress state appears during the loading. In view of that, a crack blunting effect and a significant drop in fracture ductility mostly occur during the weak bonding between the ductile matrix and the hard particles, where this bond is not adequate to execute the reinforcement in this composite system [360]. Therefore, in this case, a good bonding between the particles and matrices is very important in the reinforcement of the

composites in terms of yield strength but not fracture strength, ductility, or strain hardening exponents at large strains [371].

In contrast, in the case of a brittle matrix, the bond exerts a greater influence on the system's strength than that in a ductile matrix composite system. However, in this case, which is the brittle matrix and absence of a bond, a crack intersecting between unbonded particle certainly happens and expands immediately by an amount equal to the diameter of the particle [372]. Thus, these cracks act much like the voids, which are known to significantly reduce the strength of the brittle materials [373]. However, the strength has an inverse relationship with the volume fraction of the voids. In other words, when the volume fraction of the voids increases, the strength of the material rapidly drops down and tends to reach low values as the volume fraction increases further. As has been seen, the interface plays a crucial role in the load transfer between the matrix and the reinforcement, as well as in the dislocation particle interactions, which are significant in strengthening and stiffening the composite. Thus, the interface bonding in the composites is a complex issue, which requires the optimization of many parameters to achieve good bonding. The important parameters in the interface bonding process, as has been mentioned, are the compatibility in the chemical and physical properties of the reinforcements and matrices, a narrow particle size distribution, a highly homogenous surface area.

To understand the compatibility in the chemical and physical properties of the reinforcements and matrices and its influence on the interface bonding in the composites requires also an understanding of the reinforcement reaction and the matrix behavior during the production process. In general, and in the traditional way, the metal matrix composites (MMCs) are produced from metal matrices reinforced by ceramics fillers in order to improve their mechanical properties [277-282]. By using ceramics reinforcements, the matrix and the reinforcement have significant differences in the expansion of the thermal coefficients, and in their chemical and physical properties. Moreover, they typically induce poor bonding, where detrimental interfacial reactions often occur [283-287]. However, the ceramics have low wettability with the metal matrix, which generates particle agglomeration and porosity as well [288-291]. In order to get good and strong bonding between the metallic matrices and the reinforcements, as mentioned, a good compatibility between the chemical and physical properties in the reinforcements and matrices is imperative for the composite materials to create a strong interface bonding and to be favorable towards useful

composite. However, recently many studies have used metallic amorphous as reinforcements to the metallic matrices, and vice versa, where the metallic nature of the reinforcing phase plays an important role in achieving a good and strong bonding between the matrices and the reinforcements, by creating a suitable thermal coefficient of expansion, and compatible chemical and physical properties [264, 265, 269, 272, 281 and 283]. In view of that, in the research described in this thesis, use was made of a metallic matrix and metallic fillers in order to achieve the structural unity of the composite by improving the interface bonding between the matrix and the reinforcement, i.e., a cobalt matrix and cobalt amorphous particle reinforcement.

Additionally, the interface between the particles and matrices in the composites is largely due to the effectiveness of the compatibility in the chemical and physical properties of the reinforcements and matrices, but also there are other parameters related to the interface bonding which should be considered to achieve good interface bonding and other desired properties. These other parameters are as follows: a narrow particle size distribution, a highly homogenous surface area, and a good interface bonding between the particles and matrix, leading to a composite material that has good properties overall. Agglomerates and segregation adversely influence the physical composite properties. Without a proper dispersion of the nano- or micro-filler particles in the composite, filler aggregates will form, which tend to act as defective sites which limit the mechanical performance [374-377]. In order to acquire a well dispersed composite, the manner of combining metals matrices and particles should be considered as the most important key to gain the desired material properties. For dispersing the particles in a metallic matrix, mechanical alloying has been established to apply high shear forces during a dispersion process in order to break up agglomerates and to distribute the individual fillers homogeneously in the metallic matrix [378, 379]. This mechanism for mechanical alloying to curb the agglomerates from occurring is one of the reasons that has led to the choice of mechanical alloying known as “attrition milling” as dispersing technique in this work.

Thus, the interface between the reinforcement and matrix in metal matrix particulate reinforced composites plays a crucial role in the properties of the composite, especially in its mechanical properties. As has been stated above, it is clear that a weak reinforcement/matrix interface will lead to a failure of the composite material under use. Therefore, the interfacial failure in the composite is one of the most important issues in composite materials and we should pay a great

deal of attention to it, especially when it leads to a structural fracture in the composite. Therefore, a good interface is imperative for composite materials to perform well in their desired applications and survive under the stresses and other different circumstances. Accordingly, we have used a cobalt matrix and cobalt amorphous particles reinforcement to better understand the behavior of metallic particles enhancing metal matrices created by using the mechanical alloying (MA) method. An examination composite materials with cobalt/cobalt amorphous particles processed by MA will be discussed in one of the chapters of this work.

2.4 Magnetic Materials

Magnetic materials are ubiquitous in everyday life, with a diverse range of applications such as PCs, CD players, televisions, games consoles, loudspeakers and others, but humans have known magnetic materials since ancient times. The first recorded use of magnetism dates back to 400 BC, when early Chinese used magnets to make compasses by placing a piece of lodestone (a natural magnetic ore of iron of Fe_3O_4) on a piece of wood floating on the surface of a bowl of water. They found that the same side of its mass pointed toward the pole star [380]. However, they also found that the lodestone after being placed on the piece of wood automatically aligned itself from north to south by following the direction of the Earth's magnetic field at the point of observation horizontally because the lodestone was a naturally magnetized piece of mineral magnetite.

However, even though magnetic materials were discovered then, they remained without attention and were not well-understood until the end of the 1590s, when in 1600 William Gilbert published his classic book on magnets, considered as first real scientific study on magnetism [381]. Gilbert explained the Earth's magnetic field, and cleared away many superstitions that had clouded the subject that time by showing the relation between lodestones and the Earth's magnetic field.

After Gilbert's work, there was no further research or important discoveries on the fundamentals of magnetic materials until the nineteenth century, when the steel industry and electrical applications emerged, the beginning of future exciting applications of electromagnetic engineering and uses of magnetic materials [382]. Since the nineteenth century to date, scientists and researchers have come a long way in developing their concepts of magnetism and their applications in different fields, including power transformers, aerospace and automotive industries, electronic systems, medical equipment, data storage devices, telecommunication devices, and electrical appliances such as motors [383].

In general, magnetic materials respond to an applied magnetic field by a magnetic dipole moment associated with the intrinsic angular momentum, or spin of their electrons, and this effect is known as Faraday's Law of magnetic induction [384]. This response of materials to an applied magnetic field is dependent on a number of factors, such as the atomic and molecular structure of the material, and the net magnetic field associated with the atoms [385]. However, magnetic materials structurally consist of atoms containing electrons that move with a constant movement around atomic nuclei. This movement generates a small current and produces an electromagnetic field [386]. More importantly, electrons also spin about their own axes, which constitutes a charge in motion and thus creates another electromagnetic field [387]. Indeed, every spinning electron is like a small magnet and each pair of electrons spinning in the same direction makes a stronger magnet [387]. In contrast, a pair of electrons spinning in the opposite direction works against one another, causing their fields to cancel each other [387]. Consequently, this can explain why most substances are not magnetic, whereas in materials such as iron, nickel and cobalt the fields do not cancel one another entirely. Thus, there is no existing net magnetic field; alternately, the materials with some unpaired electrons will have a net magnetic field and will react more to an external field. In view of that, most materials can be characterized as diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic and ferromagnetic as shown in the Figure 19, while Figure 20 illustrates the magnetic properties of all elements of the periodic table at room temperature.

Diamagnetic materials have a weak, negative susceptibility to magnetic fields in that they are slightly repelled by a magnetic field and they do not retain their magnetic properties when the external field is removed [380, 386]. However, in diamagnetic materials all the electrons are paired so there is no permanent net magnetic moment per atom [380, 386]. Indeed, diamagnetic properties arise from the realignment of electron paths under the influence of an external magnetic field. Thus, most elements in the periodic table, including copper, silver, and gold, are diamagnetic.

While the paramagnetic materials have a small, positive susceptibility to magnetic fields where they are slightly attracted by a magnetic field, these materials do not retain their magnetic properties when the external field is removed [380, 386]. Moreover, the paramagnetic properties are due to the presence of some unpaired electrons and from the realignment of the electron paths caused by the external magnetic field. For example, magnesium, molybdenum, lithium, and tantalum are classified as paramagnetic materials.

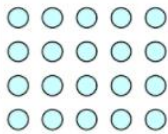
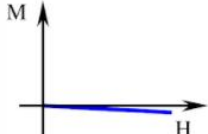
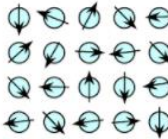
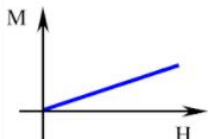
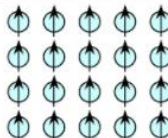
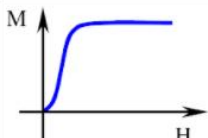
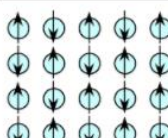
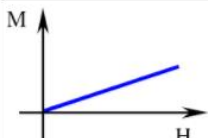
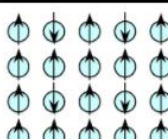
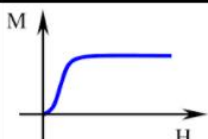
Type	Atomic / Magnetic Behavior	
Diamagnetism	 Atoms have no magnetic moment	
Paramagnetism	 Atoms have randomly oriented magnetic moments	
Ferromagnetism	 Atoms have parallel aligned magnetic moments	
Antiferromagnetism	 Atoms have anti-parallel aligned magnetic moments	
Ferrimagnetism	 Atoms have mixed parallel and anti-parallel aligned magnetic moments	

Figure 2.19: A summary of the different types of magnetic behavior [383].

As a complete contrast, ferromagnetic materials have a large, positive susceptibility to an external magnetic field where they exhibit a strong attraction to magnetic fields and are able to retain their magnetic properties after the external field has been removed [380, 386]. However, ferromagnetic materials have some unpaired electrons, so their atoms have a net magnetic moment; therefore they get their strong magnetic properties from the presence of magnetic domains. In these domains, large numbers of moments atoms (10^{12} to 10^{15}) are aligned in parallel, so that the magnetic force within the domain is strong [388]. When a ferromagnetic material is in the demagnetized state, the domains are nearly randomly organized and the net magnetic field for the part as a whole is zero [380, 386]. Conversely, when a magnetizing force is applied, the domains become aligned to produce a strong magnetic field within the part, examples of ferromagnetic materials are iron, nickel, and cobalt.

1 H																	2 He
3 Li	4 Be																
11 Na	12 Mg																
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	

Figure 2.20: The magnetic behavior of each element of the periodic table at room temperature [383].

The fourth type of the materials are antiferromagnetic materials which are mostly very similar to ferromagnetic materials, but the exchange interaction between neighboring atoms leads to the anti-parallel alignment of the atomic magnetic moments [380, 386]. Consequently, the magnetic field cancellation of the material appears to behave in the same way as a paramagnetic material. Similar of ferromagnetic materials, the antiferromagnetic materials above the Néel temperature become paramagnetic, an example of which is chromium in the periodic table at room temperature [380, 386].

In the last case of ferrimagnetic materials, the exchange interactions lead up to a parallel alignment of atoms in some of the crystal sites and anti-parallel alignment of others [380, 386]. Therefore, ferrimagnetic materials break down into magnetic domains, which is comparable behavior to that of the ferromagnetic materials, although ferrimagnetic materials usually have lower saturation magnetizations [386]. The ferrimagnetic behavior can be only observed in compounds, which have more complex crystal structures than pure elements; an example is barium ferrite ($\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$) [385-387]. However, barium ferrite has a unit cell containing 64 ions, of which the barium and oxygen ions have no magnetic moment; 16 Fe^{3+} ions have parallel-aligned moments while 8 Fe^{3+} has antiparallel-aligned moments, giving a net magnetization parallel to the

applied field, but with a relatively low magnitude as only $\frac{1}{8}$ of the ions contribute to the magnetization of the material [385-387].

It should be no surprise that most applications of magnetic materials call for ferromagnetic materials. They are very important in industry and modern technology, and are the basis for many electrical and electromechanical devices, such as electromagnets, electric motors, generators, transformers, and magnetic storage such as tape recorders, hard disks and others [382-387]. Also, as this work is based on Co-based amorphous alloys, which are considered ferromagnetic materials, more details on the ferromagnetic materials will be presented in this section. Based on the brief introduction of the ferromagnetic materials, the net magnetic moment of the ferromagnetic material can be zero by removing the external magnetic field H , and in this case, it is considered as a demagnetized material. According to Weiss's hypothesis and theory of domains, a ferromagnetic material in a demagnetized state is referred into small regions known as magnetic domains or Weiss domains [389, 390]. Each of these domains comprises a large number of atoms that are spontaneously magnetized to the saturation point M_s [380]. At the same time these domains have different directions of magnetization, which make the net magnetization of the whole specimen zero. During the magnetization process which is the applying of the external magnetic field on the specimen, these domains with many different directions of magnetization turn into a single domain for the entire specimen by being magnetized in the same direction of the applied field [387]. The allocation of domains and the results on the effective magnetization by the applied magnetic field causes a rise in initial magnetization curve, as shown in Figure 21, and is commonly known as a magnetic hysteresis loop.

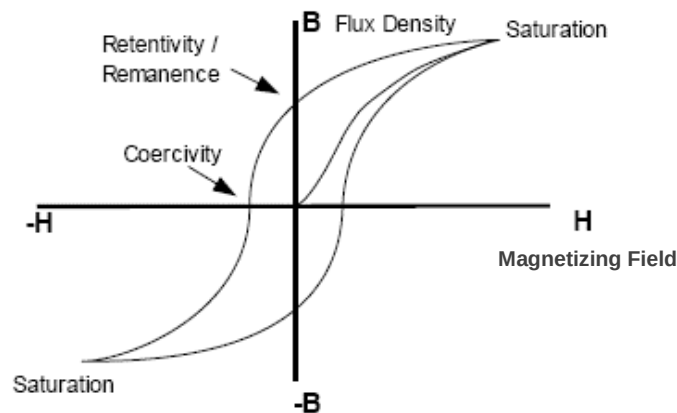


Figure 2.21: Typical hysteresis loop for ferromagnetic materials.

So, on a microscopic level, ferromagnetic material can reach the saturation point easily if the magnetic field that is applied on the specimen is large enough to induce a magnetization [380]. On the other hand, the magnetization process is considered a reversible process if the applied field is continuously varied between the two extreme values of the $\pm H$ axes, which Figure 21 shows [380]. Therefore, the initial magnetization curve, a hysteresis loop and saturation magnetization are characteristics of ferromagnetic materials [380]. Moreover, ferromagnetic materials, based on their hysteresis characteristics, can be further classified into two types, which are soft and hard magnetic materials, as shown in the magnetization curve in Figure 22. However, the hard and soft magnetic materials have different characteristics, making each one have its own applications. For example, because they have high permeability and low coercive fields, soft magnetic materials used in AC applications such as the magnetic cores of transformers, motors, inductors and related devices [391]. On the other hand, hard magnetic materials are used as permanent magnets because of their high coercive field and high residual magnetization [391].

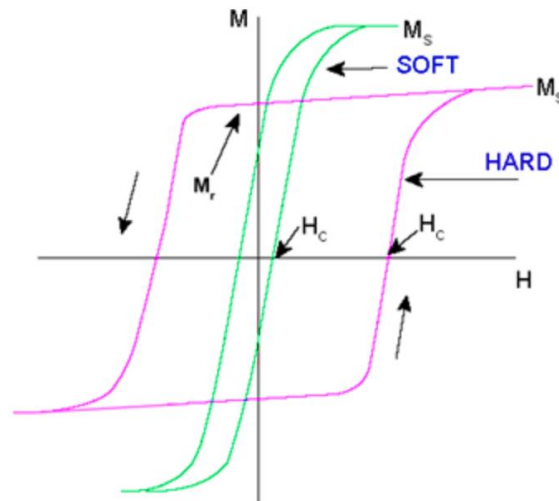


Figure 2.22: Typical magnetic hysteresis loops of soft and hard ferromagnetic materials.

2.4.1 Soft Magnetic Materials

A ferromagnetic material which can be easily magnetized at a low level of magnetic field, is classified as a soft magnetic material. In other words, soft magnetic materials are easily magnetized and demagnetized by low-strength magnetic fields. When applied field is removed, the material goes back to a state of relatively low residual magnetization [392]. However, once soft magnetic materials are exposed to a magnetic field, as shown in Figure 22, their domain walls easily migrate

and disappear until all magnetic moments are aligned in the direction of the magnetic field, which is saturation magnetization [393]. Thus, the ease in which the domain wall in a material can move during the magnetization process determines the material's response to the applied magnetic field, and mainly depends on the material's homogeneity and its microstructure [394]. In view of that, the microstructure of the soft magnetic material is fundamental to the softness of the magnetic property, where the existence of defects such as grain boundaries, inclusions or dislocations impedes the domain wall movement, thereby making it hard for the material to be magnetized and demagnetized; hence, with the loss of its softness, the material is now classified as a hard magnetic material [394]. In addition, for a ferromagnetic material to be considered soft, its magnetocrystalline anisotropy and magnetostriction constant must be low [393].

The magnetocrystalline anisotropy also has an influence on the ferromagnetic materials magnetization and its magnetic softness, and requires more energy to magnetize the material in certain directions than in others [395]. These directions are usually related to the principal axes of its crystal lattice. However, as mention above, magnetic domains in ferromagnetic materials have a random distribution of their direction of magnetization. Therefore, during the magnetization process, if the material has a high level of magnetocrystalline anisotropy and an axis along which it is easily magnetized, the magnetization in this direction uses a minimum energy for the domains [386]. On the other hand, if the direction of the applied field is different from the easy axis direction, extra energy is required to rotate the domains from the easy axis to the applied field axis [386]. Besides that, the difference between the magnetocrystalline anisotropy direction and the applied field creates an energy barrier that blocks the atoms from aligning with the applied field axis, thereby resulting in a slower response of the material to the varying field [386]. Thus, the energy required to rotate the magnetization from its easy axis is different for different materials and is described by the magnetic anisotropy constant K [386].

Since, soft magnetic materials are easily magnetized and demagnetized, they should have a high permeability μ , low coercive force H_c , and large saturation magnetization [385-387]. In general, the permeability is the measure of the ability of a material to support the formation of a magnetic field within itself [396]. Hence, it is the degree of magnetization that a material obtains in response to an applied magnetic field. However, permeability is defined as the ratio of the magnetic induction B to the magnetic field strength H that produces the induction [386, 387]. Therefore, the

maximum permeability is the maximum value of the relative permeability achieved during the magnetization cycle, as shown in Figure 23 [397]. The higher the maximum permeability, the easier it is for the material to be magnetized, and the higher the permeability, the better its magnetic performance [398].

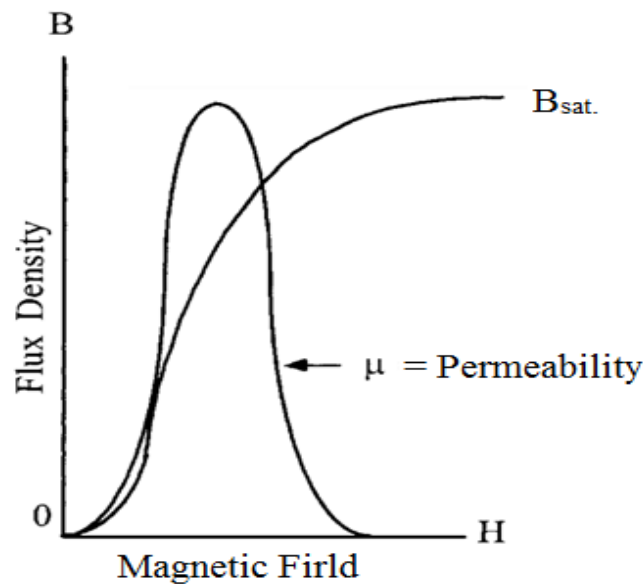


Figure 2.23: Typical magnetization and permeability curves [397].

As the permeability is a measure of how readily the material responds to the applied magnetic field, it also illustrates why soft magnetic materials have high permeability where they are easy to magnetize and demagnetize [398]. Thus, the permeability is considered as the one of the most important parameters for soft magnetic materials, since it indicates how much magnetic induction is generated by the material in a given magnetic field, and the higher the permeability, the better for these materials [398].

In contrast, soft magnetic materials show low coercivity H_c , which is a very important feature of soft magnetic materials [386, 399]. In general, the coercivity, coercive field or coercive force, is a measure of the ability of a ferromagnetic material to withstand an external magnetic field without becoming demagnetized [400]. In other words, coercivity is the magnetic field intensity that acts against the direction of spontaneous magnetization until it reaches the overall material induction $B = 0$ [401], as seen in Figure 22. Therefore, the coercivity is the degree of resistance of a magnet against demagnetization [396]. Indeed, it is well known that initial permeability and

coercivity have in broad terms an inverse relationship, so that materials with high coercivity have a low initial permeability, and vice versa [402]. In view of that, the ease of magnetization and demagnetization in soft magnetic materials gives them the features of low coercivity and high permeability, as seen earlier. As a soft magnetic material is easy to magnetize and demagnetize, it has a very low degree of magnet resistivity against demagnetization and this explains its low coercivity [386, 400-402]. As shown in Figure 22, soft magnetic materials have low coercivity H_c , and high saturation magnetization M_s but low remanence M_r . Typical soft magnetic materials have an intrinsic coercivity of less than 1000 A/m (12.5 oersted) [403], and a low value of H_c is usually desired to minimize energy losses [404].

Thus, soft magnetic materials play an essential role in many of the electrical and electronic systems that characterize our modern society today [405-407]. These materials are used in different applications such as electrical power generation and transmission, electric motors, receipt of radio signals and microwaves, relays, solenoids, magnetic shielding and electromagnets [405-415]. Indeed, the types of applications for soft magnetic materials fall into two main categories: alternating current (AC) and direct current (DC) electrical circuits. In direct current applications the main consideration for material selection is most likely to be permeability [412-415]. This would be the case, for example, in shielding applications where the flux must be channeled through a material. Where the material is used to generate a magnetic field or to create a force, then the saturation magnetization may also be significant [416].

On the other hand, in alternating current applications, the most important consideration is the amount of energy that is lost in the system, when the material is cycled around its hysteresis loop [383]. In fact, the properties of soft magnetic materials are being continuously improved as applications require it. In view of that, the initial permeability for example, is important in electronic transformers and inductors, which are improved by minimizing all sources of magnetic anisotropy, so the use of amorphous metallic alloys and zero magnetostrictive alloys are instances of that [417, 418]. In another example, the maximum permeability also is necessary for motors and power transformers, in which the alignment of the anisotropy is increased, for example, through the development of crystal texture or magnetically induced anisotropy [419]. More importantly, the energy loss that happens at these sites can originate from three different sources, all being classified as hysteresis loss, eddy current loss, and anomalous loss [383]. Initially, the

hysteresis loss, which is related to the area contained within the hysteresis loop, where it can be reduced by the reduction of the intrinsic coercivity, with a consequent reduction in the area contained within the hysteresis loop [420, 421]. Secondly, the eddy current loss is related to the generation of electric currents in the magnetic material and the associated resistive losses [418, 422 and 423]. The eddy current loss can be reduced by decreasing the electrical conductivity of the material through the alloying additions to increase the electrical resistivity [418, 424-428], as well as by laminating the material, which has an influence on the overall conductivity and is important because of skin effects at higher frequency applications [420, 422 and 424-426]. Finally, an anomalous loss is related to the movement of domain walls within the material [399, 429-433]. Such cases can be reduced by having a completely homogeneous material, within which there will be no hindrance to the motion of domain walls [434, 435].

As already seen, microstructure plays a big role in determining the magnetic properties of a material in general, and in the case of soft magnetic material, it plays the main role in determining the magnitude of the coercivity and permeability. Therefore, in order to have a soft magnetic material, minimizing the heterogeneities and imperfections of the material microstructure such as grain boundaries and inclusions are required [399, 436 and 437]. However, microstructural defects such as dislocations, inclusions and grain boundaries hinder the motion of domain walls, leading to high coercivity and low permeability [438-442]. Thus, the common goal in soft magnetic materials production is to minimize these imperfections and heterogeneities. Some of these materials that are favorable toward this criterion are amorphous metallic alloys or metallic amorphous alloys [99, 101, 105, 107, 109, 110, 135-137, 147, 150, 151, 153, 185, 198, 201, 303 and 304]. Soft magnetic properties of the metallic amorphous alloys date back to the 1967, when Duwez and Lin [33] used a quenching technique to produce a metallic amorphous structure from the composition of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ in at.%. Thus the $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ in at.% alloy was considered the first strongly magnetic amorphous alloy and the first amorphous alloy that exhibited soft magnetic properties with a low of coercivity about 3Oe. Consequently, soft magnetic properties that the metallic amorphous alloys show coming from the lack of dislocations and grain boundaries which are considered as barriers to the domain wall motion in the case of crystalline materials. More importantly, the low magnetic anisotropy constant that metallic amorphous alloys offer makes their atomic magnets rotation easy to move, even with less energy [443-445]. However, the absence of the crystalline structure in amorphous materials leads to a random and disordered state

at the atomic structure level of the material, and this random of distribution makes the magnetic orientation of the atoms easier along all axes, which explains the low anisotropy constant in amorphous materials [443-445]. In other words, the low anisotropy constant in the amorphous materials means that they have less resistance to changing magnetization under varying applied fields, compared to crystalline materials; in turn, this process makes them appropriate for soft magnetic applications [443-445].

Therefore, the increasing use of amorphous alloys today in magnetic and electric applications is due to their good soft magnetic properties [445-449]. Mainly soft magnetic materials in metallic amorphous alloys are produced from iron-based, cobalt-based and Fe-Ni-based substances with some glass formers like boron, silicon carbon, etc., as additives. Table 2 shows some of iron-based and cobalt-based metallic amorphous alloys and their magnetic properties. These metallic amorphous alloys of iron-based and cobalt-based substances with low coercivity and high permeability are extensively used in industry as magnetic heads, transformer cores, circuits and magnetic shields.

Table 2.2: Typical iron-based and cobalt-based bulk metallic amorphous alloys systems and their magnetic properties [450-466].

Alloy Composition	Saturation Magnetization (T)	Coercivity (A/m)	Curie Temperature (K)
Fe ₈₀ B ₂₀	1.65	12	-
Fe ₇₈ Si ₁₃ B ₉	1.55	9	-
Fe ₈₀ P ₁₂ B ₄ Si ₄	1.13	1.3	-
Fe ₇₆ Si ₉ B ₁₀ P ₅	1.51	1	-
Fe ₆₂ Nb ₈ B ₃₀	0.75	-	516
(Fe _{0.75} B _{0.15} Si _{0.1}) ₉₆ Nb ₄	1.2	3.7	-
(Fe _{0.75} Si _{0.1} B _{0.15}) ₉₆ Nb ₄	1.47	2.9	-
Fe ₈₀ Zr ₄ Ti ₃ Cu ₁ B ₁₂	0.94	48.5	-
Fe ₇₆ Al ₄ P ₁₂ B ₄ Si ₄	1.08	12.7	-
Fe ₇₆ Al ₄ P ₁₂ B ₄ Si ₄	1.38	3	623
Fe ₇₆ Mo ₂ Ga ₂ P ₁₀ C ₄ B ₄ Si ₂	1.32	3	-
Fe ₇₆ P ₅ (Si _{0.3} B _{0.5} C _{0.2}) ₁₉	1.44	1	680
Fe _{37.5} Ni _{22.5} Cr ₅ Co ₁₀ B ₁₅ Si ₁₀	0.89	3,720	-
Fe ₇₈ Ga ₂ P ₁₂ C ₄ B ₄	1.34	2	-
Fe ₇₈ Ga ₂ P _{9.5} C ₄ B ₄ Si _{2.5}	1.4	3	625
Fe ₇₃ Al ₅ Ga ₂ P ₁₁ C ₅ B ₄	1.24	4	-
Fe ₇₄ Al ₄ Ga ₂ P ₁₂ B ₄ Si ₄	1.03	19.1	-
Fe ₇₇ Al _{2.14} Ga _{0.86} P _{8.4} C ₅ B ₄ Si _{2.6}	1.39	9	-
Fe ₃₀ Co ₃₀ Ni ₁₅ Si ₈ B ₁₇	0.92	3	-
Fe ₅₆ Co ₇ Ni ₇ Zr ₁₀ B ₂₀	0.92	-	567
Fe ₄₀ Co ₄₀ Cu _{0.5} Al ₂ Zr ₉ Si ₄ B _{4.5}	1.18	3	736
Fe ₅₂ Co _{9.5} Nd ₃ Dy _{0.5} B ₃₅	1.26	1	-

Fe ₆₂ Co _{9.5} Gd _{3.5} Si ₁₀ B ₁₅	0.98	5	596
Fe ₆₂ Co _{9.5} Nd ₃ Dy _{0.5} B ₂₅	1.37	4	-
(Fe _{0.85} Co _{0.15}) ₇₇ Ga ₂ P ₁₀ C ₅ B _{3.5} Si _{2.5}	1.4	5	694
(Co _{0.0705} Fe _{0.045} Si _{0.1} B _{0.15}) ₉₆ Nb ₄	0.59	<3	-
(Co _{0.6} Fe _{0.4}) _{0.75} B _{0.2} Si _{0.05}) ₉₆ Nb ₄	-	-	-
Co ₄₃ Fe ₂₀ Ta _{5.5} B _{31.5}	0.51	0.9	-
Co ₄₃ Fe ₂₀ Ta _{5.5} B _{31.5}	0.49	-	-
Co ₄₃ Fe ₂₀ Ta _{5.5} B _{31.5}	0.49	0.25	-
((Fe _{0.8} Co _{0.1} Ni _{0.1}) _{0.75} B _{0.2} Si _{0.05}) ₉₆ Nb ₄	1.1	3	-
((Fe _{0.6} Co _{0.1} Ni _{0.3}) _{0.75} B _{0.2} Si _{0.05}) ₉₆ Nb ₄	0.8	2.5	-
((Fe _{0.6} Co _{0.2} Ni _{0.2}) _{0.75} B _{0.2} Si _{0.05}) ₉₆ Nb ₄	0.86	2.5	-
((Fe _{0.6} Co _{0.3} Ni _{0.1}) _{0.75} B _{0.2} Si _{0.05}) ₉₆ Nb ₄	0.9	2	-
((Fe _{0.6} Co _{0.1} Ni _{0.1}) _{0.75} B _{0.2} Si _{0.05}) ₉₆ Nb ₄	1.1	3	-

In general, producing metallic amorphous alloys commonly demands adding some glass former elements such as metalloids B, Si, C and P or the metals Ti, Zr to form an amorphous structure [9, 28, 467, 468]. Also worth mentioning, some of these metal-metalloid based metallic amorphous alloys such as iron-based and cobalt-based materials have good soft magnetic properties. But the excess of these metalloids content percentage in the system can have a detrimental impact on the magnetic properties [26, 469-476]. However, it is well-known that the composition of higher metalloids in the system facilitates the formation of amorphous structures; on the other hand, due to their poor magnetic properties, the increase of their chemical composition could lead to low saturation magnetization, effective permeability and Curie temperature, which are restricting their applications as soft magnetic materials. Therefore, in order to have higher saturation magnetization and permeability values, the chemical composition of glass former elements should be kept low [477-482]. Given the importance of the glass forming ability in the metallic amorphous alloys, it was important to find a middle ground between glass forming ability of the alloy and its magnetic properties by optimizing the chemical composition of the glass former elements that are chosen with the base metal to get a combination of all the properties [478-481].

Likewise, this present work investigates the amorphous forming ability in a Co-C system at high Co contents, in order to improve the magnetic properties as well as the mechanical properties by using this criterion. However, since the Co-based amorphous alloys are used for switch mode power supplies and for many types of magnetic sensors [483-486] because of their near-zero magnetostriction, improving their magnetic properties is always required.

2.4.2 Hard Magnetic Materials

While soft magnetic materials can be easily magnetized and demagnetized by a low-strength magnetic field, hard magnetic materials are the opposite: they are hard to magnetize and demagnetize by a low-strength magnetic field, and that is why they call them the hard magnetic materials [392, 487]. Also, hard magnetic materials are referred to as permanent magnets because they strongly resist demagnetization once magnetized and their magnetization remains as high as possible when subject to strong demagnetizing fields [444]. Hence, hard magnetic materials have a large remanent magnetization and are stable in the presence of external fields, making their magnetic properties different from soft magnetic materials [421]. Indeed, since the characteristics of hard magnetic materials are opposite those of soft magnetic materials, the key point of distinguishing between them is the coercivity H_c value, where hard magnetic materials have a higher coercivity, as seen in Figure 22. Typical hard magnetic materials have an intrinsic coercivity greater than 1000 A/m (12.5 oersted) [403]. Moreover, hard magnetic materials typically have low permeability and high remanence M_r , magnetocrystalline anisotropy and core loss, compared to corresponding values of soft magnetic materials [487, 488].

As discussed and illustrated earlier in the soft magnetic materials section, the microstructure of the material plays an important role in its magnetic properties. Also in the case of hard magnetic materials, the microstructure has an important role in the magnetic behavior of the material; it affects the migration of the domain walls by making their migration difficult, which is the opposite of what happens with soft magnetic materials [489, 490]. For this reason, hard magnetic materials are hard to magnetize and demagnetize by a low-strength magnetic field, and this result makes them to show quite different magnetic behavior from soft magnetic materials. Common examples of such materials are rare earth intermetallics include the cobalt-rare earth alloys such as SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ and neodymium-iron-boron such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ [491-495]. Another example of intermetallic permanent magnets that are classified as high performance permanent magnets are iron-platinum, cobalt-platinum, and Alnicos [494-498]. In the case of ceramic permanent magnets, hard ferrites such as $\text{SrO-Fe}_2\text{O}_3$ and $\text{BaO-6Fe}_2\text{O}_3$ are classified as high performance permanent magnets [440, 499-503].

Thus the applications of permanent magnets in daily life has increased significantly in the last three decades in different fields. For example, they are used to apply (generate) tractive and

repelling forces, as found in magnetic separators, latches, torque drives, bearings, etc. [504-507]. They are also found in energy conversion equipment such as the magnetos, generators, alternators, eddy current brakes, motors and actuators [494, 504-506]. Permanent magnets are good in directing and shaping particle beams and electromagnetic waves, including cathode ray tubes, traveling wave tubes, klystrons, cyclotrons, and ion pumps, etc. [504-506]. In addition, permanent magnets are used to provide magnetic bias fields for a wide range of RF, microwave, and mm-wave devices as isolators, circulators, phase shifters, filters, etc. [494, 504-506].

2.5 Amorphization of Metals

As was seen in the historical review of the amorphous metallic alloys section, the production of amorphous metallic phases has been of interest to the researchers for many years because of their fundamental scientific importance and engineering application potential. In order to improve their forming ability and production, several methods have been used to produce amorphous alloys, such as rapid quenching, irradiation, solid state amorphization reaction (SSAR), and mechanical alloying. Generally, a metallic amorphous phase can be created through two mechanism: (1) a liquid-to-solid mechanism, such as a rapid quenching or casting of molten metal [26, 356, 508 and 509], and (2) a solid-to-solid, such as solid state amorphization reactions (SSAR) and mechanical alloying [160, 162, 510-512]. In the case of a liquid-to-solid mechanism, the process mostly depends on the rapid solidification by cooling the molten metal so quickly that crystallization has not enough time to occur [513]. However, with continuing cooling, the temperature goes down and the viscosity of the molten goes up, leading to reduction of the atoms' mobility, which ends with the solidification of the molten material [356]. Therefore, if the cooling process has a low cooling rate, the molten material is able to crystallize, but if the cooling is sufficiently rapid, the crystallization can be avoided by a progressive freezing of the molten configuration [513]. Thus, during the solidification process with a high cooling rate, the viscosity becomes so high and the atoms' mobility so slow, at that moment the molten cannot change its structure rapidly enough to maintain the internal equilibrium, and ultimately the final product is a solid with a liquid-like atomic arrangement which is in disordered structure, this is called the metallic amorphous phase [356].

In contrast, in the case of a solid-to-solid mechanism, the process does not involve the melting of constituents. However, this technique energizes the material highly by a rapid atomic diffusion

of one of the components of the alloy in the other components through the crystals lattices [514, 515], using a high driving force, such as irradiation [516], hydrogen diffusion [511], diffusion induced amorphization in multilayers [162], and mechanical alloying [170, 172 and 173]. In other words, increasing the energy of the starting crystalline material by the addition of some externally provided energy causes the material to store this energy in the crystal up to a point at which it becomes unstable with respect to the amorphous state. Therefore, the highly energized material lowers its energy by being transformed into a different atomic structural arrangement, i.e., the metallic amorphous phase [517].

2.5.1 Rapid Quenching

Rapid quenching normally involves a rapid solidification to the molten metal, using extremely high cooling rates from 10^6 to 10^{10} K/s, in order to suppress the nucleation and growth process of a crystalline phase in the super-cooled liquid region, and to solidify an amorphous phase from the liquid phase [23, 518 and 519]. The super-cooled liquid region is a region between the melting temperature T_m and the glass transition temperature, T_g , the temperature at which a metal has a viscous flow [520]. In other words, when the extraction of heat is so rapid, the molten material undergoes a significant undercooling [519] and, as a result of the limited atomic mobility and the structural disorder of the liquid phase, the liquid is retained (quenching-in) as a glassy material. Turnbull [37, 38 and 83] proved that metals have glass transition temperatures T_g and also explained the similarities between metallic glasses and non-metallic glasses. Turnbull also modeled a criterion for glass formability in metals: $T_g/T_m = 2/3$ [521]. One important limitation in the rapid quenching, however, was that the composition of the alloy must be near a deep eutectic [23, 518 and 522]. Thus, amorphous metallic substances produced by rapid quenching were confined to compositions surrounding these eutectics. In view of this narrow criterion for selecting the alloy elements, the rapid quenching technique was shown to have a reduction in the cooling rates of binary compositions; however they were not enough to produce anything other than powders, thin films and ribbons. Subsequent research took advantage of these criteria to find material systems that would form metallic glasses at lower cooling rates [523].

2.5.2 Metallic Mold Casting

Metallic mold casting involves lower cooling rates of approximately $<10^4$ K/s, compared to rapid quenching, and allows to use molds. Metallic mold casting is the most frequently used

method to prepare bulk metallic amorphous alloys with a thickness of only a few millimeters or greater. Indeed, there have been several contributions to this technique to lower the cooling rates and increase the size of the amorphous metallic produced. For example, the contribution of Turnbull et al. was one of the most important contributions to this technique to lower the cooling rates for the quenching alloys, by placing emphasis on the constituents of the system [10]. Inoue et al. [217] also made a significant contribution by establishing empirical rules for the formation of the bulk metallic amorphous alloys, which are summarized as follows:

1. A multicomponent alloy with at least three components.
2. Large negative enthalpy of mixing among the major constituent elements.
3. Atomic size difference larger than 12% among the main constituent elements.

Therefore, any alloy or system that satisfies and accepts these three empirical rules will have a difficult atomic rearrangement in that it ends up with a randomly packed structure. However, upon cooling, the undercooled liquid will form new local atomic configurations and have a high solid/liquid interfacial energy, which is favorable for suppression of nucleation of a crystalline phase. Also, the atomic rearrangement on a long-range scale for crystallization will be impossible, because it will suppress the growth of the crystalline phase and decrease the atomic diffusivity and increase the viscosity. So the multicomponent alloy or system, which satisfies these three empirical rules will always have a deep eutectic point with a low melting temperature, leading to a high T_g/T_m and a large supercooled liquid region, thereby creating a better glass forming ability. Figure 24 gives an overview of the influence each of the empirical rules has on the glass forming ability of the alloys and the resulting effects on T_g and T_m . In view of that, it is clear from Figure 25 that the reduced glass transition temperature (T_g/T_m) has a significant effect on the critical cooling rate R_c (which is defined as the minimum rate at which an alloy must be cooled from its liquid state in order to retain the amorphous structure) and the maximum thickness. Despite these advancements, the casting of bulk metallic glasses is still complicated and limited by cooling rates in the fabrication of intricate geometric shapes.

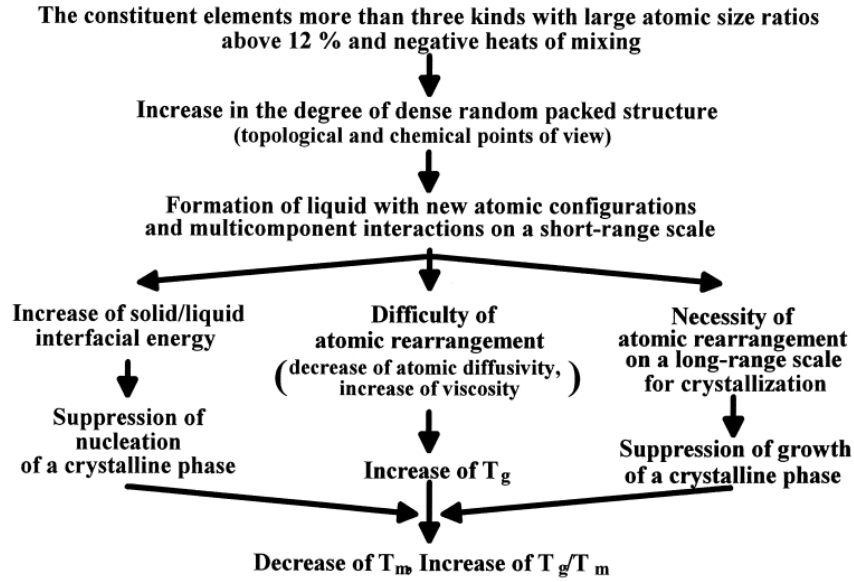


Figure 2.24: A flow diagram showing the influence of the three empirical rules on the glass formability of alloys [217].

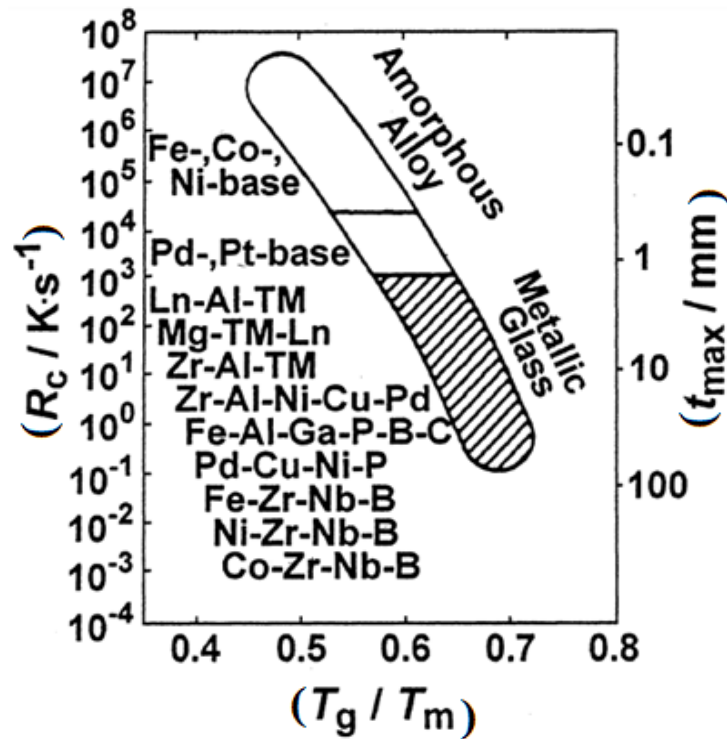


Figure 2.25: Correlation in different glass-forming alloys between the critical cooling rates (R_c) reduced glass transition temperature (T_g/T_m) and thickness of glass (t_{max}) [217].

2.5.3 Solid State Amorphization

As stated above, solid state amorphization reactions (SSAR) follow the mechanism of solid-to-solid to produce metallic amorphous alloys, which does not involve the melting of alloy constituents. Therefore, SSAR techniques are mainly based on the rapid atomic diffusion through metal lattices to create metallic amorphous alloys [514, 515]. However, solid state amorphization processes depend critically on the fact that the amorphous phase has a free energy which is lower than the non-equilibrium state of the crystalline solid. Thus a thermodynamic driving force for the formation of the metallic amorphous phase exists. Irradiation [516], hydrogen diffusion [511], diffusion induced amorphization in multilayers [162] and mechanical alloying [170, 172 and 173] are a few examples of SSAR.

Amorphization by irradiation is based on destroying the crystal lattice of the material by bombarding it with fast moving ions, electrons, or neutrons, creating defects on the crystal structure, such as interstitial-vacancy pairs, vacancy loops, and others [516, 524]. The accumulation of lattice defects eventually demolishes the crystal lattice, makes the material in the amorphous phase rather than crystalline phase. However, due to the increase of the free energy in the material under the irradiation, the critical defect concentration destabilizes the crystalline phase, promoting a spontaneous transformation of the material to the amorphous phase. The increase of the free energy that is induced by the irradiation will appear in the material as atomic disorder [525], or in the form of a higher concentration of point defects [526-530]. Indeed, the best materials to undergo this technique are intermetallics, which could easily transform into amorphous materials even though they are at low temperatures, as a result of irradiation-induced damage. The amenability of the intermetallic materials to the irradiation of the amorphization is due to their ability to store enthalpy by means of Frenkel pairs, and to the reduction in short and long-range atomic order, and limited migration of defects [531].

Another example of solid state amorphization is hydrogen diffusion, which was invented by Oesterreicher et al. in 1976 [532]. They reported that the amorphous alloys of La-Ni were produced when the crystalline compounds of LaNi, LaNi₂ and La₂Ni₃ were exposed to hydrogen at high pressures leading to amorphization. Further studies in the hydrogen diffusion amorphization technique were done in the early 1980s, using the earth elements in the alloys system [533]. However, all these studies during that time didn't foster further research until the systematic study

that Yeh et al. did in 1983, where they showed that Zr_3Rh was thermodynamically driven when going from crystalline to amorphous states upon exposure to hydrogen [26]. Later on, Yeh's work was the first example of what has since become known as glass formation by means of a solid state diffusion reaction, or reaction amorphization, or more recently known as solid state amorphization reaction (SSAR).

Amorphization by multilayer interdiffusion is also another method based on the SSAR. In this method, the amorphous phase results due to the fast diffusion of one element into other element in a thin multilayers system. The first amorphization by multilayers interdiffusion was observed by Schwarz and Johnson [162] in 1983. They established that the annealing of Au-La multilayers was found to result in the formation and growth of an amorphous phase. This unusual reaction in forming an amorphous phase was explained by Schwarz and Johnson that anomalously fast diffusion of one species in the other and the large negative heat of mixing are responsible for the transformation from a crystalline to an amorphous phase. According to the results of this study, Schwarz and Johnson developed criteria for the SSAR in a metallic multilayered system, which involve in two important points:

1. The heat of mixing between the two species must be large and negative.
2. One species must diffuse anomalously fast into the other.

In solid state amorphization by interdiffusion from multilayers, the driving force results from the large negative heat of the mixing of the individual elements. The formation of a metastable amorphous phase, rather than the more stable equilibrium crystalline phases, occurs as a result of kinetic considerations [534]. In this way, the amorphous alloy forms long before the collective rearrangement of the two species, which is necessary for intermetallic nucleation to occur [534]. Thus, this solid state amorphization by interdiffusion of initially crystalline elemental metals has subsequently been found to be rather ubiquitous [531, 535]. Examples of alloy systems that meet these criteria and have been shown to amorphize by SSAR include Ni-Ti [536, 537], Cu-Ti [538], Co-Ti [539], Ni-Hf [165], Ni-Zr [164, 537], Co-Zr [166], and Au-Y [163].

As another example of solid state amorphization reactions, a mechanical alloying technique is utilized to produce an amorphous powder from elemental mixtures of metal powders mechanically alloyed. However, the real discovery of amorphization by mechanical alloying was done in 1983

by Koch et al. [170], who found that an amorphous phase is induced after the mechanical alloying of elemental mixtures of crystalline metal powders of Ni-40 at.% Nb. Subsequently, many amorphous alloys have been formed by mechanical alloying/milling both the mixtures of two pure elements and the homogeneous intermetallic compounds. This technique is very promising for the formation of numerous new metastable phases. A detailed description of this technique will be discussed later. According to Schwarz and Johnson [162], who reported on the mechanism of amorphous phase formation by mechanical alloying, the results of amorphous phases that are formed by the mechanical alloying processes were rationalized on the basis that amorphization occurs under a chemical solid state reaction by the formation of a multilayer structure during milling, wherein the asymmetric interdiffusion couple and the negative heat of mixing, were considered to be the driving force for diffusion. Moreover, the defects created by the mechanical process in the ball mill play a major role in the amorphization process [540]. However, deformation is well known to create defects, such as vacancies, dislocations, atomic site defects, antiphase boundaries or grain boundaries. In the meantime, these defects will increase the free energy of the crystalline phase, which is considered responsible for amorphization during mechanical alloying/milling [540]. Indeed, the role of these defects in this process is similar to the role of those defects in the ion and electron irradiation technique.

More broadly, since 1983, amorphization by mechanical alloying, or milling, has created widespread research interest, owing to its advantages compared with other methods. For example, its ability to produce a large amount of amorphous material with equiatomic compositions have made it an effective amorphous material producer. Also, the composition range for the amorphous phase is much wider in alloys produced by mechanical alloying than in those obtained by rapid solidification processing [541]. Thus, the amorphization process by mechanical alloying has been followed in detail for Ni-Ti [172], Fe-Zr [173], Ni-Zr [542, 543] and Ni-Nb systems [170]. Amorphous phase formation by mechanical alloying was noted for multi-component Zr-, Mg- and Al-based alloy systems [544]. On the other hand, the amorphous phases in the Fe-based system (Fe-Zr-B) that formed by mechanical alloying were studied by Schultz [545]. Additionally, Schlorke et al. [546] studied the multi component system of Fe-Al-P-B-C alloys that were prepared by mechanical alloying. In the same way, amorphization by mechanical alloying has been reported in Fe-Co-Ni-Zr-B [547], Fe-Cu-Nb-Si-B [548], Fe-Ni-P-Si [549], Fe-Ni-P-B-Si [550] and Fe-Co-Zr-Mo-W-B [551], among others.

2.6 Mechanical Alloying

Mechanical alloying (MA) is a solid state powder processing technique used to produce homogeneous materials by blending and alloying dissimilar elemental powder mixtures. However, MA is a high energy ball milling process technique based on the principle of the deforming, fracturing, welding, and rewelding, which repeatedly occur to the trapped powder particles between two or more colliding balls, to create a homogeneous alloyed microstructure or uniformly dispersed particles in a matrix [552]. This technique was developed in the late 1960's by John Benjamin and co-workers at the International Nickel Company (INCO) to produce complex oxide dispersion-strengthened (ODS) alloys [552-555]. In general, MA techniques are based on the mechanical effects of the grinding media (vial and balls) and the agitating source (shaking, vibration and attrition) [544]. However, during MA processing, powders are loaded into a vial along with hard wear-resistant charge balls and milling by one of the agitating sources for the desired time and the charge ratio (weight of charge balls divided by weight of powders). The high energy impacts between the balls and the powder that is trapped between them or with the vial walls induces a continuous deforming, fracturing, welding, and rewelding when the agitating process, as seen in Figure 26. Causing deformation to the powder particles, leading to reduction in the particles size and work hardening. At a constant rate, the collisions occur repeatedly by fracture, deformation and interdiffusion thereby cold welding on the powder particles, and forming a lamellar structure [544, 556]. Over time, a steady state particle size is achieved, while structure refinement continues as shown in Figure 27.

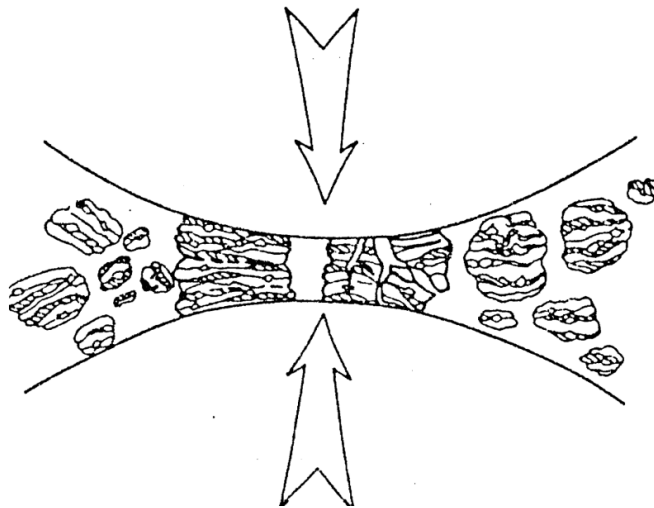


Figure 2.26: Illustration of a collision between two balls and trapped powder [554].

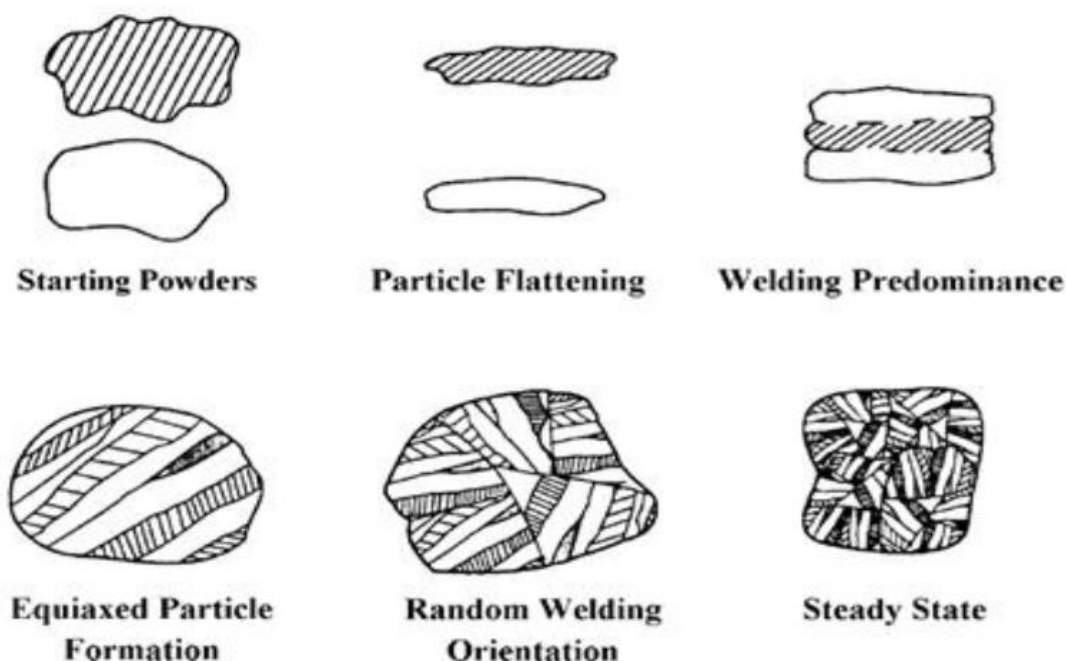


Figure 2.27: Particle microfracture evolution during mechanical alloying [557].

Different types of milling equipment have been developed for mechanical alloying such as SPEX mill, planetary ball mill and attritor mill. The SPEX mill is functionally described as a shaker mill or high-energy ball mill; this Mixer/Mill shakes a vial loaded with 10-20g of the powder of known composition that needs to process with hard wear-resistant balls by using movable arm to generate different movements back, forth, and lateral at approximately 1200Hz as shown in Figure 28 [544].

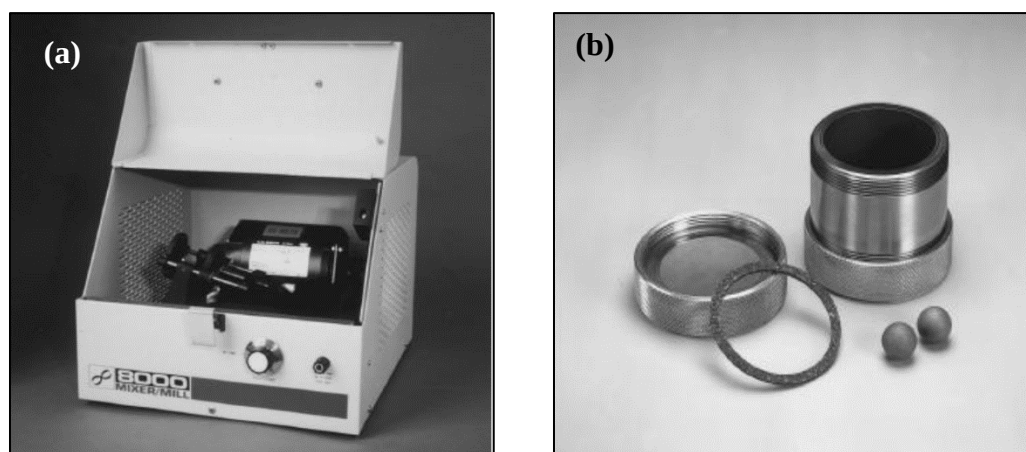


Figure 2.28: (a) SPEX 800 mill. (b) Vial and grinding media (Tungsten carbide).

The planetary ball mill, also known as centrifugal or ball mill, simply consists of a set of vials that are arranged on a rotating support disk. The vials are rotated on their axis in one direction and also on a disk the opposite direction producing planetary motion and centrifugal force, as seen in Figure 29 (b). Since the vials and the supporting disk rotate in opposite directions, the centrifugal forces alternately act in opposite directions. This motion causes both impact and friction effects as the balls collide with the vial wall and run down the side.

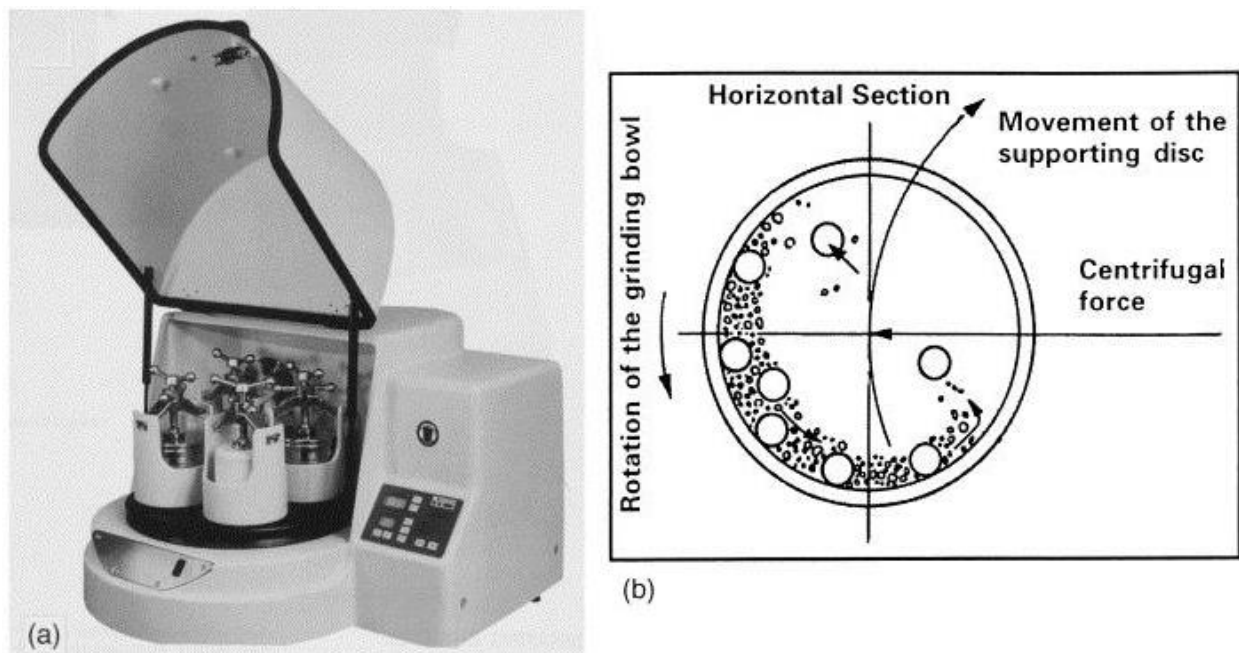


Figure 2.29: (a) Fritsch Pulverisette P-5 four station ball mill. (b) Schematic depicting the ball motion inside the ball mill [544].

In the Szegvari attritor mill, used in this study, the powder to be milled is charged into a vertical tank filled with grinding media. Both the powder and grinding media are then agitated by an impeller with arms causing the media to exert shearing and impact forces on the powder particles leading to repeated fracture and welding as seen in Figures 30 and 31. This action produces extremely fine and homogeneously dispersed powder particles. Attritors have the advantage of large-scale production with capacities between 0.5 and 40 kg which can be milled at a time. The velocity of the grinding medium in the attritors as linear velocity is much lower (about 0.5 m/s) than in the planetary or SPEX mills, and consequently the energy of milling in the attritors is low [544].

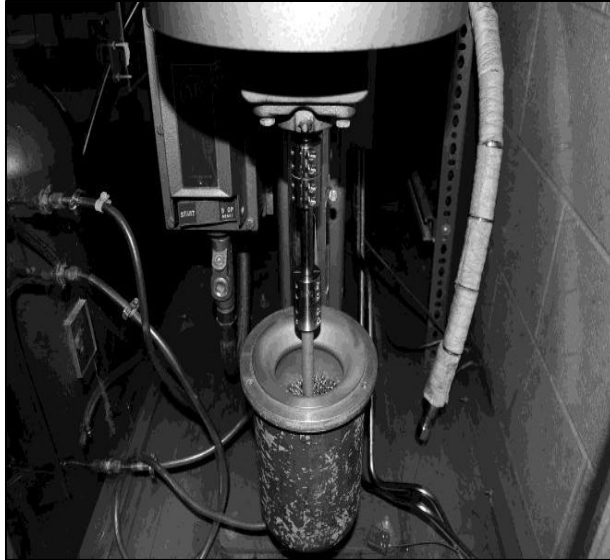


Figure 2.30: The Szegvari attritor mill.

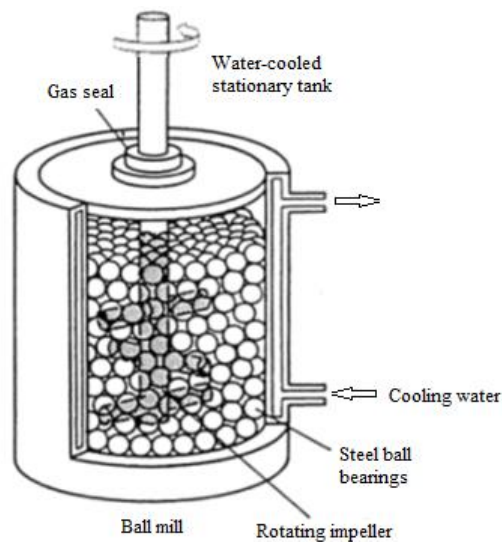


Figure 2.31: Diagram of the components of the stationary tank of an attritor mill [544].

High-energy ball milling is a complex process, which requires optimization of many parameters to achieve the desired product. The parameters of important during the mechanical alloying process are grinding or milling media type, atmosphere, process control agent (PCA) and the input energy parameters such as charge ratio, milling time, milling speed, and milling temperature [544].

Grinding media, the contamination arising from the grinding media (vial and balls) is of great importance during the material processing. The degree of contamination depends largely on the

mechanical properties of the powder that is being milled, as well as the chemical affinity of the material to some of the chemical elements of the milling media [558]. For example, during the milling of Ni for 24h by SPEX milling a hardened tool-steel vial and 440 C martensitic stainless steel balls, the Fe contamination was 13.6 wt.%, while Nb, milled at the same parameters developed only 4.03 wt.% Fe contamination [559]. Also, high energy mills systems such as the SPEX mills with longer milling times have larger effects on the milled material due to the increased amount of contamination [544]. Occasionally, the level of contamination could be significantly high. For example, over the synthesis of Ni-AL alloys by using stainless steel vials and balls, the Fe contamination can be as high as 18% [560]; Fe contamination has also been as high as 33% in some Tungsten milling experiments [561]. The suggestions to control and reduce this issue are: use low energetic mills whenever possible, inert milling media, and tungsten carbide vials and balls are also preferred. Sometimes, the milling media are made up from the same material as the powders, although this can often become technologically difficult and expensive [544].

The control of the milling atmosphere is also an important issue during the milling process and involves prevention of any undesired reactions of mechano-chemical nature or contamination that could happen in the product materials. When using milling process in air atmosphere, the product will contain a significant amount of contamination from oxygen and nitrogen [544]. Usually these effects are not desirable, and the best way to overcome this issue is by carrying out the milling process under the vacuum or in an inert gas, such as argon or helium [544].

Mechanical alloying may not be a successful and feasible process if the balance between the cold welding and fracturing of the powder particles is not achieved [544]. Without adding a process control agent (PCA) into the powder matrix during milling, cold welding will dominate and the particles will agglomerate [544]. A PCA acts as a lubricant or surfactant, absorbs on the surface of the powder particles, and limits cold welding; and a typical PCA used in high-energy ball mills is stearic acid, with a concentration of 1-5 wt.% of the total powder charge [544].

Other important parameters, which should be considered, are those called input energy parameters (milling time, charge ratio, milling speed, and milling temperature). The time that is spent on the milling is the most important of such parameter. However, the milling time used to achieve a steady state between the fracturing, cold welding and diffusion of the powder particles have influence on the powder microstructure and phase evolution when changing milling time and

milling system type [562- 564]. In fact, the milling time required for a mechanical alloying process varies depending on the type of milling system used, the type of material, the ball-to-powder ratio and the temperature of milling [544].

Charge ratio is the ratio of the weight of the balls to the powder and it has a significant effect on the milling time. However, the milling process with higher charge ratio has shorter processing time because of the increasing of the number of impacts events which means more energy transferred to the powder particles which is explained by increasing the kinetic energy per unit mass of ball mill powder, and consequently milling process takes place faster [544]. For example, the Ti-Al powder mixture was milled by SPEX to produce amorphous phase took 7 hours with charge ratio of 10:1, and it took 2 hours by using charge ratio of 50:1, and only 1 hour by using charge of 100:1 [544]. Lisboa et al. showed that when milled $\text{Al}_{50}\text{Si}_{30}\text{Fe}_{15}\text{Ni}_{15}$ by SPEX 8000 for 40 hours with charge ratio of 15:1 and 95 hours with charge ratio of 10:1, both the milled gave almost similar patterns considering phases, position of crystalline peaks and relative intensities [565].

Milling speed is one of the important parameters that affects mechanical alloying products. The mechanical alloying processes with the higher milling speed have higher input energies compared with the lower milling speed because of the increasing the number ball collisions with the charge powder and therefore increasing mechanical alloying process [544]. Therefore, it is easy to form a homogeneous alloyed microstructure or uniformly dispersed particles in the matrix, and amorphous due to the increase of the strain and defects concentration as the milling speed increased [508]. Sadrnezhad et al. reported that the amounts of amorphization and diffusion for Ni-Ti powder mixture that was milled by a vertical attritor, are functions of the milling speed and other input parameters [566]. In contrast, very low rotational speeds lead to very long periods of milling and a large inhomogeneity in the alloy because of inadequate energy input [567]. On the other side, very high milling speed leads in a reduction of milling time and thus effectiveness of alloying decreases because of the decrease in time available for diffusion of the solute. Also, very high milling speeds originate greater contamination due to the excessive heat and wear between the balls by themselves or with the vial walls [567].

Milling temperature is also an important parameter, and must be considered during the mechanical alloying process because of its influence on the final structure of the milled powder.

However, during mechanical alloying, some of the mechanical energy converts to heat through plastic deformation. Also, the nature of the exothermic chemical reactions that happen during the milling process is another cause to the increase of the temperature. The increasing of the temperature, higher concentration on the lattice defects, and larger grain boundary surface accelerate the diffusion processes [544]. Since diffusion processes are involved in the formation of alloy phases irrespective of whether the final product phase is a solid solution, intermetallic, nanostructure, or an amorphous phase, it is expected that the milling temperature will have a significant effect in any alloy system [544]. For example, “during planetary ball milling of a Cu-37at%Ag powder mixture, it was noted that a mixture of an amorphous and crystalline (supersaturated solid solution) phases was obtained on milling at room temperature; instead, only a Cu-8at%Ag solid solution was obtained on milling the powder at 200°C. Similar results were also reported by others in the Cu-Ag, Zr-Al, and Ni-Ag alloy systems and were explained on the basis of the increased diffusivity and equilibration effects at higher temperatures of milling [544].” Milling at lower temperatures, such as cryomilling, has been shown to reduce the time required to produce nanocrystalline materials. For example, Al powder was milled for 20 hours by a high-energy ball mill at room temperature produced a grain size of approximately 25 nm, while it took 8 hours of milling in a Szegvari cryomill to achieve the same result [568].

Mechanical alloying has achieved great success as a processing technique for preparation of alloyed powders or composites in powder form [544, 566]. In the early 1980s, the era of the 'Solid State Amorphization reactions' (SSAR) was started by using a mechanical alloying technique [569] which did not confine on the SSAR materials only, but also it drove up and spreaded to include many different synthesized materials, such as nanocrystalline materials [570], stable and metastable materials [544], composites and nanocomposites materials [265, 266], and intermetallic compounds [571]. MA widely applied to metallic systems, but in the late 1980s, and early 1990s Shaw and coworkers studied the possibility to use mechanical attrition to the polymeric materials for blending and alloying and its effects on the structure and properties of the processed material [572-575]. Subsequently, others have studied milling-induced changes in the structure of several semicrystalline and amorphous homo-polymers [576-589].

Thus, the MA is an important technique for producing larger amounts of metallic amorphous phases and with a wider chemical composition range. In this work, SPEX mill was used to obtain

Co-C amorphous powders with different chemical compositions and also to study this process by means of some process parameters and their influence on some of the material properties.

2.6.1 Amorphization by Mechanical Alloying

As stated above, amorphization by mechanical alloying is not purely a mechanical process and the amorphous phase is formed by reactions within the solid state. However, the mechanical alloying amorphization is a solid state amorphization reaction, which is a technique capable of amorphizing materials below their crystallization temperature, using interdiffusion mechanisms [162, 170 and 590]. Moreover, amorphization by mechanical alloying has a wider glass forming composition range in many binary alloy system; therefore equiatomic compositions are most favorable for amorphization by mechanical alloying [591, 592]. On the other hand, in the rapid quenching technique, amorphization is restricted to the compositions near the eutectic, due to kinetic restraints [591].

This process can be well illustrated in a hypothetical binary phase diagram between elements **A** and **B**, as shown in Figure 32. Figure 32 (a) shows a presence of terminal solid solutions α and β , with an intermetallic phase γ and liquid phase **L**. Gibb's free energy of these phases at temperature T_r , is shown as a function of the composition in figure 32 (b), on the assumption that the free energy of the amorphous phase is equivalent to that of the liquid. So in this case, variables α , β , γ , and mixtures of these phases at a temperature T_r are thermodynamically stable, whereas **L** is metastable, which means that the amorphous phase is also metastable. As seen in Figure 32 (b), the free energy of the equiatomic blended elemental powder mixture G_c is represented as a point **1**, while both the free energy of amorphous phase G_a are presented as point **2**, and the free energy of the formation of γ , the intermetallic phase G_i as point **3**. Although thermodynamically the γ phase is seen to be the most stable phase which is the lowest free energy state, kinetically it can be prevented from occurring, by raising the energy of the system beyond point **2** through the structural defects during the mechanical alloying. Therefore, for an equiatomic composition, mechanical alloying essentially creates an elemental powder mixture with Gibbs free energy corresponding to point **1** in Figure 32 (b). As a result formation of the amorphous phase is energetically favorable, though less favorable than the intermetallic phase. Further, the reaction leading the crystalline elemental mixture to form the intermetallic phase can be a prevented by proper choice of metals, the reaction temperature and the reaction time.

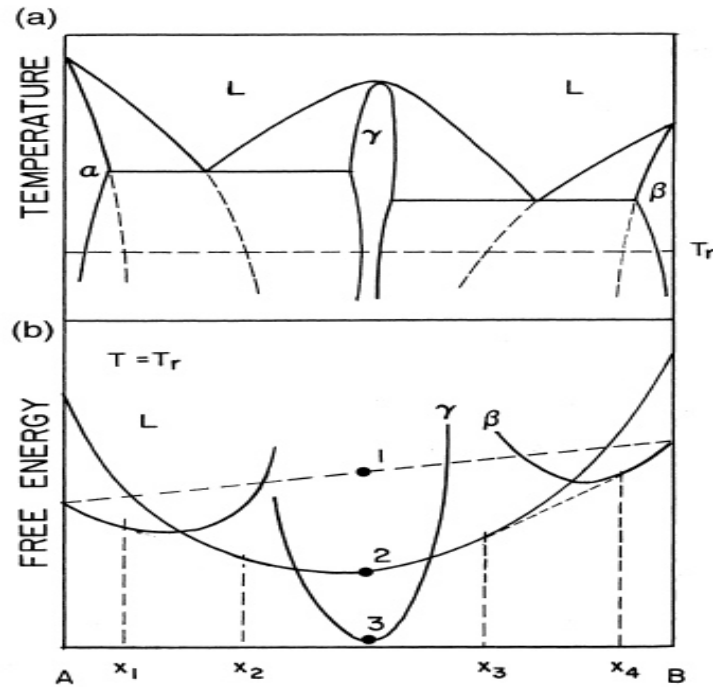


Figure 2.32: (a) Hypothetical binary phase diagram exhibiting limited solid solubility on both ends and also showing the presence of an intermetallic phase. (b) Gibb's Free energy vs solute composition at a temperature corresponding to T_r . Note that points **1**, **2** and **3** represent the free energy values of the mixture of **A** and **B**, the amorphous phase, and the intermetallic phase, respectively [544].

Under these circumstances, amorphization by means of mechanical alloying becomes possible to reach, but the more important issue is how to keep this metastable amorphous phase without transforming it to the equilibrium phase. However, the stable state of a system can be thermodynamically defined as the state when the Gibbs free energy G of the system is at the lowest possible value. In general, below the melting temperature and at the equilibrium, the crystalline phase is classified as a stable phase with a Gibbs free energy G_x , which is always lower than that of the amorphous phase. Therefore, the amorphous phase is a metastable state, i.e., an energy barrier that prevents the amorphous phase from spontaneous crystallization. So, in order to achieve the amorphous phase by mechanical alloying and maintain it, let's assume an initial state of high free energy G_0 in the system, as schematically shown in Figure 33. In this case, the initial state is the blended elemental mixture which consists of a layered system of mixture crystalline system [517].

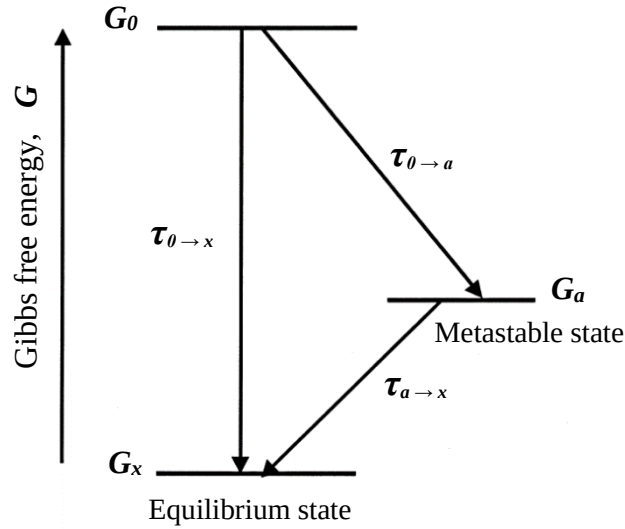


Figure 2.33: Schematic representation of the basic principles of amorphization by solid state reaction [517, 593].

As thermodynamics concepts, this high free energy G_0 will go down to the equilibrium state. In the presence of the mechanical alloying process, there are two ways to lower the free energy of the system either by the formation of the metastable amorphous phase with free energy G_a or by the formation of the equilibrium crystalline phase G_x . The crystalline phase is definitely thermodynamically favored since the driving force for crystallization $\Delta G_x = (G_0 - G_x)$ is larger than that for amorphization $\Delta G_a = (G_0 - G_a)$. However, as is known the formation of crystalline or amorphous phases depends on thermodynamic as well as kinetics factors. Consequently, if the system is kinetically restricted from reaching the crystalline state, which is the lowest form of free energy, the amorphous phase is possible to form and reach it, so long as the amorphization reaction is carried out faster than the formation of the equilibrium crystalline phase. However, the amorphization reaction from the initial state G_0 to the metastable amorphous phase G_a ($G_0 \rightarrow G_a$) should be much faster than the formation of the equilibrium crystalline phase ($G_0 \rightarrow G_x$). Concurrently, this metastable state of the amorphous phase must be not crystallize as the reaction continues. As Schultz and Eckert [517, 593] explained, the time scale for crystallization of the amorphous phase must be longer than that of amorphous phase formation: they summarize these kinetic constraints as follows:

$$\tau_{0 \rightarrow a} \ll \tau_{0 \rightarrow x}$$

Eq. 20 [517, 593]

$$\tau_{0 \rightarrow a} \ll \tau_{a \rightarrow x} \quad \text{Eq. 21 [517, 593]}$$

Where $\tau_{0 \rightarrow a}$ and $\tau_{0 \rightarrow x}$ are the characteristic reaction times for the formation of the amorphous and equilibrium crystalline phase, respectively, and $\tau_{a \rightarrow x}$ is the time scale for the crystallization of the amorphous phase.

It was previously stated and according to Schwarz and Johnson's suggestions [162], the amorphization by mechanical alloying cannot occur until two conditions are obtained. First, the system components must have a large negative heat of mixing, and they should have asymmetrical diffusion coefficients, i.e., one species must diffuse anomalously fast into the other. The second condition of asymmetric diffusion has been seen to favor amorphization by mechanical alloying and is related to the atomic size difference for different elements [594]. Subsequently, the scientists and researchers found that the heat of mixing is a very important condition in the rapid quenching process for amorphization to occur, but is not an essential condition for the mechanical alloying process, since some alloy systems with a positive heat of mixing have been amorphized by mechanical alloying. However, the scientists and researchers now believe that amorphization by mechanical alloying mostly occurs as a consequence of the increase in the free energy of the crystalline phase of the system during the mechanical alloying. This increase in the free energy results from the deformation and the structural defects that the mechanical alloying process produces on the system during the processing. Indeed, this destabilization in the crystalline phase occurs because of the accumulation of structural defects, such as vacancies, dislocations, grain boundaries, and antiphase boundaries during mechanical alloying processing. However, the increase of the grain boundary area results from the continued declining in the grain size; moreover, the lattice expansion contributes to the increase of the free energy of the system [595]. As a consequence, these structural defects elevate the free energy of the intermetallic system to a level higher than that in the amorphous phase, so that under these circumstances, the amorphous phase formation becomes possible to form. In view of that, it has been reported that amorphization by the mechanical alloying process can occur when the strain in the slow diffusing species reaches a maximum [596], while, in the case of ordered alloys, amorphization occurs when the long range order parameter is less than 0.6, with a corresponding volume of expansion of about 2% [597].

2.6.2 Amorphization of Cobalt-Based Alloys by Mechanical Alloying

Amongst the metallic amorphous alloys that are prepared by means of mechanical alloying are the Co-based amorphous alloys, which are of considerable interest because of their magnetic and mechanical properties. As already mentioned, the Co-based amorphous alloys exhibit excellent soft magnetic properties such as low coercivity, high permeability and low hysteresis losses, and these soft magnetic properties result from their near zero magnetostriction and magnetocrystalline anisotropy [598, 599]. Consequently, mechanical alloying has been successfully utilized as a technique to produce Co-based amorphous powders of several binary, ternary, quaternary and multi component systems, and a proven effective technique to obtain Co-based amorphous powders [600, 601]. For example, Hellstern and Schultz [602] were able to amorphize Co-Zr system by mechanical alloying. In their work they confirmed that the $\text{Co}_{55}\text{Zr}_{45}$ in at.% alloy after 20 hours of milling can be easily amorphized by mechanical alloying. Also, they demonstrated that the amorphous transition metal-transition metal (TM-TM) systems can be produced by mechanical alloying, as long as both elements are sufficiently ductile. Work done by Kimura et al. [603] was also on the Co-Zr system, and as used a mechanical alloying attritor to amorphize $\text{Co}_{85}\text{Zr}_{15}$ in at.% alloy at different flow rates of cooling water. Kimura et al. reported that the full amorphous phase of $\text{Co}_{85}\text{Zr}_{15}$ in at.% alloy could be formed after 8 to 14 hours of milling depending on the attrition temperature; therefore, he concluded that the degree of amorphous phase transformation depended on the milling time as well as the attrition temperature.

In another work, Kimura et al. [604] succeeded in amorphizing several binary cobalt-rich systems of Co-Zr, Co-Nb and Co-Ti by mechanical alloying. In this work Kimura and his group developed magnetic amorphous powders of $\text{Co}_{90}\text{Zr}_{10}$, $\text{Co}_{85}\text{Nb}_{15}$ and $\text{Co}_{80}\text{Ti}_{20}$ in at.% using a mechanical alloying attritor, and they found that the amorphous cobalt-rich powders have lower coercivity compared with their crystalline phase.

In contrast, Xueming et al. [605] studied the mechanical alloying amorphization of a Co-Nb system using high energy planetary ball milling. Xueming et al. reported that a perfect amorphous phase of the Co-Nb alloy powders was obtained after 40 hours of milling at room temperature. Also, they mentioned that the amorphous alloys that were formed showed soft magnetic properties. Xueming's group concluded that mechanical alloying is a promising and feasible way to produce amorphous magnetic materials for a wide variety of applications. Similarly, Machado et al. [606]

studied the amorphization of the Co-Nb system using as SPEX 8000 shaker mill as a mechanical alloying technique. Machado et al. confirmed that the Co-Nb system with a typical composition of $\text{Co}_x\text{Nb}_{100-x}$ in at.% (where $x = 25, 57$, and 80 after 40 hours of milling) was transformed into amorphous powders with soft magnetic properties.

Meanwhile, Corrias et al. [607] discussed $\text{Co}_{67}\text{B}_{33}$ in at.% alloy that was mechanically alloyed using high energy planetary ball milling. The results showed that a partially amorphous phase occurred and Corrias et al. concluded that the different milling or process conditions cannot lead to a complete amorphous phase transformation. However, they made this conclusion based on similar results [608] reported about SSAR induced by annealing of multilayers of nickel and boron, where the amorphous phase was a few nm thick. In complete contrast, Kubalova et al. [609] reported that the $\text{Co}_{87}\text{B}_{13}$ in at.% alloy after 70 hours of milling by using high energy planetary ball milling underwent a complete amorphous phase transformation, as shown in Figure 34. Kubalova et al. explained that the dissolution of the B in the fcc Co phase that occurred during the milling process led to a complete amorphous phase transformation, and this fcc supersaturated solid solutions of Co (B) could be a interstitial or substitutial-interstitial mixed type. Thus, this complete amorphous phase transformation resulted from the increase of the stacking faults concentration that was caused by the continuous milling of the fcc solid solutions of the Co (B).

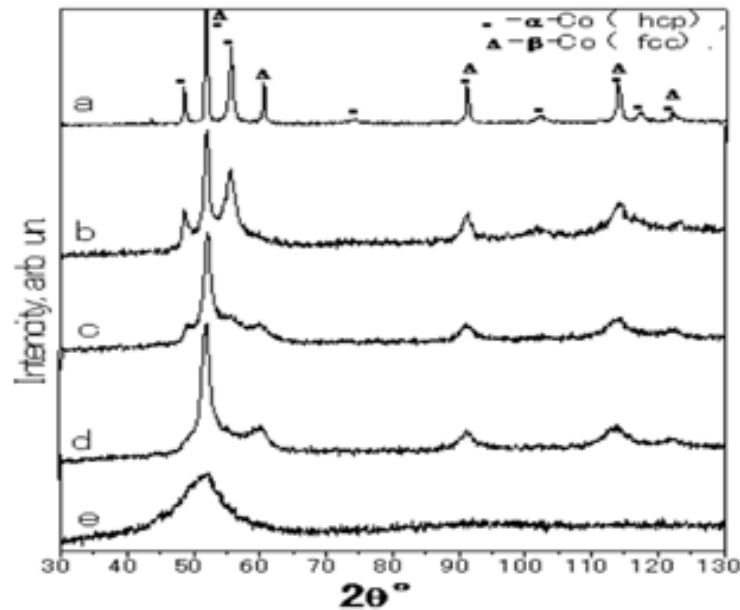


Figure 2.34: XRD patterns of $\text{Co}_{87}\text{B}_{13}$ in at.% after various periods of milling: (a) as received powder. (b) Milled 20 min. (c) milled 70 min. (d) milled 3hr. (e) milled 70hr [609].

Ruuskanen et al. in a study of mechanical alloying for $\text{Co}_{100-x}\text{Gd}_x$ in at.%, where in ($x = 10, 15, 20$, and 25) [610] reported that the mechanically processed Co-G showed a complete amorphous phase transformation after 12 hours of milling by SPEX 8000 shaker.

In the amorphization of multi component systems of cobalt-based alloys by mechanical alloying, work has been conducted and continues, designed to improve the cobalt-based amorphous alloys in terms of structure and application as well. For example, Bolarín-Miró et al. [611] worked on amorphization of Co-Cr-Mo system by mechanical alloying. Bolarín-Miró et al. concluded that a complete amorphous phase transformation in the $\text{Co}_{60}\text{Cr}_{30}\text{Mo}_{10}$ in at.% can be obtained if the Cr and Mo are milled for 9 hours to get the solid solution of $\text{Cr}_{80}\text{Mo}_{20}$ first and then Co is added to them and all of them milled for 14 hours. On the other hand, the Co-Cr system cannot lead to an amorphous phase.

Another example of the amorphization of multi component systems of cobalt-based alloys by means of mechanical alloying is the Co-Nb-B system done by Nascimento and Melnyk [612]. In this work Nascimento and Melnyk were able to amorphize the alloy $\text{Co}_{87}\text{Nb}_{46}\text{B}_{15}$ in at.% by mechanical alloying using high energy planetary ball milling.

Wu et al.'s work [613] is another example, in which they studied the $\text{Co}_{62-x}\text{Fe}_x\text{M}_8\text{B}_{30}$ in at.%, (where $\text{M}=\text{Ti}, \text{Zr}$ and $x = 0, 5, 10, 15, 20$, and 25); amorphization by mechanical alloying took place using a SPEX 8000 shaker. Wu et al. reported that the milling time to reach the amorphous phase was iron content-dependent, which means that substituting the Co amount in the system with a higher amount of Fe would retard the amorphization reaction. Wu and his associates explained that the differences in atomic size and heat of mixing of the system were affected when the chemical composition of the system was changed by increasing the amount of Fe. This change made the alloy less tolerant to the empirical component rules of the glass forming ability [217], making the system less glass-forming, and therefore a long milling was required to cover this incompatibility. Wu et al. also worked on milling Co-M-Ti-B ($\text{M}=\text{Fe}, \text{Nb}$) using SPEX 8000 shaker to produce a ferromagnetic Co-based amorphous alloy [614]. In this work Wu et al. succeeded in amorphizing $\text{Co}_{70-x}\text{M}_x\text{Ti}_{25}\text{B}_5$ in at.% (where $\text{M}=\text{Fe}, \text{Nb}$ and $x = 5, 10, 15, 20$, and 25), but substituting the Co amount in the system with an amount of Fe or Nb led to the reduction of the thermal stability of the amorphous powders.

Taghvaei et al. [615] also were able to amorphize a multi component of Co-rich alloy of $\text{Co}_{87}\text{Nb}_{46}\text{B}_{15}$ in at.% after 200 hours of milling, using a high energy planetary ball milling. They reported that the amount of the amorphous phase in the system increased by increasing the milling time, and after 200 hours of milling finished with a full amorphous phase, as shown in Figure 35.

Moreno et al. reported a study about mechanical alloying amorphization of $\text{Co}_{62}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ in at.% [616]. In this study, they carried out the mechanical alloying in a high energy planetary ball milling and using three different types of boron powders in the starting mixture. However, they were using a crystalline β -B, commercial amorphous B and optimized amorphous B, which facilitated the mechanically alloying. The results showed that the amorphous phase was successfully produced in the three types of boron. However, they found that using the optimized amorphous B was more efficient for the amorphization process of the alloy, but its disadvantage was inserting some iron contamination into the system.

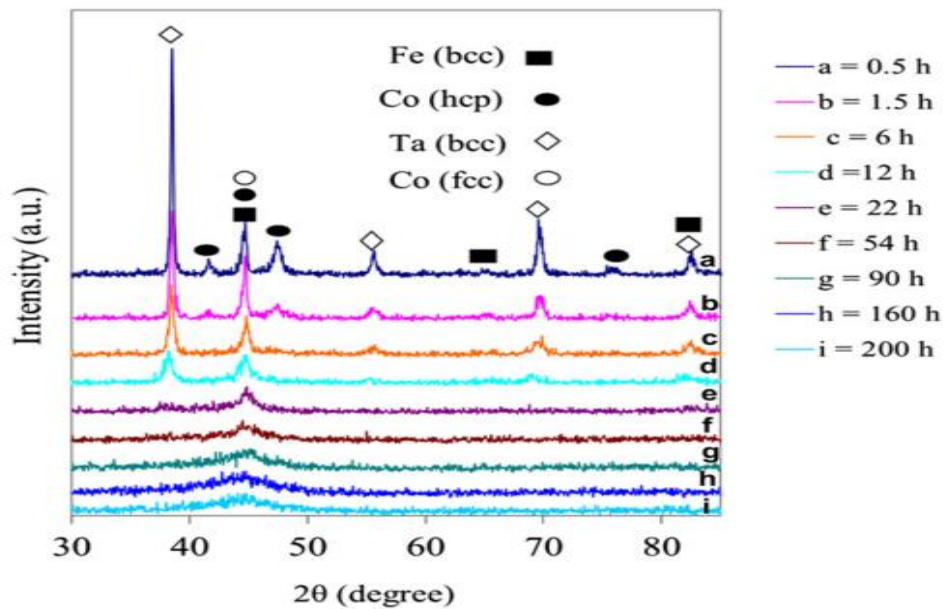


Figure 2.35: X-ray diffraction patterns for the elemental powders of $\text{Co}_{87}\text{Nb}_{46}\text{B}_{15}$ in at.% milled for up to 200 hours [615].

Other work done by Neamtu et al. [617] involved using a wet high energy planetary ball milling to amorphize $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_9$ in at.%, resulting full amorphization after 40 hours of milling. In fact, after this work Neamt et al. developed a new amorphous alloy by adding Zr and Ti to the system. In this new work Neamtu et al. [618] also used a wet high energy planetary ball

milling to amorphize alloys with chemical compositions of $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_4\text{Zr}_5$, $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_4\text{Ti}_5$, $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{10}\text{B}_9\text{Zr}_5$ and $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{10}\text{B}_9\text{Ti}_5$ in at.%. The results showed that the complete amorphization reaction to the powders was achieved after 40 hours of milling. Also, they found that the substitution of Zr or Ti for Si lead to an increase of the crystallization temperature of the alloys by 18% and 21%, respectively, but the substitution of the Ti or Zr for B did not have a significant effect on the crystallization temperature of the amorphous phase.

A Co-based amorphous binary system of Co-C is another system which has a very small share in the amorphization by mechanical alloying. However, in general there are a limited number of studies that have been performed on the production of Co-based amorphous alloys by the mechanical alloying processing, compared to the use other methods of processing; in particular, a very limited number of studies in the Co-C system have been performed using the mechanical alloying processing. For example, Yang et al. [619] characterized the mechanical milling for Co-C system by mechanically alloying $\text{Co}_{50}\text{C}_{50}$ in at.% by SPEX 8000 shaker. Yang et al. reported that a full amorphous phase was obtained from the mixture of pure cobalt and carbon powder by using a mechanical alloying process. However, Yang et al. concluded that after 12 hours of milling a complete amorphous phase transformation occurred and they confirmed the results from the X-ray diffraction, as shown in Figure 36.

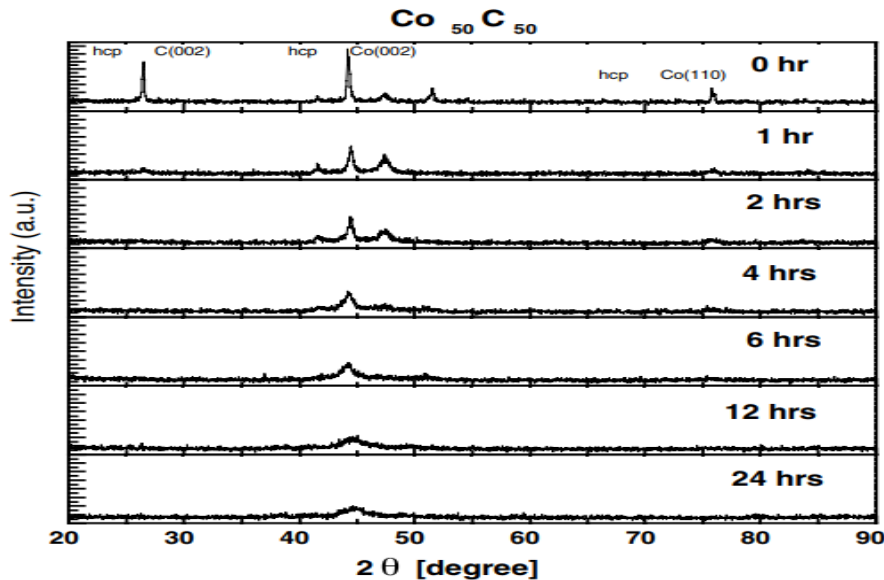


Figure 2.36: X-ray diffraction patterns for the elemental powders of $\text{Co}_{50}\text{C}_{50}$ in at.% milled for up to 24 hours [619].

In contrast, Jiang et al. [620] reported on the mechanical alloying of C-Co system. In this study they milled alloys of $\text{Co}_x\text{C}_{100-x}$ in at.%, (where $x = 1, 2, 3, 4$, and 5), up to 100 hours by SPEX 8000 shaker. Jiang et al. believed that the X-ray diffraction results showed an amorphous C matrix with small embedded Co particles after a long time of milling, as seen in Figure 37; they also believed that a phase transformation occurred during the $\text{Co}_{\text{hcp}+\text{fcc}}$ phases to the Co_{hcp} phase.

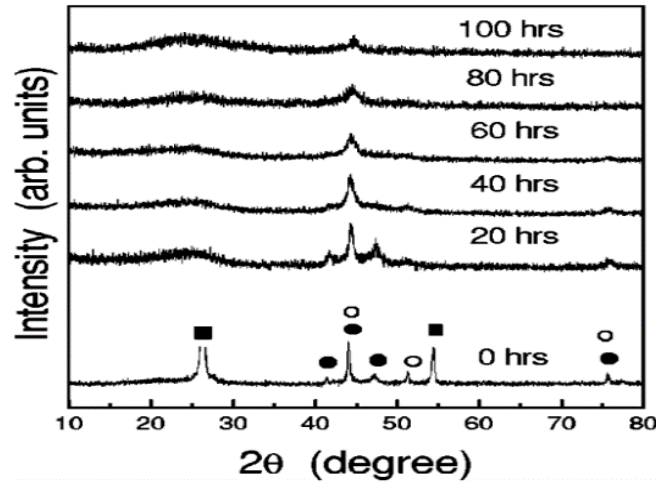


Figure 2.37: X-ray diffraction patterns for the elemental powders of Co_5C_{95} in at.% milled for up to 100 hours [620].

Although the majority of amorphous alloys are conventionally produced by the rapid quenching method, the mechanical alloying technique is a promising alternative method to synthesize these alloys. However, mechanical alloying proved to be an effective technique to prepare Co-based powders by milling of the amorphous ribbons obtained by rapid quenching technique [600], [601]. Conversely, as seen in the Co-C system, only a very limited number of Co-C alloy amorphizations by mechanical alloying have been developed and evaluated. Therefore, this work focuses on the amorphization of the binary system of Co-C by mechanical alloying, in view of an understanding of the amorphous phase transformation development and how the chemical composition and mechanical alloying parameters affect the resulting microstructure and properties.

2.7 Metallic Amorphous Composites

Bulk metallic amorphous composites have attracted considerable attention due to both scientific and engineering aspects in the two past decades because of their unique mechanical properties. Recently, many researches have focused on introducing the metallic amorphous to the composite

microstructures to suppress the fracture while preserving the high strength, because they typically combine a strong metallic amorphous with ductile crystalline matrix reinforcements, or vice versa to increase the strength, hardness and wear resistance of the ductile crystalline matrix [264-276]. Traditionally metal matrix composites (MMCs) are produced from metal matrices reinforced with ceramics particles or fibers such as Al_2O_3 or SiC to enhance their mechanical properties [277-282]. In this case, however, and with the significant differences in the thermal coefficient of expansion, chemical and physical properties between the metals and ceramics, typically induce poor bonding, where detrimental interfacial reactions often occur [283-287]. However, ceramics come with low wettability on account the metal matrix, which generates particle agglomeration and porosity as well [288-291].

So, in order to get a perfect bonding between the metallic matrices and the reinforcements and good mechanical properties, many researches these days are using the metallic amorphous as reinforcements to the metallic matrices, and vice versa, where the metallic nature of the reinforcing phase plays an important role in achieving a good bonding between the matrices and the reinforcements, by creating a suitable coefficient of thermal expansion, and compatible chemical and physical properties [264, 265, 269, 272, 281 and 283].

With regard to the production, development and application of the metallic amorphous composites, several works have been conducted and others are still underway, designed to improve the metallic amorphous composites in terms of structure and application as well. The first attempt to use amorphous metals to reinforce metal matrices was by Takayama and Fehrman in 1980 [621], they produced metallic amorphous composites by wrapping a layer of $\text{Fe}_{78}\text{Mo}_2\text{B}_{20}$ in at.% metallic amorphous on the copper and aluminum wires. Takayama and Fehrman observed that there was a significant increase in the strength of the wires as a result of the incorporation of the amorphous metal and that there was a slippage between the wires and metallic glass, which means there was a poor interfacial bonding. In 1981, Cytron [622, 623] reported on the production of the first bulk metallic amorphous composites, using vacuum hot pressed $\text{Ni}_{60}\text{Nb}_{40}$ in at.% metallic glass strips reinforcements with an aluminum alloy matrix. Cytron concluded that the metallic amorphous could be a good reinforcement to the metallic matrix, where the composite samples had showed a good bonding between the aluminum matrix and metallic amorphous reinforcements. He also surmised that this method could be a promising technique for use with metal matrix composite

materials in the future. Similarly, many other studies on different systematic approaches appeared later along the lines of Cytron's approach [5, 264-270, 276, and 624-626].

With the goal of maintaining a systematic approach to increase the strength, hardness, stiffness and wear resistance of the ductile crystalline matrix, several works such as amorphous particulate reinforced lightweight metals and alloys were conducted. In the case of aluminum and Al-based alloy matrices, studies were done using the metallic amorphous particle reinforcement, such as the Fe-based metallic glasses [269, 270 and 624-626], Mg-based metallic glasses [627, 628] and Al-based metallic glasses [276, 629]. Other examples of lightweight metals and alloys that were reinforced by amorphous particulates were magnesium and Mg-based alloys, concerning which several studies were conducted by using many different amorphous particles such as Ni-Nb, Ni-Ti, etc. [630-632]. Meanwhile, some attempts were made to reinforce titanium and Ti-based alloys, using amorphous particulates [633, 634]. At the same time, other experiments on amorphous particulate reinforcements in different systems were done successfully, including matrices of Fe reinforced with amorphous particulates of Fe-W [265], Ni by Ni-W [266], Cu by Cu-Zr-Al-Ni-Ti and Ni-Zr-Ti-Si-Sn [635, 636].

The W matrix also had a share of this work, but different systematic approaches were used. The idea behind using the amorphous particulate to reinforce the W matrix was to force the branching of shear bands by creating interfaces [637-641], which meant increasing the shear localization effects to control the tungsten fracture behavior [641]. In this approach, work has been reported attempting to fabricate materials for kinetic energy penetrators by using an amorphous particulate to reinforce the W matrix such as the metallic glass of Zr-Nb-Cu-Ni-Al [637], Zr-Ti-Cu-Co-Be [638, 640] and Hf-Cu-Ni-Ti-Al [641].

Another systematic approach to produce bulk metallic amorphous composites was by enhancing the amorphous matrix with the soft crystalline phase [264, 642]. However, although the bulk metallic glasses have a very high strength, they showed very limited plasticity and catastrophic failure, which restricted their widespread use in applications [5, 642-644]. Thus, it was necessary to solve this problem by forming a ductile crystalline phase in the metallic glass matrix through an either in-situ method by (forming precipitates dispersed [642], or an ex-situ method in the form of particles [645] and fibers [646]). So this ductile crystalline phase works as boosting a strain localization at different sites throughout the matrix, which acts as a

microstructural arrest barrier to the shear band propagation [642, 647 and 648]. From this point of view, many investigations have been reported on embedding a crystalline phase in the metallic matrix. For example in the case of the toughening strategies of the bulk metallic glass composites, a large compressive plasticity was successfully achieved in different metallic glass composites such as the Zr-Ni-Cu-Ta-Al bulk metallic glass reinforced by precipitates of Ta-rich solid solution particles [642, 649], Zr-Nb-Cu-Ni-Al with bcc β -Ti phase [650] and Zr-Ti-Cu-Ni-Be with Ti-Zr-Nb bcc β phase [651].

A slightly different approach later on was followed along the lines of increasing tensile ductility and superior fracture toughness by controlling the dendrite spacing of the primary phase, using properly prepared methods and good control over the alloy compositions [268, 652-654]. The results have been positive, where a significant tensile ductility and superior fracture toughness have been achieved in many different metallic glass matrix composites, especially with the Zr- and Ti-based metallic glass composites [655-657]. An example of that was work done by Flores et al. [658], using a ductile phase of dendritic Zr-Ti-Nb to reinforce the bulk metallic glass matrix of Zr-Ti-Ni-Cu-Be. The results showed that both the fracture resistance and the fatigue lifetime relative to the monolithic glass were significantly improved, caused by the effects of the separation distance between the second phase on the shear band formation and distribution. Other work done by Kühn et al. [659] using ductile bcc precipitates β -Ti-type phase to enhance the Zr-Nb-Cu-Ni-Al bulk metallic glass matrix resulted in significantly improved mechanical behavior compared to monolithic glass. It has been observed that the alloy composition and the cooling rate lead up to different volume fractions and dendrite sizes of the ductile bcc phase, which in turn affects the yield strength, elastic and plastic strain. On the other hand, Hofmann et al. [660] in his work on Zr-Ti-Nb-Cu-Be metallic glass matrix system that was reinforced with β -Ti solid solution (dendrites) demonstrated that bulk metallic glass matrix composites through thermoplastic processing could achieve high tensile ductility and ultra-high toughness.

Moreover, Qiao et al., using Bridgman solidification have created another work on a Zr-Ti-Nb-Cu-Be metallic glass matrix composite system [661], and reported that the sizes and volume fractions of the β -Zr dendrites phase in the composites are controlled by adjusting the withdrawal velocities. Therefore, Qiao's results confirmed that the large plasticity and tensile ductility could be achieved by only controlling the cooling conditions. Narayan et al. [662] also worked on Zr-Ti-

Nb-Cu-Be metallic glass matrix composite system and dendritic bcc b-Ti phase as reinforcements, where the results showed that the higher ductility was reached in the presence of the large dendrite size. They was noticed that a remarkable improvements in both the ductility and yield strength in the case of the finer interdendritic spacing, due to the confinement of shear band nucleation in the smaller volumes of the glass matrix. In contrast, Fan et al. studied the casting of Co-Fe-Ta-B metallic glass matrix composite system with an in-situ precipitated crystalline dendrite phase [663]. As a result, Co-based metallic glass composites could be promising high performance materials with both high strength and good plasticity.

Finally, Wang et al., in another work on the Fe-Co-Ni-Cr-Cu-C-Y metallic glass matrix composite system, reported that the micro scale of dendritic phases and nanoscale crystalline particles have been created as reinforcements by using a strategy of copious nucleation, positive mixing heat and high entropy of mixing [664]. Therefore, this Fe-based metallic glass composite with a hierarchical microstructure has exhibited extraordinarily high strength and large ductility, high resistance to oxidation and corrosion.

In sum, the combination of the high strength, toughness, large elastic limit, excellent corrosion resistance, and superplastic forming ability has made the metallic glass composites of great importance because of their promising usage across a broad range of industries, including aerospace, aeronautical, nautical, medical tools, automotive, sporting goods, defense, and others [656, 665-667].

2.8 Amorphous Magnetic Materials

Over the past several decades, amorphous materials have been investigated for applications in magnetic devices requiring magnetically soft materials such as power electronics and consumer electronics (including transformers, inductors, saturable reactors, magnetic amplifiers, chokes, etc.) [405-415]. These significant uses of amorphous materials in the magnetic application devices are due to the combination of the unique magnetic properties found in them. As mentioned in the description of the properties of bulk amorphous metal alloys and soft magnetic materials, research on the amorphous soft magnetic alloys has dramatically increased after Gubarov's theoretical prediction in 1960 [31, 668] that the short-range order in the crystal structure of the material played a dominant role in the magnetic properties of the material and not the longer-range ones; thus, he predicted that the amorphous metals could be effective ferromagnetic materials. However, the

tempo of research work on bulk metallic amorphous alloys as soft magnetic materials increased worldwide only after Duwez and Lin's work in 1967 [33]. As a result, a significant number of binary, ternary, and multicomponent systems of amorphous metallic alloys have been widely studied and subsequently used in industry.

As explained in the previous sections, amorphous materials exhibit excellent soft magnetic properties due to their low of magneto-crystalline anisotropy and lack of microstructural defects (grain boundaries, dislocations or precipitates), which make their domain walls move easily, leading to a low level of magnetization. Thus, the key beneficial feature of amorphous alloys lies in their high permeability μ , low coercive force H_c , and low energy losses due to their disordered structure. But, with respect to the development of soft magnetic materials, from a practical and technical point of view, the core loss and saturation flux density B_s are cooperative factors, demonstrating that B_s decreases/increases with the decreasing/increasing core loss [247, 403 and 659]. Technically, magnetic materials with high permeability and low core loss are accepted as soft magnetic materials including ferrite, Co-based amorphous alloys, Ni-Fe alloys and nanocrystalline, as seen in Figure 38 [247, 659 and 670].

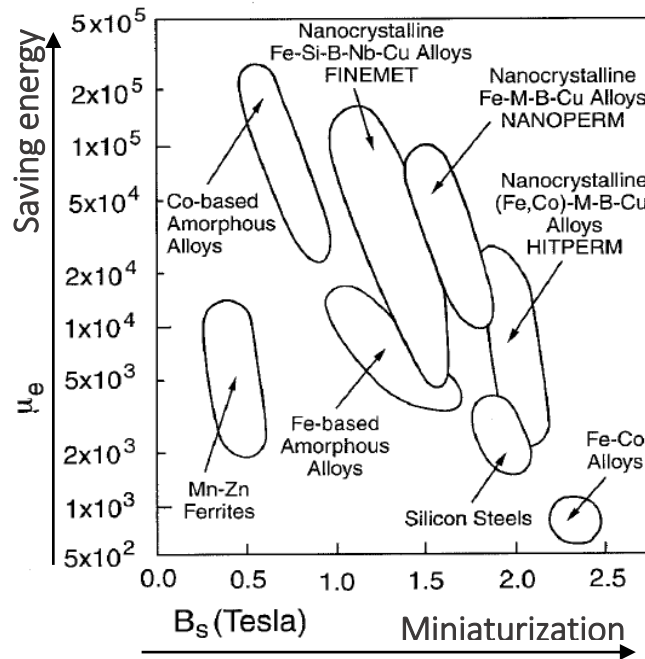


Figure 2.38: The relationship between permeability and saturation flux density in several soft magnetic alloys [247, 669 and 670].

However, these materials generally have a B_s value of approximately only 0.1 of pure iron, which produces an extremely high B_s . In contrast, iron and silicon steel with high B_s exhibit a low permeability of the order of 0.1 of Co-based amorphous alloys which have higher permeability. However, the amorphous metal alloys not only provide good soft magnetic behavior, similar to the polycrystalline NiFe alloys, but also, at the same time, exhibit significantly lower eddy current losses than their crystalline counterparts. This is illustrated in Figure 39, which compares the core losses of soft magnetic materials used in high frequency power transformers [671]. Thus, the discovery of the combination of the superior soft magnetic properties and the low losses, in particular, prompted the research interest in amorphous metal alloys.

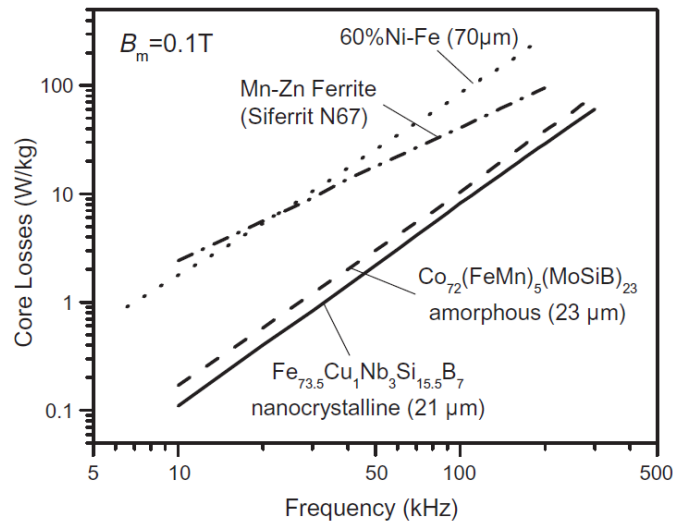


Figure 2.39: The relationship between core losses and frequency for soft magnetic materials used for high frequency power transformers [671].

Cobalt-based metallic amorphous alloys exhibit exceptional performances with respect to high permeability, low coercivity, and negligible magnetostriction, but these alloys suffer from a low polarization saturation. On the other hand, iron-based metallic amorphous alloys exhibit a higher saturation, but at the cost of permeability and coercivity. However, the combination of higher saturation, higher permeability and lower coercivity facilitates good designing, such as the alloy composition and processing. For example, the addition of about 20% of cobalt to iron-based alloy can lead to a desirable combination of high saturation and permeability but low coercivity [672], while the design of a nanocrystalline soft magnetic material from an amorphous alloy is an example of appropriate processing of a soft magnetic material [669, 671, 673 and 674]. Likewise,

this present work investigates the amorphous forming ability in a Co-C system at high Co contents, in order to improve the magnetic and mechanical properties by using this criterion. Therefore, the detailed composition and processing can vary widely, which allows for the coverage of a large spectrum of soft magnetic properties according to the demands of the applications.

2.8.1 Cobalt-Based Amorphous Soft Magnetic Materials

Cobalt-based metallic amorphous alloys are well known for their excellent soft magnetic properties, such as low coercivity, high magnetic permeability and nearly zero magnetostriction [453, 456]. However, in many special applications, the requirements for low core losses come together with that of a multi-use magnetic behavior. Therefore, these requirements may be satisfied by the based-cobalt metallic amorphous alloys even though they have lower saturation flux densities than the iron-based alloys. Consequently, depending on the alloy composition, the cobalt-based metallic amorphous alloys are characterized as soft magnetic properties because their magnetostriction is very small or almost zero. In view of this, at low frequencies applications, the magnetic values of cobalt-based metallic amorphous alloys are comparable to or better than those of Permalloys, while at high frequency applications, the cobalt-based metallic amorphous alloys are superior to ferrites. These materials are therefore highly suited for high frequency applications [675]. However, the main drawback with the cobalt-based metallic amorphous alloys is the relatively high manufacturing cost resulting from their high cobalt contents. So the choice remains a matter of economic issues.

Cobalt-based metallic amorphous alloys are ideal materials as cores of inductive components because of their excellent high frequency permeability characteristics which make them suitable to be used, for example, in digital telecommunications circuits with high frequency ranges upwards several MHz [676]. In view of that, several research projects have reported on fabricating magnetic materials for high frequency applications by using cobalt-based metallic amorphous alloys. One significant example is Metglas, which was introduced in the 1970s by Allied Signals Inc. Metglas Products [403]. However, Metglas 2705 M ($\text{Co}_{69}\text{Fe}_4\text{Ni}_1\text{Mo}_2\text{Si}_{12}\text{B}_{12}$), and Metglas 2714 A ($\text{Co}_{66}\text{Fe}_4\text{B}_{14}\text{Si}_{15}\text{Ni}_1$) exhibit excellent soft magnetic properties at high frequency levels applications with saturation inductions of 0.77T and 0.57T, and the specific core losses are about 6 W/kg and 3 W/kg, respectively, at 10 kHz sinusoidal excitation of 0.3T [403]. Metglas is commercially available and manufactured by Hitachi Metals, Japan. Another example, Vitrovac

6025 ($\text{Co}_{66}\text{Fe}_4\text{B}_{12}\text{Si}_{16}\text{Mo}_2$), and Vitrovac 6030 ($\text{Co}_{70}(\text{FeMo})_2\text{Mn}_5(\text{SiB})$) have also showed good soft magnetic properties at high frequency levels applications, which are commercially available and offered by Vaccumschmelze [403].

Co-Fe-Zr-B alloys are another example of cobalt-based metallic amorphous alloys. Inoue [677] reported that the amorphous alloys with a typical composition of $\text{Co}_{72-x}\text{Fe}_x\text{Zr}_8\text{B}_{20}$ in at.%, where in ($x = 16-20$), exhibited good soft magnetic properties with saturation inductions of 0.77- 0.83T, 6.3- 8.3 A/m for coercivity, and $7.6- 10 \times 10^{-6}$ for saturated magnetostriction. Inoue also indicated that the cobalt-based amorphous alloys with a typical composition of $\text{Co}_{63}\text{Fe}_9\text{Zr}_8\text{B}_{20}$ and $\text{Co}_{56}\text{Fe}_{16}\text{Zr}_8\text{B}_{20}$ in at.% exhibited high magnetic permeability in the high-frequency range (up to 1 MHz) but decreased with a further increase in frequency to 10 MHz, compared to other commercial amorphous alloys, as seen in Figure 40. Therefore, he concluded that the magnetic permeability values of the Co-Fe-Zr-B amorphous alloys are higher than those for the Co-Fe-Ni-Mo-Si-B amorphous alloy with zero saturated magnetostriction in the high-frequency range above 100 kHz.

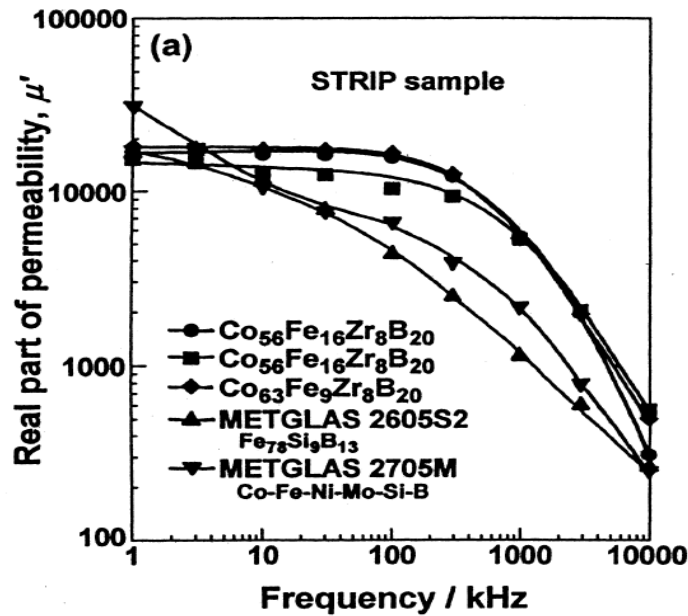


Figure 2.40: Permeability versus frequency of different magnetic materials [677].

In addition, Taghvaei et al. conducted studies showing that the Co-based amorphous alloys ($\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$, and $\text{Co}_{40}\text{Fe}_{22}\text{Ta}_8\text{B}_{30}$ in at.%) work as good soft magnetic materials, which presented a very low coercivity of 0.8 A/m and polarization of 0.5 T [678- 681].

Furthermore, Fiorillo et al. [682], in their review of soft magnetic materials, provided a summary of the basic properties and the essential phenomenology of application-oriented soft magnetic materials. However, the Co-based amorphous alloys were part of this review, including the common amorphous alloys, such as $\text{Co}_{80}\text{B}_{10}\text{Si}_{10}$, $\text{Co}_{71}\text{Fe}_4\text{B}_{15}\text{Si}_{10}$, and $(\text{CoFe})_{70}(\text{MoSiB})_{30}$. Fiorillo et al. stated that the $\text{Co}_{80}\text{B}_{10}\text{Si}_{10}$ amorphous alloy exhibited good soft magnetic properties with saturation inductions of 0.9T, 7 A/m for coercivity, and -4×10^{-6} for saturated magnetostriction. On the other hand, he indicated that the $\text{Co}_{71}\text{Fe}_4\text{B}_{15}\text{Si}_{10}$ alloy showed low saturation inductions 0.87 and 0.5 A/m coercivity values, respectively, with -0.2×10^{-6} for saturated magnetostriction. The $(\text{CoFe})_{70}(\text{MoSiB})_{30}$ alloy showed much lower saturation inductions and coercivity, (0.55 and 0.4 A/m respectively), and -0.2×10^{-6} for saturated magnetostriction.

As can be seen, the cobalt-based metallic amorphous alloy for a given soft magnetic material applications is based on the attainment of the optimum combination of the magnetic properties, such as saturation magnetization, permeability, coercivity, magnetostriction, and, most importantly, cost. Therefore, the continuous improvement in the magnetic properties of the existing cobalt-based amorphous alloys, and the discovery of new alloys with a new chemical composition has led to severe competition among the soft magnetic materials for a given application. Table 2.3 shows some more examples of cobalt-based metallic amorphous alloys and their magnetic properties.

Table 2.3: Typical examples of cobalt-based bulk metallic amorphous alloys and their magnetic properties [683, 684].

Alloy Composition	Saturation Magnetization (T)	Coercivity (A/m)	Magnetic permeability	Magnetostriction
$\text{Co}_{70.3}\text{Fe}_{4.7}\text{Si}_{15}\text{B}_{10}$	0.8	0.48	8500	0
$\text{Co}_{75.3}\text{Fe}_{4.7}\text{Si}_4\text{B}_{16}$	1.1	1.2	20000	0
$\text{Co}_{65.7}\text{Fe}_{4.3}\text{Si}_{17}\text{B}_{13}$	0.53	0.48	55000	0
$\text{Co}_{61.6}\text{Fe}_{4.2}\text{Ni}_{4.2}\text{Si}_{10}\text{B}_2$	0.54	0.16	120000	0
$\text{Co}_{69.6}\text{Fe}_{4.6}\text{Mo}_{1.8}\text{Si}_8\text{B}_{16}$	0.63	-	10000	0
$\text{Co}_{72}\text{Mn}_4\text{B}_{24}$	0.95	0.4	26000	0
$\text{Co}_{81.5}\text{Mn}_{9.5}\text{Zr}_9$	0.73	0.24	21000	0
$\text{Co}_{87}\text{Nb}_9\text{Zr}_4$	1	2	1000	Below 0.5×10^{-6}

2.8.2 Mechanically Alloyed Cobalt-Based Amorphous Soft Magnetic Materials

As was stated in the previous sections, the use of mechanical alloying to fabricate metallic amorphous alloys is scientifically and economically advantageous. However, a wide variety of amorphous magnetic alloys prepared by mechanical alloying has been investigated including Fe-based [545-551], and Co-based [600-620].

In the case of Co-Based amorphous soft magnetic materials prepared by mechanical alloying, several studies have been reported. For example, Taghvaei et al. investigated the structural morphology and magnetic, and thermal properties of $\text{Co}_{40}\text{Fe}_{22}\text{Ta}_8\text{B}_{30}$ in at.%, produced by mechanical alloying [615, 685 and 686]. Taghvaei et al. observed that the thermal stability was decreased by milling, while the magnetic properties were significantly affected by increasing the saturation magnetization, Curie temperature and coercivity. Therefore, Taghvaei pursued the matter to explain that the evolution of the coercivity was based on different phenomena, such residual stresses, grain refinement, amorphous phase formation, surface anisotropy and particle surface irregularities.

Wu et al.'s [613] also studied alloys of $\text{Co}_{62-x}\text{Fe}_x\text{M}_8\text{B}_{30}$ in at.%, (where $\text{M}=\text{Ti}$, Zr and $x = 0, 5, 10, 15, 20$, and 25); they conducted the amorphization by mechanical alloying using a SPEX 8000 shaker. Wu et al. reported that the $\text{Co}_{62-x}\text{Fe}_x\text{Zr}_8\text{B}_{30}$ alloys showed lower coercivity values than those of the $\text{Co}_{62-x}\text{Fe}_x\text{Ti}_8\text{B}_{30}$ alloys, while the saturation magnetization increased as the amount of Fe substituted for Co in the $\text{Co}_{62-x}\text{Fe}_x\text{M}_8\text{B}_{30}$ alloys increased. Wu and his associates explained that the higher amount of Fe would retard the amorphization reaction, thereby increasing the coercivity values. These results imply that for a fixed period of milling, the degree of amorphization decreases as the amount of Fe increases and leads to an increase in the coercivity values as well as saturation magnetization. Wu et al. also worked on milling Co-M-Ti-B ($\text{M}=\text{Fe}$, Nb), using a SPEX 8000 shaker to produce a ferromagnetic Co-based amorphous alloy [614]. They succeeded in amorphizing $\text{Co}_{70-x}\text{M}_x\text{Ti}_{25}\text{B}_5$ in at.% (where $\text{M}=\text{Fe}$, Nb and $x = 5, 10, 15, 20$, and 25), but substituting the Co amount in the system with a certain amount of Fe or Nb led to the reduction of the thermal stability of the amorphous powders. Moreover, the amorphous alloys of $\text{Co}_{70-x}\text{Fe}_x\text{Ti}_{25}\text{B}_5$ exhibited better soft magnetic properties than did the $\text{Co}_{70-x}\text{Nb}_x\text{Ti}_{25}\text{B}_5$ alloys by showing lower coercivity values and higher saturation magnetization.

Moreno et al. also reported on the mechanical alloying amorphization of $\text{Co}_{62}\text{Nb}_6\text{Zr}_2\text{B}_{30}$ in at.% [616]. They carried out the mechanical alloying in a high energy planetary ball milling by using three different types of boron powders in the starting mixture. However, they used a crystalline β -B, commercial amorphous B, and optimized amorphous B that facilitated the mechanically alloying. The results showed that the amorphous phase was successfully produced in three types of boron. However, they found that using the optimized amorphous B was more efficient for the amorphization process of the alloy, main drawback was inadvertently inserting some iron contamination into the system. Furthermore, the samples that were milled with amorphous B in the initial mixture showed about a 50% reduction in the coercivity with respect to the samples that were prepared using crystalline B.

Other work done by Neamtu et al. [617] involved using a wet high energy planetary ball milling to amorphize $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_9$ in at.%, resulting in full amorphization after 40 hours of milling. They concluded that this method of wet mechanical mixing was a useful technique for preparing amorphous powders of $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_9$, with distinctive soft magnetic properties. In another work, Neamtu et al. [618] developed the amorphous alloy of $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_9$ in at.%, by adding Zr and Ti. In this work they used a wet high energy planetary ball milling to amorphize alloys with chemical compositions of $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_4\text{Zr}_5$, $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_4\text{Ti}_5$, $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{10}\text{B}_9\text{Zr}_5$ and $\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{10}\text{B}_9\text{Ti}_5$ in at.%. The results showed that the complete amorphization reaction to the powders was achieved after 40 hours of milling. They also found that the substitution of Zr or Ti for Si led to an increase of the crystallization temperature of the alloys by 18% and 21%, respectively, but the substitution of the Ti or Zr for B did not have a significant effect on the crystallization temperature of the amorphous phase. Also Neamtu et al. reported that the Curie temperature of the substituted alloys increased as compared to the reference sample ($\text{Co}_{70}\text{Fe}_4\text{Ni}_2\text{Si}_{15}\text{B}_9$) and the highest temperature observed was for the alloy in which Si was replaced with Zr. Moreover, the saturation magnetization increased from 14% to 20%, as compared to the reference sample, when either Ti or Zr was substituted for Si or B.

In contrast, Xueming et al. [605] studied the mechanical alloying amorphization of a $\text{Co}_{70}\text{Nb}_{30}$ alloy using high energy planetary ball milling. They reported that a perfect amorphous phase of the Co-Nb alloy powders was obtained after 40 hours of milling at room temperature. They mentioned that the amorphous alloys that were formed showed soft magnetic properties.

Xueming's group concluded that mechanical alloying is a promising and feasible way to produce amorphous magnetic materials for a wide variety of applications.

As can be concluded from these studies, mechanical alloying is now recognized as a powerful tool in the development of new materials, such as amorphous soft magnetic materials. However, mechanical alloying offers the potential to produce alloys that were not possible to produce by the conventional melting technology because of the wide differences in melting points, and liquid or solid-state immiscibility. Therefore, in the present study, the formation of the metallic amorphous phase in the Co-C system using mechanical alloying amorphization is investigated. $\text{Co}_{100-x}\text{C}_x$ in at.%, (where $x = 2, 5, 10, 15, 20, 30$, and 40) alloys were selected for the present study. For the first time, a detailed analysis of the influence of milling time on the alloying behavior, phase evolution, thermal behavior and magnetic properties of these alloys is clearly represented.

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3. Experimental Procedure

3.1 Material Selection

Since the discovery of the first metal amorphous alloy in the 1960s as seen in the historical review of the amorphous metals alloys section, metallurgists and researchers have tried in many different ways to produce amorphous alloys in huge quantities, using less energy and expense, so that they could be used in different applications. Metallurgists and researchers had pushed for the production of huge quantities of such amorphous metallic alloys precisely because they exhibited promising attributes in their microscopic properties in mechanical, magnetic, physical, and other properties. In contrast to crystalline metals, amorphous metals contain no crystal defects such as grain boundaries, dislocations, excretions of other phases, etc., in contrast to the properties of conventional metallic alloys [1]. Amongst the metallic amorphous alloys are the Co-based amorphous alloys, which are of considerable interest because of their magnetic and mechanical properties. As already mentioned, the Co-based amorphous alloys exhibit excellent soft magnetic properties such as low coercivity, high permeability and low hysteresis losses, and these soft magnetic properties result from their near zero magnetostriction and magnetocrystalline anisotropy [2, 3].

Therefore, this work focuses on the amorphization of the binary system of Co-C by mechanical alloying, in view of an understanding of the amorphous phase transformation development and how the chemical composition and mechanical alloying parameters affect the resulting microstructure and properties. Though, the difficulty of making an amorphous metal-carbon phase is well-known. However, due to the extremely high cooling rate that the metal-carbon alloys need to form an amorphous phase, their amorphous phases are extremely hard to reach them by the rapid-quenching techniques [4-8]. Moreover, the high melting temperature of carbon (3367 °C) [9] also makes it extremely difficult to form the metal-carbon amorphous alloys for a wide composition range using the rapid-quenching techniques (Figure 3.1). In addition, the Co-C system to some extent has a low negative heat of mixing, which makes it not fully meet the requirements for the large negative heat of mixing (Figure 3.2) and asymmetrical diffusion needed for solid state amorphization reaction (SSAR).

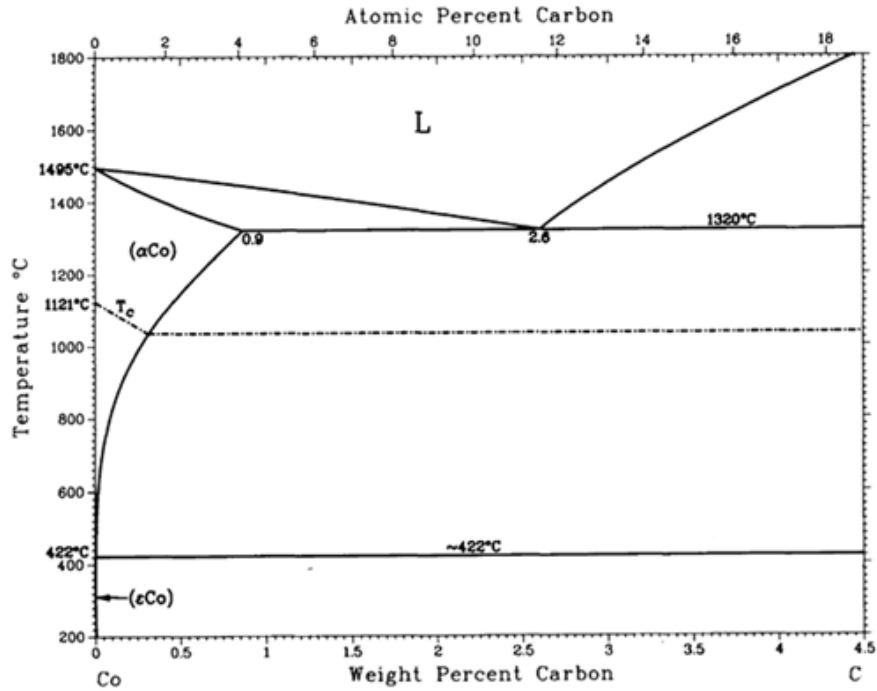


Figure 3.1: Phase diagram of the Co-C system [10].

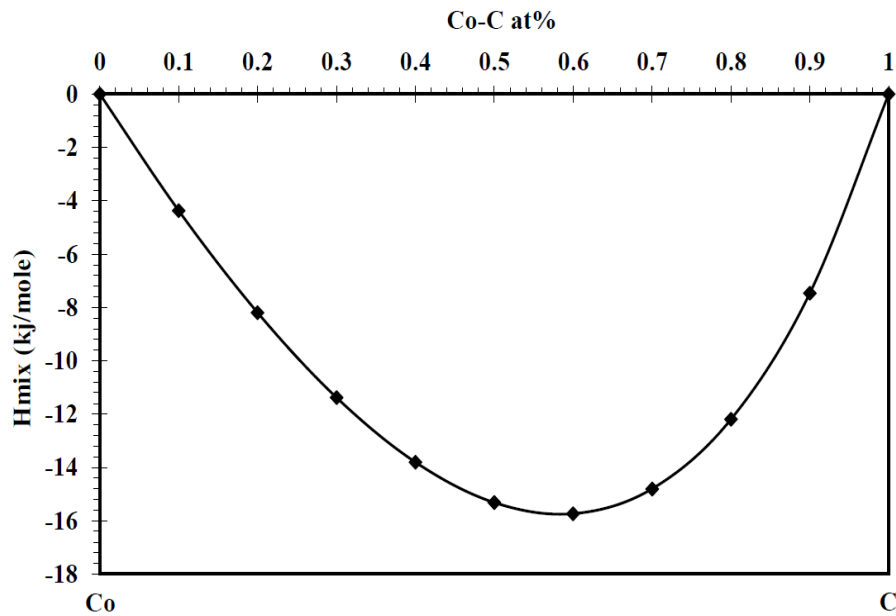


Figure 3.2: The calculated heat of mixing for the Co-C system using Miedema's heat of mixing formulas.

In general, the Co-C system amorphization process is not an easy task and it is a major challenge. However, metal-carbon amorphous alloys can be manufactured this way by adding a

third element, such as silicon or phosphorus, in order to obtain the amorphous state [4, 7 and 11]. Consequently, most of the studies that have reported on the metal-carbon binary amorphous alloys have used the vapor phase to create an amorphous phase, which is the direct deposition of the alloy using ion beams or DC and RF sputtering techniques [4, 6, 7, 12-14]. Thus, these methods can provide an extremely very high cooling rate that ensures the formation of a metal-carbon amorphous phase with a wide composition range [4, 6, 7, 15 and 16]. Several studies have reported Co-C amorphous alloys being prepared using ion beams or co-sputtering [4, 6, 7, 12-14], but these Co-C amorphous alloys were only thin films. These thin films are inadequate for most usages and do not meet the applications requirements because of their small size. With the good of providing a larger bulk size of the metallic amorphous alloys with a wider compositional range, a mechanical alloying process has been used as an approach to solve this issue [17-19]. Likewise, this present work investigates the amorphous forming ability in a Co-C system at high Co contents, in order to improve the magnetic properties as well as the mechanical properties by using this criterion. However, since the Co-based amorphous alloys are used for switch mode power supplies and for many types of magnetic sensors [20-23] because of their near-zero magnetostriction, improving their magnetic properties is always desired.

Therefore, in the present study, the formation of the metallic amorphous phase in the Co-C system using mechanical alloying amorphization was investigated. However, the materials selected for this work consists of – 400 mesh cobalt powder (99.5%, 57 μm) supplied by Alfa Aesar and carbon powder (99.999%, 74 μm) supplied by Strem Chemicals, Inc. The cobalt powder was subsequently reduced in a hydrogen atmosphere for 2h at 250°C. This cobalt reduction was done to remove surface oxides that may be present.

3.2 Powder Processing and Sample Preparation

Reduced cobalt powder and 2, 5, 10, 15, 20, 30, and 40 at.% carbon powders were mechanically alloyed for up 40h to produce Co-C amorphous powders. The mechanically-alloyed powders were then characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). Further, compositions of 1, 2, 5, 10 and 20 vol.% C mechanically alloyed powders of $\text{Co}_{60}\text{C}_{40}$ that had prior milled for 40h were subsequently blended in a attritor mill for 2h with a pure cobalt matrix to produce amorphous Co-C-reinforced crystalline Co-matrix composites powders. The composite

powders were then consolidated by spark plasma sintering (SPS) to produce composite bulks of Co-C/Co and characterized. Characterization included X-ray diffraction (XRD), differential scanning calorimetry (DSC), optical microscopy, scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), density measurements and hardness testing.

3.2.1 Mechanical Alloying and Production of the Co-C Amorphous Powders

Mechanical alloying was conducted using a laboratory SPEX 8000M Mixer/Mill® operating at about 1200 Hz for up to 40 hours as shown in Figure 3.3. A 55 mL tungsten carbide grinding vial was used. The vial is 2 ¼" diameter x 2 ½" (5.7 cm x 6.35 cm) with tungsten carbide-lined body, two screw-on tungsten carbide-lined caps and two gaskets as seen in Figure 3.3.



Figure 3.3: SPEX 8000M Mixer/Mill® with a tungsten carbide vial set.

The initial powder mass of each run was 12.8 g with a ball to powder ratio of 2.5:1, and it was sealed in the tungsten carbide vial with two 1/2" (12.7mm) diameter ultra-hard tungsten carbide balls in a glove box in an argon gas atmosphere. The mechanical alloying procedures were carried out to investigate the effect of milling time and carbon at. % content in the milled powder as shown in Table 3.1.

Table 3.1: The mechanical alloying experimental design. The check (x) indicates to the experiments that were performed.

Carbon content (at. %)	Milling Time (Hours)				
	0h	5h	20h	30h	40h
Co-0 at.% C	X	X	X	X	X
Co-2 at.% C		X	X	X	X
Co-5 at.% C		X	X	X	X
Co-10 at.% C		X	X	X	X
Co-15 at.% C		X	X	X	X
Co-20 at.% C		X	X	X	X
Co-30 at.% C		X	X	X	X
Co-40 at.% C		X	X	X	X

3.2.2 Production of the Composite Powder

Cobalt powder serves as the matrix for the composites with a density of 8.90 g/cc. The cobalt amorphous reinforcement powder ($\text{Co}_{60}\text{C}_{40}$ milled for 40h) was measured to have a density of 6.993 g/cc using a helium Micromeritics Accupyc 1330 Pycnometer. The two powders were blended to form composites with up to 20 volume percent reinforcement as shown in Table 3.2.

Table 3.2: Five composite blends with differing reinforcement volumes.

Reinforcement (vol.%)	Matrix (vol.%)	Reinforcement (wt.%)	Matrix (wt.%)	Reinforcement Weight (g)	Matrix Weight (g)
0	100	0.00	100.00	0.000	25.000
1	99	0.25	99.75	0.197	24.803
2	98	0.50	99.50	0.394	24.606
5	95	1.25	98.75	1.001	23.999
10	90	2.50	97.50	2.008	22.992
20	80	5	95	4.120	20.880

A Union Process Szegvari Attritor with a vertical stainless steel milling tank (Figure 3.4) was used to blend the reinforcement and matrix powders with a total mass of 25g per run and ball mass of 500g with powder ratio of 20:1. Stainless steel balls (Winsted Precision Ball Company 440C) size of 1/4" (6.35mm) were used for this study. The agitator's rotational speed was set at 300 rpm, and the duration time was 2h. The mixing can was cooled with a water jacket so as to avoid crystallization of the amorphous phase and was filled with argon flowing at 10-50 ft³/h to minimize oxidation.

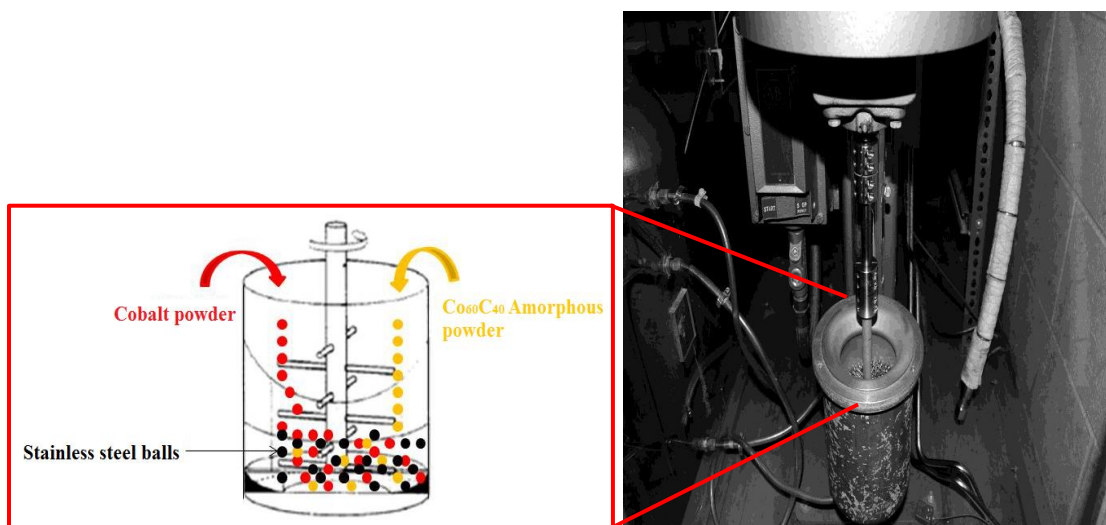


Figure 3.4: The Szegvari attritor mill that was used in this work.

3.2.3 Consolidation of the Composite Powders

Densification of the composite powders in this work was achieved using spark plasma sintering (SPS) so as to avoid crystallization of the amorphous phase. The SPS is a sintering technique that employs uniaxial force and pulsed electrical DC under a vacuum to perform a high-rate of sintering for powders [24], as shown in Figure 3.5 and 3.6. Therefore, SPS has significant advantages in material processing that traditional sintering methods do not have. The SPS can simultaneously apply high temperature, high applied pressure, and low-mode (low voltage, high current) field (plasma) assisted sintering [25]. Joule heat, which is generated from the electric field, provides the conditions of hot compaction; densification and the final grain structures are also enhanced significantly by the current [26, 27]. The SPS process potentially maintains the microstructure and final grain size in nanosized powder materials after consolidation [26, 27]. Furthermore, it significantly shortens the processing time and improves performance. The application of very high

heating and cooling rates is possible because of this direct manner of heating, and densification is enhanced over grain-growth-promoting diffusion mechanisms. Thus, the intrinsic properties of nanopowders in their fully-dense products are maintained [28, 29]. In general, the samples are placed between the graphite die and punch in the vacuum chamber and held between electrodes. Under pressure and energized pulse, the temperature can quickly increase to 1000-2500°C, and the heating rate can reach 1000 °C/min [28, 29].

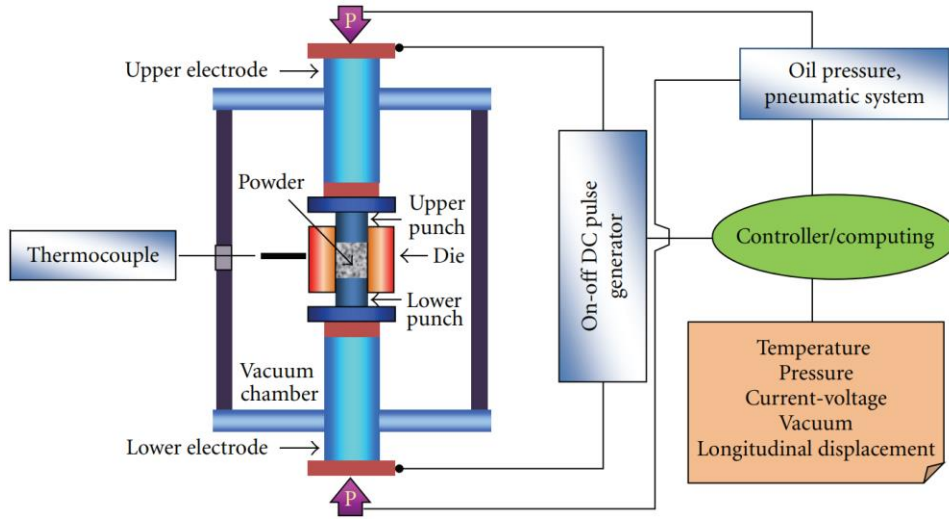


Figure 3.5: Schematic of Spark Plasma Sintering setup [30].

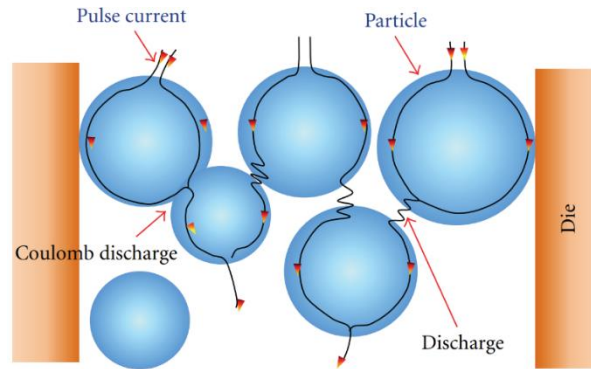


Figure 3.6: Schematic of joule heating mechanism and coulomb discharge between powder particles upon applying pulsed current [30].

The consolidation process of the composite powders (Co/Co₆₀C₄₀) performed by spark plasma sintering (SPS) was subcontracted to California Nanotechnologies, Inc. in Cerritos, California. Approximately 3.5 grams of each composite powder were compacted into a disk 1/2" (12.7mm)

in diameter and 0.140" (3.56mm) in thickness. The pressure and temperature of the SPS was set at 300 MPa and 350°C for 10 minutes with heating rate of 50°C/min.

3.3 Characterization

Mechanically alloyed Co-C powders and the composite powders (Co/Co₆₀C₄₀) as well as their bulk samples were characterized to investigate the effect of the milling and carbon content on the amorphization process and the structure properties.

3.3.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was conducted on the milled pure cobalt and mechanically alloyed Co-C powders using a Netzsch STA 449 C Jupiter TG-DSC. DSC measurements were used to determine the thermal properties of the mechanically alloyed Co-C powders. The samples were placed in an alumina crucible and then placed on the tray at the DSC chamber. In the next step, the DSC chamber was sealed, two evacuation cycles applied, and then purged with argon gas. The samples were heated in an argon atmosphere from 25°C to 1200°C at rates of 5, 10, 20 and 40 °C/min. The DSC data showed an exothermic peak which was analyzed using the Proteus software as exemplified in Figure 3.7. The maximum deviations for the DSC data are in the range of 2% according to the Netzsch's specifications.

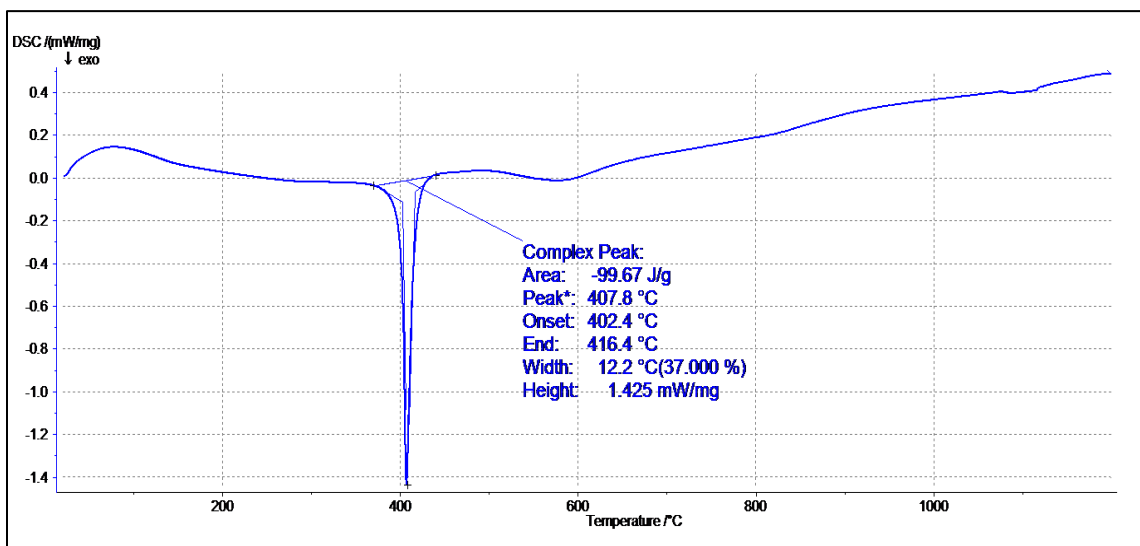


Figure 3.7: An example of DSC data analyzed for exothermic peak of mechanically alloyed Co₆₀C₄₀ powder milled 40h with heating rate of 10 °C/min using the Proteus software.

3.3.2 X-Ray Diffraction (XRD)

Panalytical X'pert Pro PW 3040 diffractometer generator was used in this work to obtain X-ray diffraction patterns. Panalytical X'pert Pro PW 3040 diffractometer generates the X-rays ($k\alpha$) from Cu source using a generator power of 45 kV and 40 mA. for this work, was used the nickel filter, 10 mm mask, 1° anti-scatter slit, and Bragg angle (2θ) range from 10° to 95°. X-ray diffraction spectra were collected for Co powder and Co-C samples before and after mechanical milling processing. Also, X-ray diffraction spectra were collected for the mechanically alloyed Co/Co₆₀C₄₀ composite powders before and after SPS processing. X-rays diffraction spectra were done for all the samples in order to compare crystalline index values as well as crystal structure information using X'Pert High Score Plus and MDI Jade softwares.

3.3.3 Optical microscopy

SPS samples (bulk of the mechanically alloyed Co/Co₆₀C₄₀ composite powders) were analyzed for microstructure development using a Carl Zeiss Axiovert 200 M MAT optical microscope with differential interference contrast (DIC). Therefore, the preparation for the optical microscopy entailed first mounting the bulk composite samples in the epoxy or bakelite, a thermosetting polymer. These mounts were then ground and polished with alumina powder in a number of steps (down to 0.05 μ m alumina). The optical micrographs were taken in order to assess the microstructure evolution and investigate the effect of the amorphous powder volume fraction on the microstructure.

3.3.4 Scanning Electron Microscopy (SEM)

The same samples of the SPS (bulk of the mechanically alloyed Co/Co₆₀C₄₀ composite powders) that prepared and used with optical microscopy were imaged using a FEI Quanta 600 FEG Environmental Scanning Electron Microscope (SEM) equipped with a backscatter detector and a Bruker energy-dispersive X-ray spectroscopy (EDS) unit with a silicon drift detector. The FEI Quanta 600 FEG was set at a working distance of 8mm and the electron gun set to 20 kV. A range of magnifications were used to assess the microstructure evolution as well as the amorphous particles morphology and distribution in the samples matrix. EDS maps and point analysis were generated to identify elements shown in the micrographs.

3.3.5 Transmission Electron Microscopy (TEM)

Selected mechanically alloyed Co-C powders (2, 5 and 10 at. %C milled 40h), samples were first imbedded and mounted in an epoxy then cut it into thin sections using a RMC Boeckeler PowerTome PC: Cryo-ultramicrotome microtome. These thin sections were then attached to a TEM grid, then high resolution TEM was performed on the prepared samples using a JEOL 2100 TEM at 120kV equipped with an EDAX energy-dispersive X-ray spectroscopy (EDS) system. The preliminary purposes for using the TEM characterization is to detect the presence of an amorphous phase through bright and dark field micrographs and selected area diffraction patterns. In addition, the EDS was used to identify the elemental composition for the amorphous phase.

3.3.6 Vibrating Sample Magnetometer (VSM)

Room temperature vibrating sample magnetometer (VSM) was used in this work to determine the magnetic properties of the mechanically alloyed Co-C powders using a Princeton Measurements Corporation vibrating sample magnetometer (VSM Model 3900) operated by IRM at University of Minnesota. However, the magnetic properties of the mechanically alloyed Co-C powders were extracted from magnetic hysteresis loops as measured by a magnetometer. Consequently, saturation magnetization (M_s), remanent magnetization (M_r), remanent-to-saturation ratio (M_r/M_s) and the coercive field (H_c) of the mechanically alloyed Co-C powders were determined for the samples in order to assess the magnetic properties and investigate the effect of the carbon content and milling time on the magnetic properties.

3.3.7 Density Measurements

The bulk density of each SPS composite sample was determined by Archimedes' principle in order to assess densification. However, the traditional Archimedes' density approach was used by taking the weight of the compact sample in air, W_{air} , and then in ethanol, $W_{ethanol}$, along with the known density of ethanol, $\rho_{ethanol} \approx 0.79$ g/cc at the given temperature and the density of air, $\rho_{air} = 0.0012$ g/cc to estimate the density of the compact sample, $\rho_{compact}$. These values are related to each other by Equation 3.1:

$$\rho_{compact} = \frac{W_{air}}{W_{air} - W_{ethanol}} * (\rho_{ethanol} - \rho_{air}) + \rho_{air} \quad \text{Eq. 3.1 [31]}$$

While the theoretical density, ρ_{th} , was calculated using Equation 3.2:

$$\rho_{th} = ((V_{matrix}) * (\rho_{matrix})) + ((V_{reinforcement}) * (\rho_{reinforcement})) \quad \text{Eq. 3.2 [32]}$$

Where V_{matrix} is the volume fraction of the matrix, $V_{reinforcement}$ is the volume fraction of the reinforcement, ρ_{matrix} is the density of the matrix which is the density of the cobalt 8.9 g/cc and $\rho_{reinforcement}$ is the theoretical density of the reinforcement (Co- 40 at.% C) which is 6.592 g/cc. The calculation of the theoretical densities of the Co/Co₆₀C₄₀ composites are shown in Table 3.3.

Table 3.3: Theoretical density of the Co/Co₆₀C₄₀ composites.

Reinforcement (vol. %)	Matrix (vol. %)	Theoretical density of the composites (g/cc)
0	100	8.89
1	99	8.894
2	98	8.888
5	95	8.870
10	90	8.840
20	80	8.780

3.3.8 Hardness Testing

Microhardness testing were used to assess mechanical properties on micro scales, as a function of reinforcement volume fraction. However, the hardness testing was performed on the microscopy samples after they had been analyzed. A Phase II Micro Vickers Hardness tester was used at 0.98N for 15 seconds. At least ten tests were run per sample, with more runs on some samples for statistical reliability.

3.3.9 Particle Size Analysis

A Horiba Partica LA-950 Laser Diffraction Particle Size Analyzer was performed to evaluate and measure the mean particle size of the Co-C mechanically alloyed powders. However, the particles of the Co-C mechanically alloyed powders were dispersed in ethanol, and the suspension was sonicated twice cycles for 10 minutes each cycle to break any agglomerations if present. Each sample was repeated with at least five runs to provide confidence in the results, which were output as plots of frequency on a linear y-axis versus particle diameter on a logarithmic x-axis.

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4. Amorphization of Co-C Alloys by Mechanical Alloying

4.1 Introduction

The difficulty of making an amorphous metal-carbon phase is well-known. However, due to the extremely high cooling rate that the metal-carbon alloys need to form an amorphous phase, their amorphous phases are extremely hard to reach by the rapid-quenching techniques [1-5]. Moreover, the high melting temperature of carbon also makes it extremely difficult to form the metal-carbon amorphous alloys for a wide composition range using the rapid-quenching techniques. Therefore, in order to form metal-carbon amorphous alloys this way, a third element, such as silicon or phosphorus, is needed in order to obtain the amorphous state [1, 4 and 6]. Consequently, most of the studies that have reported on the metal-carbon binary amorphous alloys have used the vapor phase to create an amorphous phase, which is the direct deposition of the alloy using ion beams or DC and RF sputtering techniques [1, 3, 4, 7-9]. Thus, these methods can provide an extremely very high cooling rate that ensures the formation of a metal-carbon amorphous phase with a wide composition range [1, 3, 4, 10 and 11]. Therefore, an important result of obtaining extremely high cooling rates was the metal-carbon binary amorphous could only be produced as ribbons, foils, or thin films, so the heat could be extracted quickly enough to achieve the necessary cooling rate [1, 3, 4, 10 and 11]. Several studies have reported [1, 3, 4, 7-9], Co-C amorphous alloys being prepared using ion beams or co-sputtering, but these Co-C amorphous alloys were only thin films. These thin films are inadequate for most usages and do not meet the application requirements because of their small size. To that end of large bulk sizes for the metallic amorphous alloys with a wide composition range, a mechanical alloying process has been used as one of these methods and approaches to solve this issue. In the case of Co-C amorphous alloys in particular, we used the mechanical alloying SPEX mill technique in this work to obtain Co-C amorphous powders with different chemical compositions. This process was steadied as a function of processing parameters and their influence on some of the material properties.

Mechanical alloying (MA) has proven to be an effective technique to synthesize several of the equilibrium and non-equilibrium alloy phases, such as amorphous, quasicrystalline, and nanocrystalline alloys, or composites [12]. In the case of amorphous alloys in particular, MA has achieved great success as a processing technique for preparation of amorphous alloyed powders

[12-16]. However, since 1983, amorphization by mechanical alloying, or milling, has created widespread research interest, owing to its advantages compared with other methods. For example, its ability to produce a large amount of amorphous material with equiatomic compositions have made it an effective amorphous material producer. Also, the composition range for the amorphous phase is much wider in alloys produced by mechanical alloying than those obtained by rapid solidification processing [17].

According to recent literature [12, 13], in MA amorphization occurs under a chemical solid state reaction by the formation of a multilayer structure during milling. The asymmetric interdiffusion couple to the negative heat of mixing are the driving force for this diffusion. Moreover, the defects created by the mechanical process in the ball mill play a major role in the amorphization process. Defects such as vacancies, dislocations, atomic site defects, antiphase boundaries or grain boundaries, will increase the free energy of the crystalline phase, which is considered responsible for the amorphization during mechanical alloying/milling [18]. Indeed, the role of these defects in this process is similar to the role of those defects in the ion and electron irradiation techniques.

Among the metallic amorphous alloys that are prepared by means of mechanical alloying are the Co-based amorphous alloys, which are of considerable interest because of their magnetic and mechanical properties [19]. However, numerous studies have demonstrated the effectiveness of mechanical alloying to promote the amorphization of different Co-based amorphous alloy powders of several binary, ternary, quaternary and multi component systems, such as Co-Nb [20], Co-B [15], Co-B-Si [21], Co-Cr-Mo [22], Co-Fe-Si-B [14], Co-Fe-Ta-B [23], Co-Fe-(Zr,Ti)-B [24], Co-M-Ti-B (M= Fe, Nb) [25] and Co-Nb-Zr-B [26]. On the other hand, only a very limited number of studies exist regarding the cobalt-carbon amorphous alloys despite their scientific and technological importance.

So far, there have been no serious attempts to synthesize a cobalt-rich Co-C amorphous alloy by MA for magnetic and mechanical applications. However, in general there are a limited number of studies that have been performed on the production of Co-based amorphous alloys by the MA processing, compared to the use of many other methods of processing; in particular, a very limited number of studies in the Co-C system have been performed using the MA processing. Yang et al. [27] demonstrated that ball milling induces a complete amorphous phase transformation in a

system of Co-50 at.% C. Such study dealt with a middle chemical composition range between the elements, with a high negative heat of mixing, which was thought to be an important parameter determining the glass forming ability in a solid state reaction [14]. Yet the study did not cover the other side of the high cobalt composition. In contrast, Jiang et al. [28] studied the mechanical alloys of $\text{Co}_x\text{C}_{100-x}$ in at.%, where in ($x = 1, 2, 3, 4$, and 5), and they demonstrated that a prolonged ball milling process led to an amorphous C matrix with embedded small Co particles, but the experiment did not achieve a complete amorphized structure.

The aim of the present work is to study the solid state interaction between the elemental powders of Co and C during high-energy ball milling in order to understand their chemical composition influence on the amorphization process of Co-C alloys. It is important to note that in the literature, there is not enough information on the amorphization of cobalt-rich Co-C alloys, thus the mechanical alloying technique was used to obtain an amorphized Co-C alloy with the propose of investigating the extent to which adequate results could be achieved using this method.

4.2 Experimental procedure

The materials selected for this work consists of cobalt powder (99.5%, 57 μm) supplied by Alfa Aesar and carbon powder (99.999%, 74 μm) supplied by Strem Chemicals, Inc. to ensure the absence of any cobalt oxide, the cobalt powder was reduced in a hydrogen atmosphere for 2 hours at 250°C. The elemental blended powders of compositions $\text{Co}_{100-x}\text{C}_x$ in at.%, (where $x = 2, 5, 10, 15, 20, 30$, and 40) were prepared by ball milling in a laboratory SPEX 8000 shaker/mill with different milling times (5, 20, 30, and 40h). The initial powder mass of each run was 12.8g with a ball-to-powder ratio of 2.5:1, and it was sealed in a tungsten carbide vial with tungsten carbide balls in a glove box in an argon gas atmosphere.

X-ray diffraction (Panalytical X'pert Pro PW 3040 diffractometer generates) was performed using $\text{CuK}\alpha$ ($\lambda=1.54 \text{ \AA}$) radiation to investigate the phase transformation in the mechanically alloyed powders. Differential scanning calorimetry (Netzsch STA 449 C Jupiter TG-DSC) was conducted at a heating rate of 10 °C/min to understand the devitrification phenomena in the mechanically alloyed amorphous powders. The formation of the amorphous phase was validated by means of transmission electron microscopy (JEOL 2100 TEM at 120kV.).

4.3 Results and Data Analysis

4.3.1 X-ray Diffraction Analysis

The evolution of the mechanically alloyed powders of nominal composition $\text{Co}_{100-x}\text{C}_x$ in at.% as a function of x and milling time is demonstrated by X-ray diffraction patterns shown in figures 4.1- 4.8. Figure 4.1 shows X-ray diffraction patterns of mechanically alloyed powders of $\text{Co}_{60}\text{C}_{40}$ in at.% milled for up to 40h. As expected, the X-ray diffraction pattern of the powder mixture at 0h milling time (blended powder) shows only sharp peaks corresponding to the starting metal mixture Co and C, which are the hexagonal phase hcp of C, and two allotropic structures of Co, hcp and fcc, as shown in Figure 4.1. After 5h of milling, the main C peak (002) disappears, whereas the Co-fcc peaks (200), (111), (220), and (311) dramatically decrease and shift to lower diffraction angles, as well as Co-hcp peaks (100), (002), (101), (110) and (112), reflecting the increase in the lattice parameter of cobalt due to the dissolution and grain refinement.

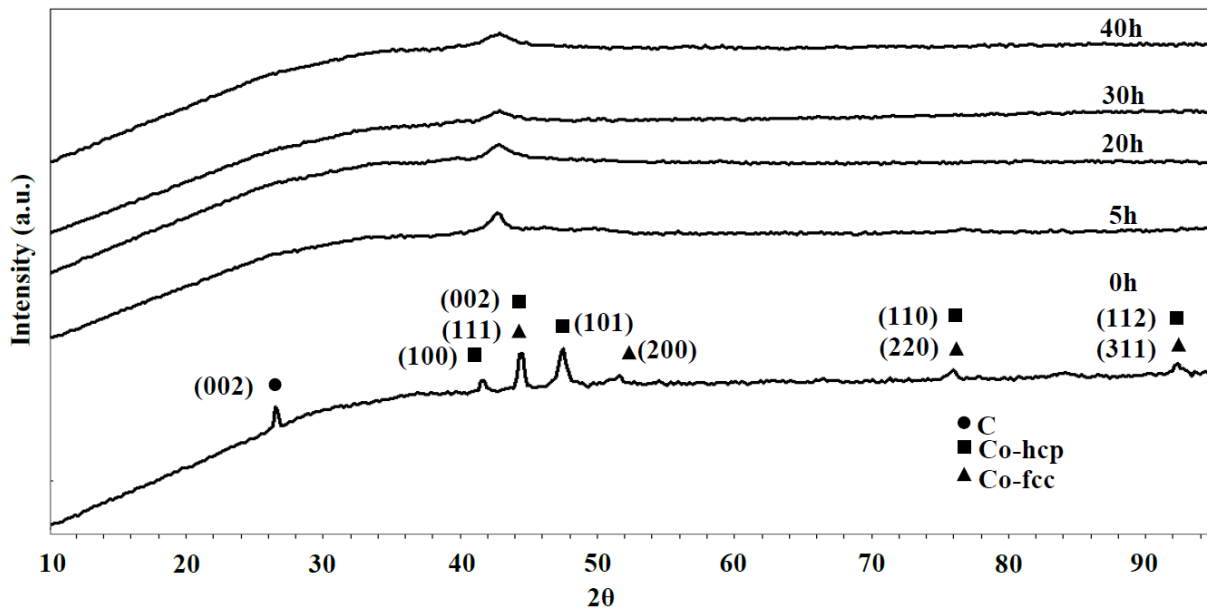


Figure 4.1: X-ray diffraction patterns for $\text{Co}_{60}\text{C}_{40}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.

In the meantime, the cobalt peaks also show peak broadening resulting from the nonuniform strain as well as grain size reduction [12, 13, 22, 29], both of which are known to be caused by MA. With continued milling, the cobalt peaks keep broadening and after 20h of milling all cobalt peaks completely disappear without crystalline sharp Bragg peaks except the (002 and 111) peak, which stays as single broad peak. According to previous studies [12, 29], this single broad peak indicates

that an amorphous phase has occurred, which is a cobalt amorphous containing dissolved carbon. After milling for 40h, the (002 and 111), the peak reaches its maximum broadening and shifting to a lower diffraction angle, thus indicating that a complete amorphous phase transformation has occurred. This transformation was independently corroborated by differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Consequently, Figures 4.2 through 8 show the X-ray diffraction patterns of the mechanically alloyed powders at various compositions and milling stages along the path to the final amorphous state.

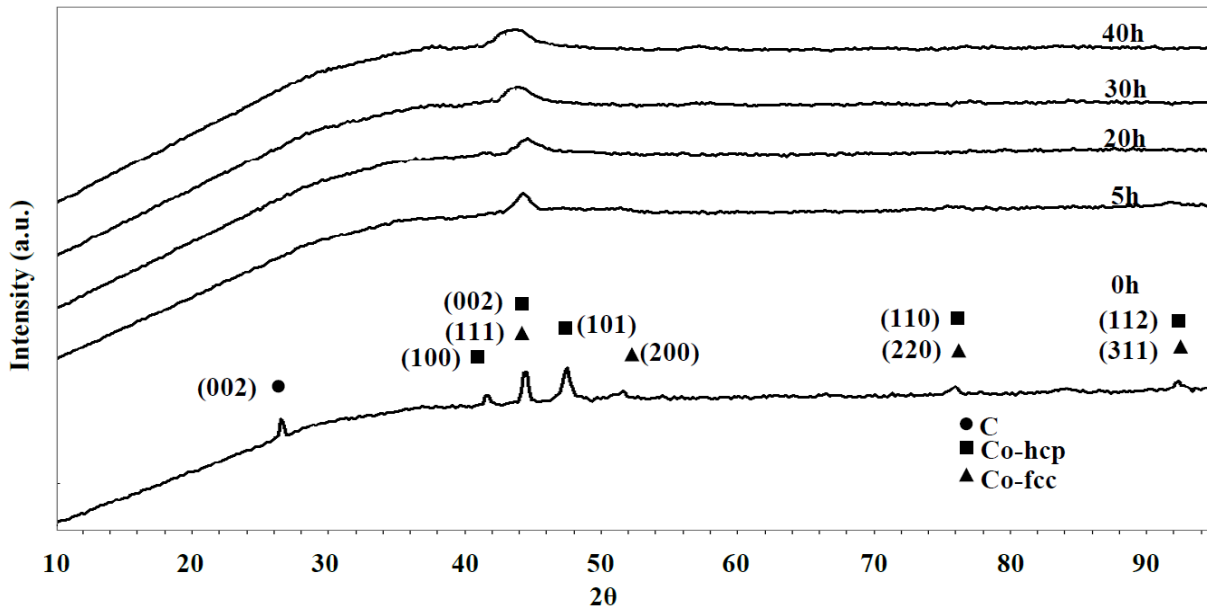


Figure 4.2: X-ray diffraction patterns for $\text{Co}_{70}\text{C}_{30}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.

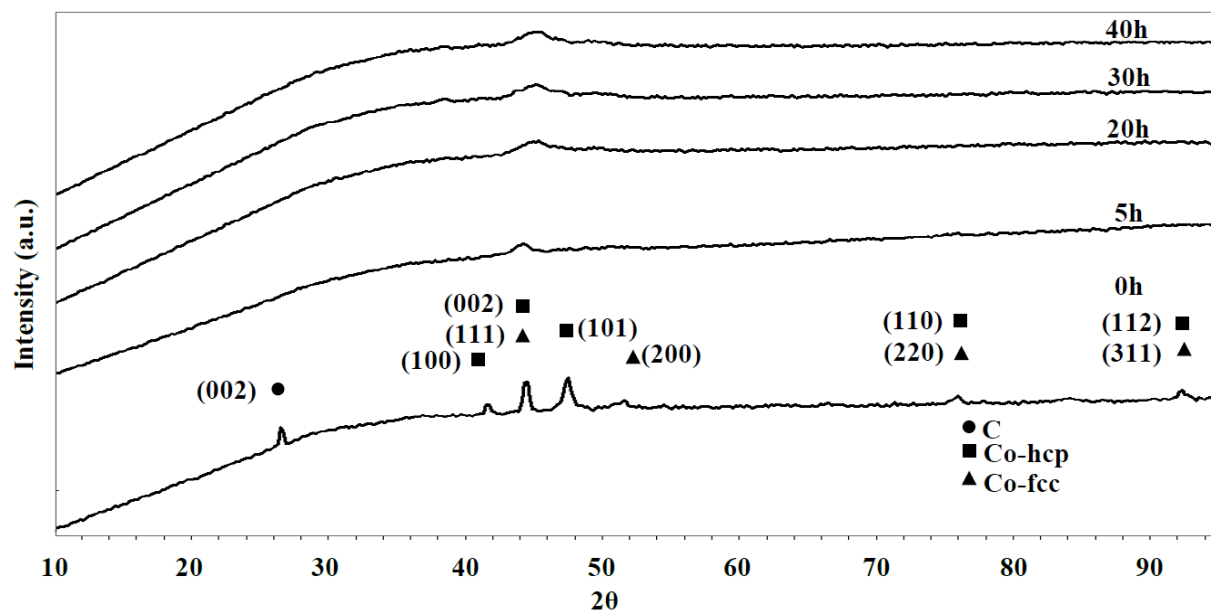


Figure 4.3: X-ray diffraction patterns for $\text{Co}_{80}\text{C}_{20}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.

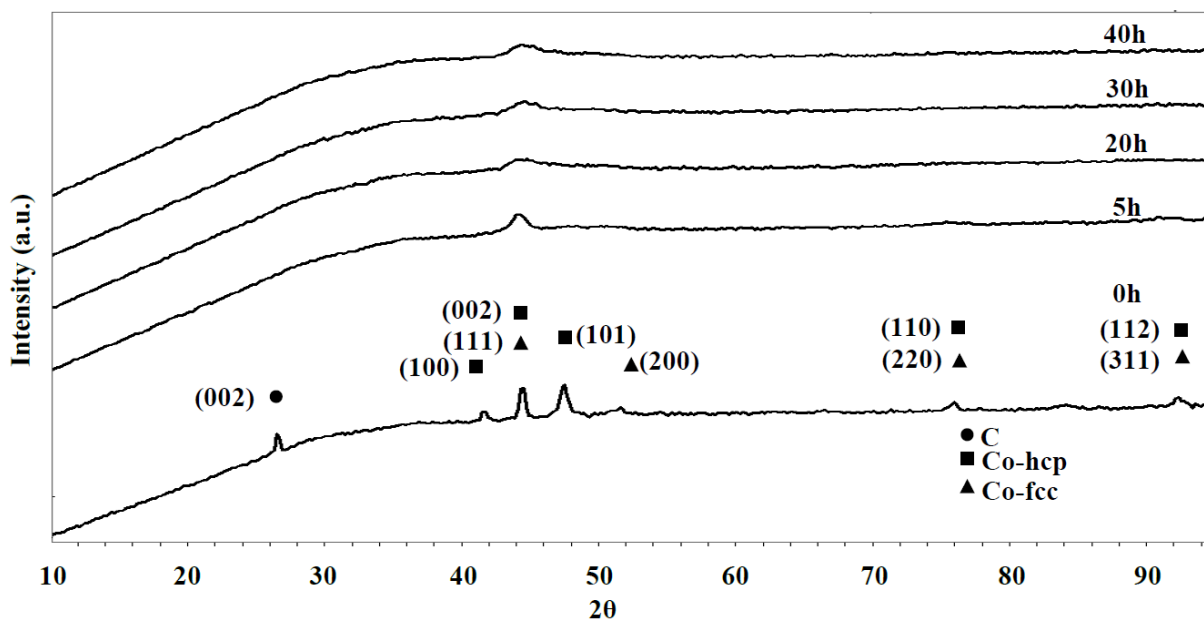


Figure 4.4: X-ray diffraction patterns for $\text{Co}_{85}\text{C}_{15}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.

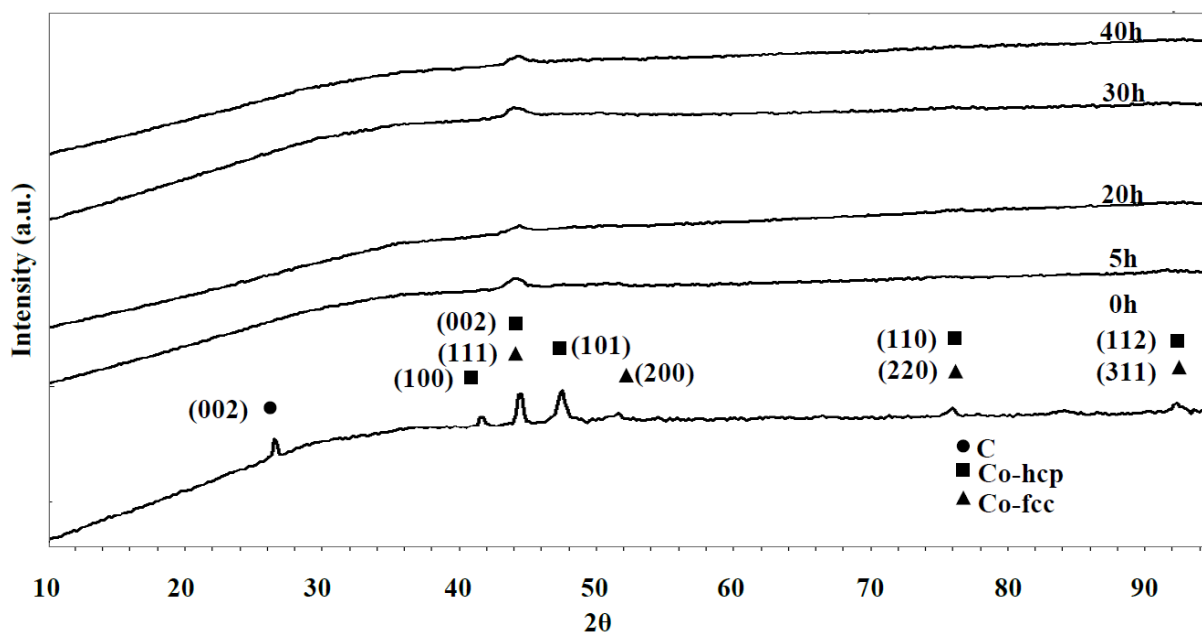


Figure 4.5: X-ray diffraction patterns for $\text{Co}_{90}\text{C}_{10}$ in at.% milled for up to 40 hours, compared with the blended powder of Co-C.

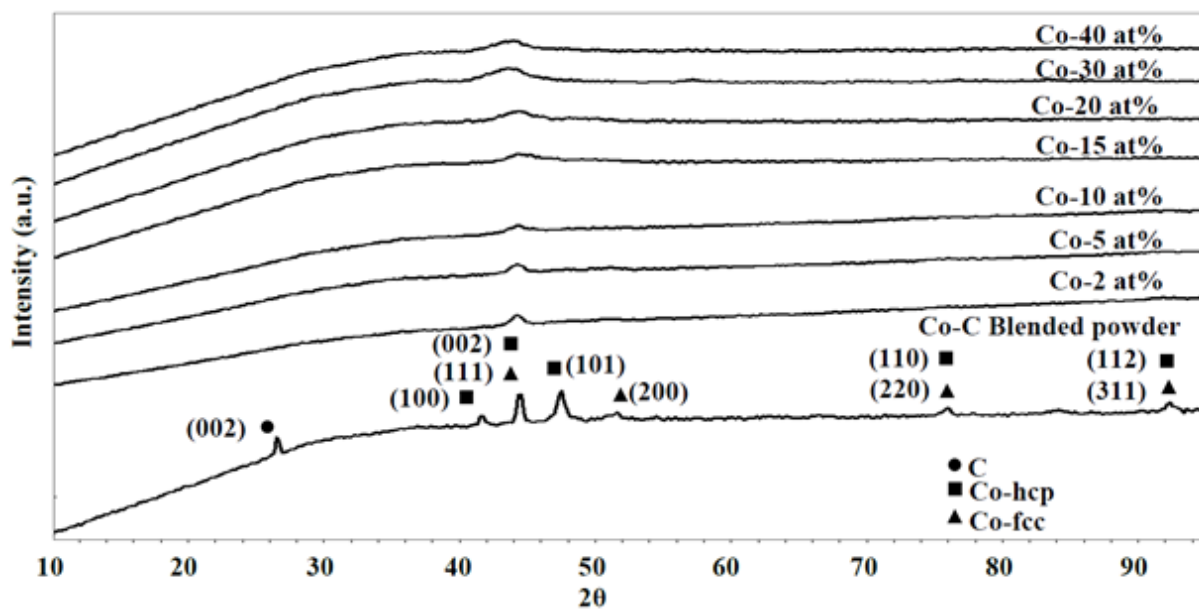


Figure 4.6: X-ray diffraction patterns for Co-C and alloyed for 40 hours, compared with the blended powder of Co-C.

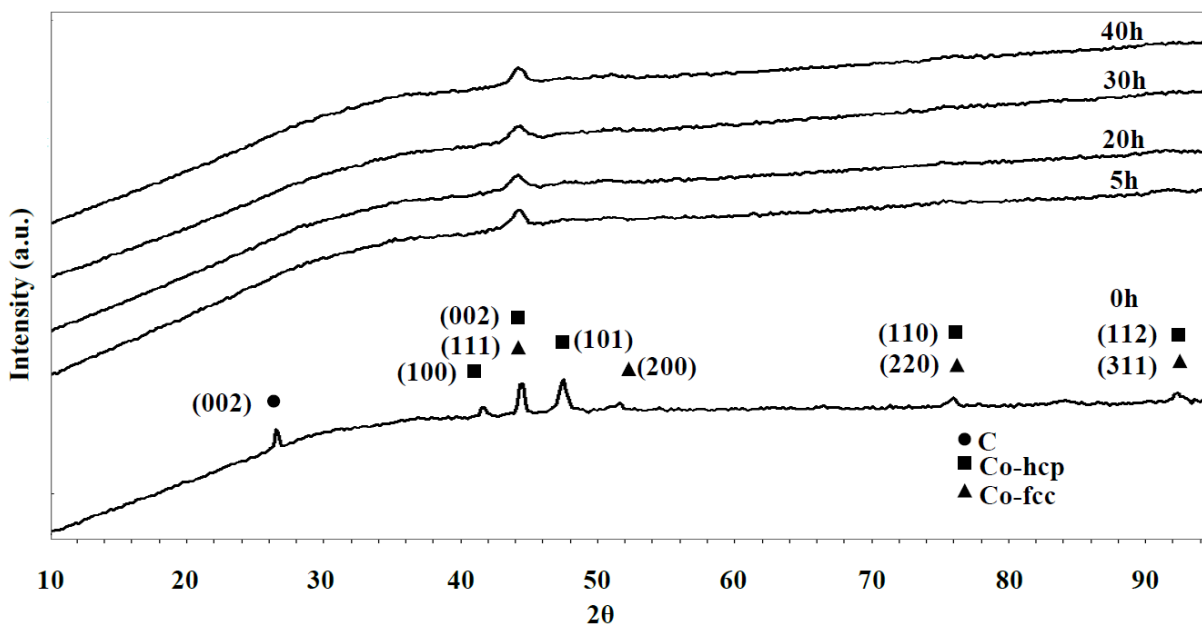


Figure 4.7: X-ray diffraction patterns for Co_{95}C_5 in at.% milled for up to 40 hours, compared with the blended powder of Co-C.

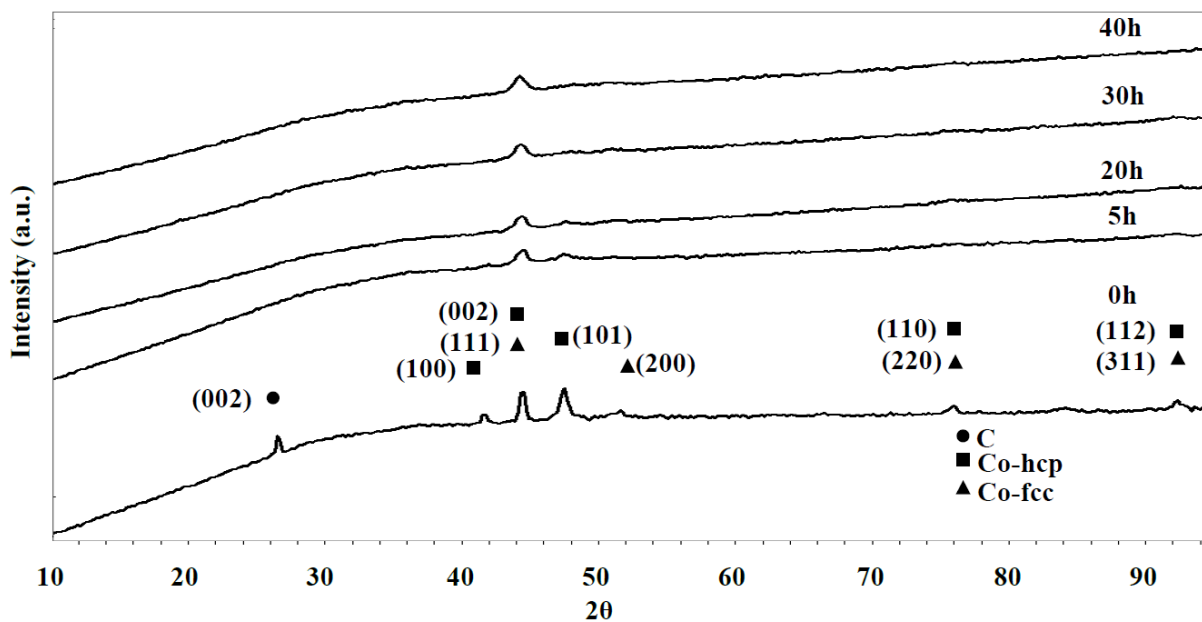


Figure 4.8: X-ray diffraction patterns for Co_{98}C_2 in at.% milled for up to 40 hours, compared with the blended powder of Co-C.

Figure 4.5 exhibits X-ray diffraction patterns of mechanically alloyed powders of $\text{Co}_{90}\text{C}_{10}$ in at.%, milled for up to 40h. Actually, the mechanically alloyed powders of $\text{Co}_{90}\text{C}_{10}$ show similar

X-ray diffraction patterns to those of the $\text{Co}_{60}\text{C}_{40}$ mechanically alloyed powders. After milling for 40h, it appears that a complete amorphous phase transformation occurred in the alloy, similar to the composition of $\text{Co}_{60}\text{C}_{40}$, which was confirmed by the DSC and TEM results. The only difference between the $\text{Co}_{60}\text{C}_{40}$ and $\text{Co}_{90}\text{C}_{10}$ compositions during the mechanical alloying was that the $\text{Co}_{60}\text{C}_{40}$ composition reached the amorphous phase faster than the $\text{Co}_{90}\text{C}_{10}$ composition did because of the amount of C in the system. However, the amorphization process in the present system is due to the negative heat of mixing between the constituent elements, which is considered to be the driving force for the diffusion. Moreover, the defects that were created by the mechanical alloying process were also considered responsible for the amorphization by increasing the free energy of the crystalline phase. In the case of composition of $\text{Co}_{60}\text{C}_{40}$, the negative heat of mixing was higher value than the one in composition of $\text{Co}_{90}\text{C}_{10}$, as seen in Figure 4.9, which are about -13.8 KJmol^{-1} and -4.37 KJmol^{-1} , respectively, as related to Miedema's model [30]. However, the composition of $\text{Co}_{60}\text{C}_{40}$ had a higher negative heat of mixing than the lower C composition, which means it has a large amorphous forming ability compared with the low C composition, according to the solid state reaction requirement, and therefore this property makes it easy for $\text{Co}_{60}\text{C}_{40}$ to form an amorphous phase.

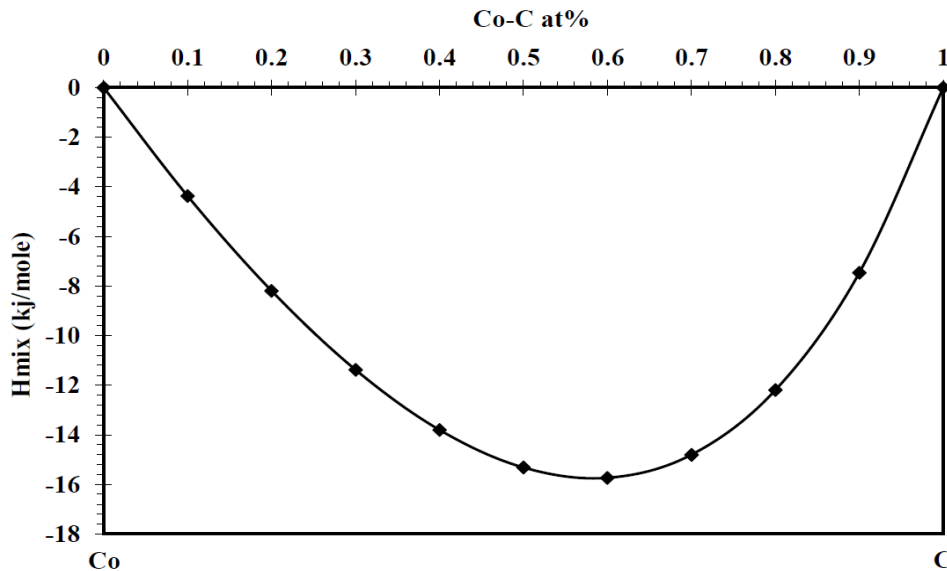


Figure 4.9: The calculated heat of mixing for the Co-C system using Miedema's heat of mixing formulas.

Figure 4.6 shows the X-ray diffraction patterns of mechanically alloyed powders of $\text{Co}_{100-x}\text{C}_x$ in at.% as a function of x after 40h of milling. For all of these samples, no crystalline sharp Bragg peaks of elemental powders were detected and only typical broad diffuse maximums of the amorphous state appeared. These results show that mechanically alloyed powders with compositions of 60 to 90 at.% Co are perfectly amorphous after 40h milling also show in Figures 4.1 through 4.5, as demonstrated by the DSC and TEM results. Whereas the cobalt-rich samples of mechanically alloyed powders of Co_{95}C_5 and Co_{98}C_2 show a single broad peak in their X-ray diffraction patterns, in fact these single broadening peaks are not peaks of a perfectly amorphous phase, but rather an amorphous phase and nanocrystalline structure. However, Figures 4.7 and 4.8 show the X-ray diffraction patterns of mechanically alloyed powders of Co_{95}C_5 and Co_{98}C_2 milled for up to 40h. It is clear that the maxima of the single broad peaks of mechanically alloyed powders of Co_{95}C_5 and Co_{98}C_2 are smaller than those with higher C content thereby illustrating what these broadening peaks are, as confirmed by what the TEM results showed.

4.3.2 Thermal behavior and Differential Scanning Calorimetry (DSC) Analysis

The thermal behavior analysis and typical differential scanning calorimetry (DSC) results are shown in Figures 4.10- 4.34. Figure 4.10 shows differential scanning calorimetry (DSC) curves of the mechanically alloyed powders of $\text{Co}_{60}\text{C}_{40}$ milled for up to 40h at a heating rate of $10^\circ\text{C}/\text{min}$. According to Konno et al. [1] and many other studies afterwards, the exothermic peaks that can clearly be seen at 377 , 393 and 407°C are a crystallization peaks of the amorphous phase for the milled powders of the three different milling times of 20, 30, and 40h, respectively. Meantime, the shallow exothermic peak that was released after 20h of milling slightly shifted to a higher temperature with increasing the milling time and became apparent after 40h of milling, as seen in Figure 4.10. While the $\text{Co}_{60}\text{C}_{40}$ powder milled for 5h, no exothermic peak was detected, and this result confirmed that no amorphous phase occurred during this milling time.

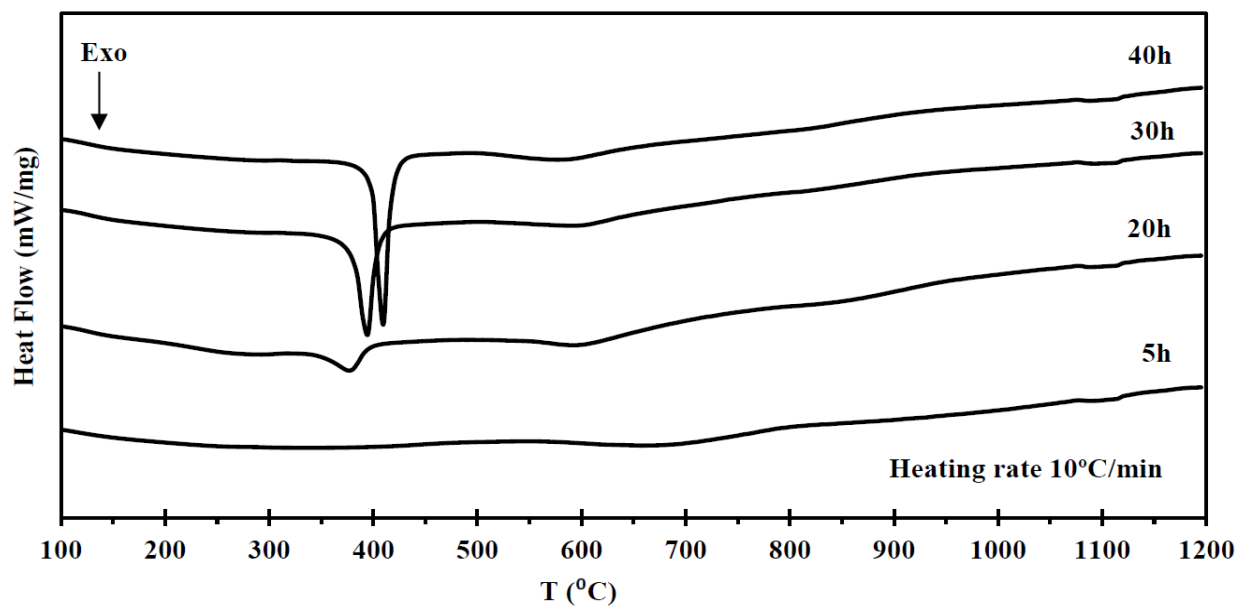


Figure 4.10: Differential scanning calorimetry curves of $\text{Co}_{60}\text{C}_{40}$ in at.%, milled for up to 40 hours at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

These exothermic peaks that have been seen in the high milling times correspond to the heat released by the precipitation of crystalline hcp phase [1] and fcc cobalt in the amorphous carbon. This result agrees with the observation of XRD patterns of the $\text{Co}_{60}\text{C}_{40}$ powder, milled 20h after heated at 325, 495, and 725 $^{\circ}\text{C}$, respectively, in an argon atmosphere, with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and cooled to room temperature under the same conditions. At that point, we found a strong fcc cobalt structure, concomitant with some of the hcp cobalt, as shown in Figure 4.11. The agreement between the results of Konno et al. [1] and those of this study is qualitatively good.

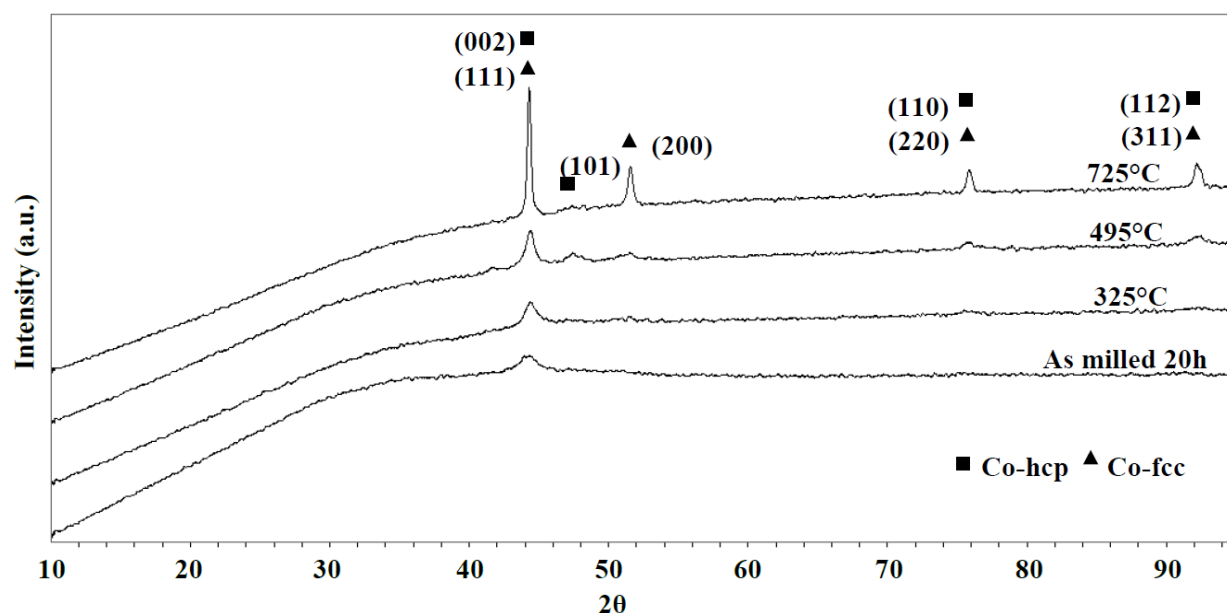


Figure 4.11: X-ray diffraction patterns for $\text{Co}_{60}\text{C}_{40}$ in at.% milled 20h and heated in different temperatures.

However, Konno et al. reported that the C-rich Co-C amorphous alloys, prepared using co-sputtering, showed exothermic peaks of the precipitation of the crystalline hcp cobalt phase in the amorphous carbon at a range of 325 to 450°C, depending on the composition. They confirmed their results using the TEM diffraction patterns and d-spacing techniques, so they concluded that these exothermic peaks correspond to the heat released by the precipitation of crystalline heavily-faulted hcp cobalt. On the other hand, in this study, the X-ray diffraction method has confirmed that the precipitation of the crystalline cobalt is a predominantly fcc phase. However, the Jade6 and X'Pert High Score Plus software was used to determine the d-spacing of the X-ray diffraction patterns and compared with the International Center for Diffraction Data (ICDD) database, as seen in Figures 4.12 and 4.13. It is clear that the peaks obtained for the $\text{Co}_{60}\text{C}_{40}$ powder milled 20h after being heated up to 725°C very closely resemble those of the Co-fcc that were found in the database. Therefore, the difference in the crystalline structure reported in the previous studies and in the present study may be due to the structure of the amorphous phase itself, where the co-sputtered amorphous alloys should have a relatively lower level of cobalt stacking faults structure due to the process mechanism [31, 32], compared to the structure of the mechanically alloyed amorphous alloys. Thus, this difference could be the reason for the existence of the fcc phase, even though the temperature was much lower than the hcp-to fcc-phase transformation temperature (417°C). Also,

the grain size of the Co-C milled powder could have played a dominant role here, since the grain size of the milled powder was very small (on a nanometer scale [33]). In accordance with Edwards and Lipson's theory [34] and Owen and Jones' work [35], the stable structure should be fcc cobalt, even if annealed further at 700°C, the stable phase would be the fcc phase [33, 35]. In addition, the dissolution of carbon in the cobalt could also lead to the stabilization of the fcc-Co phase at room temperature [31, 32, 36, and 37].

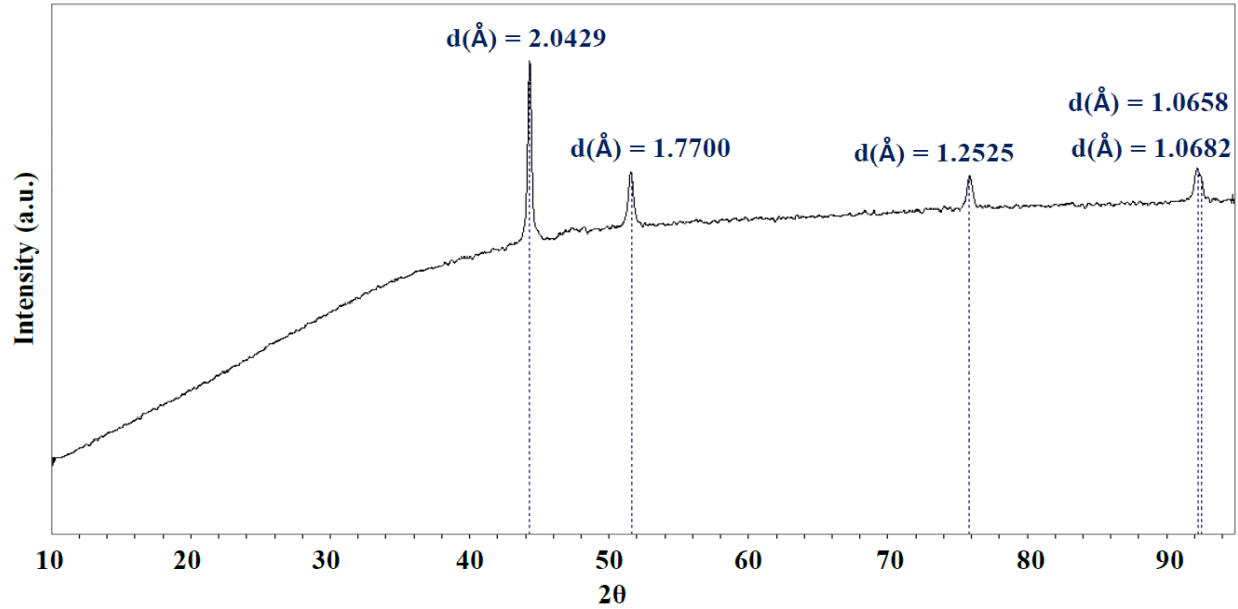


Figure 4.12: X-ray diffraction pattern and d-spacing values of the $\text{Co}_{60}\text{C}_{40}$ powder, milled 20h after heated up to 725°C.

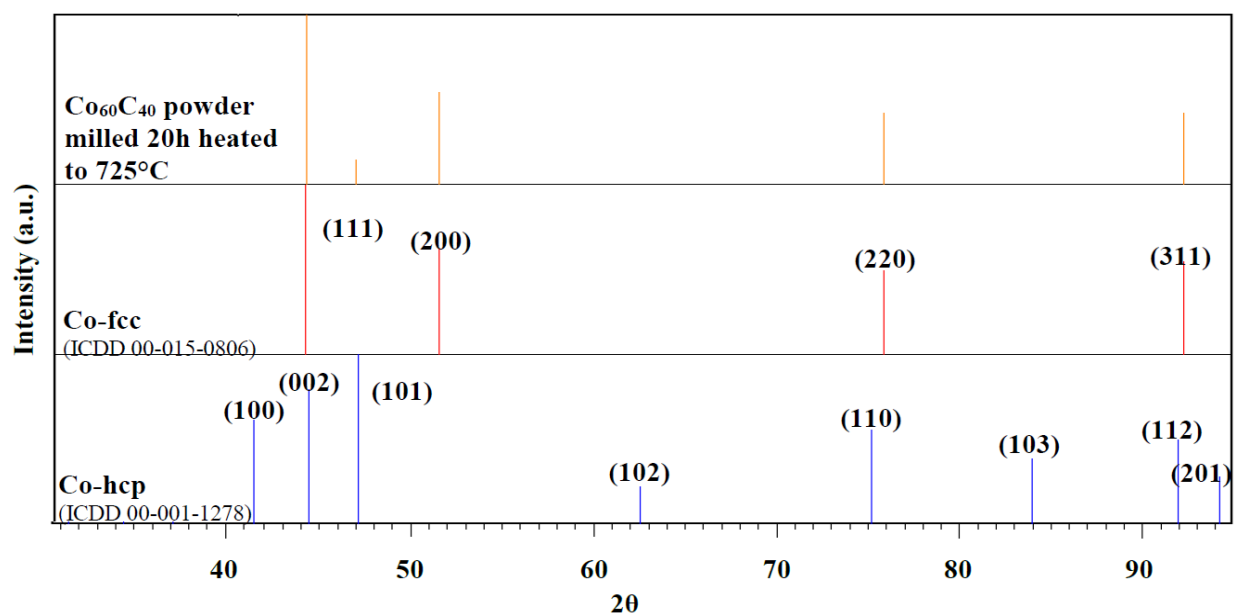


Figure 4.13: X-ray diffraction pattern of the $\text{Co}_{60}\text{C}_{40}$ powder milled 20h after being heated up to 725°C , compared with the ICDD numbers of 00-015-0806 and 00-001-1278.

Interestingly, the carbon phase was not observed in the XRD profiles of the annealed specimens, as shown in Figure 4.11. However, the lack of detection of the carbon phase in the XRD profiles may be due to the detector (PANalytical PW3015/20 X'Celertator) used in this study not being sensitive enough to pick up the carbon phase. Another possible reason is that the amorphous structure of the carbon could have had a very broad XRD profile and its broadening peaks could have been hidden in the background noise. Therefore, to verify the presence of carbon, energy-dispersive X-ray spectroscopy (EDS) point analysis was performed on the $\text{Co}_{60}\text{C}_{40}$ sample milled for 20h and annealed at 725°C , as seen in Figure 4.14. As shown in Figure 4.14, the EDS spectra clearly demonstrate that, in addition to the strong peaks of the Co, the C peaks were obviously present.

Therefore, from this chemical analysis that shows up in the EDS data, we find that the elemental composition for this data clearly and quantitatively corresponds to the pristine elemental composition of the sample ($\text{Co}_{60}\text{C}_{40}$), confirming the presence of both elements (Co and C) in the sample chemical composition. Moreover, in order to check the extent of the impurities in the system which may have transferred from the grinding media to the system (in addition to the carbon and cobalt chemical analysis) a chemical analysis was executed on the elements of oxygen, iron and tungsten. However, besides the cobalt and carbon amounts that were found in the test

results, as seen in Figure 4.14, a trace amount of oxygen was detected and may have been incorporated during the preparation for the EDS test or be present as impurity in the starting powders.

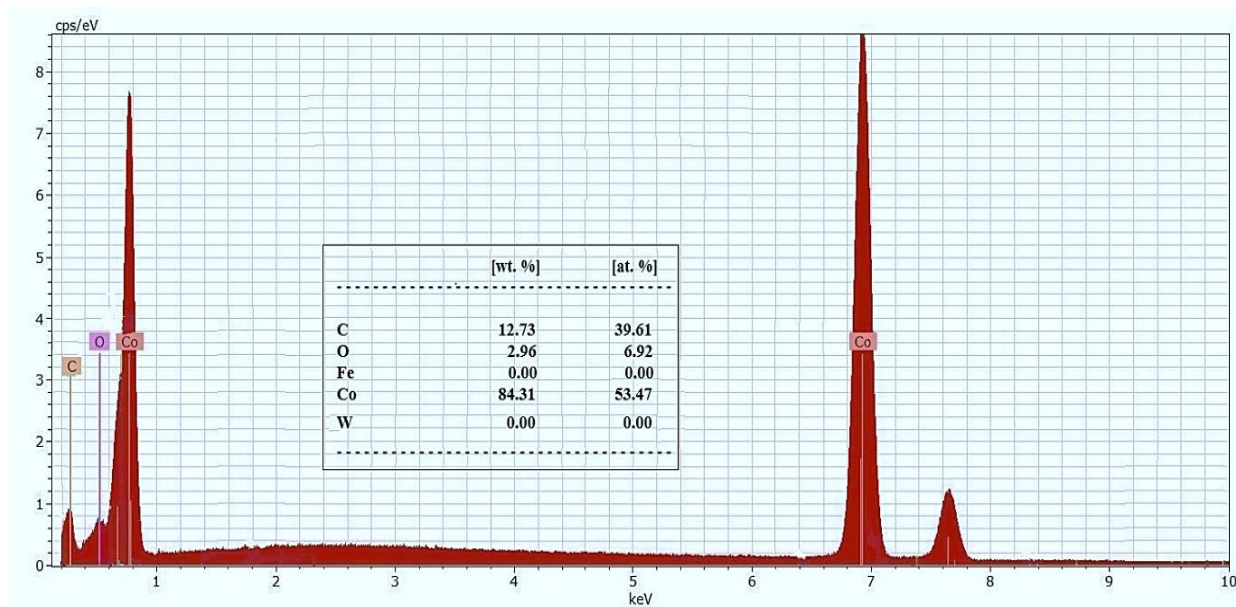


Figure 4.14: EDS spectra from the mechanically alloyed powder of $\text{Co}_{60}\text{C}_{40}$ (milled 20h and annealed at 725°C) shows intense cobalt peaks, a minor carbon peak and nothing else in more than a trace amount of oxygen.

The crystallization characteristics of amorphous $\text{Co}_{60}\text{C}_{40}$ alloy powders indexed by the crystallization temperature, T_x (temperature of the exothermic crystallization reaction peak), and the enthalpy of crystallization, ΔH_x (total area under the exothermic crystallization reaction peak), are presented as a function of the milling time in Figure 4.15. It is clear in Figure 4.15 that the crystallization enthalpy ΔH_x of amorphous $\text{Co}_{60}\text{C}_{40}$ alloy increases dramatically during the early and intermediate stages of milling, as well as slightly increasing in the temperature of the exothermic crystallization reaction T_x . This increase in ΔH_x and T_x is attributed to the continuous changing in the composition of the amorphous phase that occurs with the increasing milling time. Therefore, within the ultimate stage of milling (which is 40h), both T_x and ΔH_x are closely approaching the saturation value. However, the T_x nearly approaches the saturation value by 407°C . Meanwhile, the ΔH_x moves dramatically and monotonically with the increase of milling time to the saturation value, and saturates at a value of about 6.2 KJmol^{-1} , suggesting the formation of a single phase amorphous alloy. This value is comparable to the enthalpy of crystallization of

Co-C alloys [1]. However, these DSC results clearly prove that the amorphous phase in $\text{Co}_{60}\text{C}_{40}$ mechanically alloyed became chemically and topologically homogeneous with the increasing milling time.

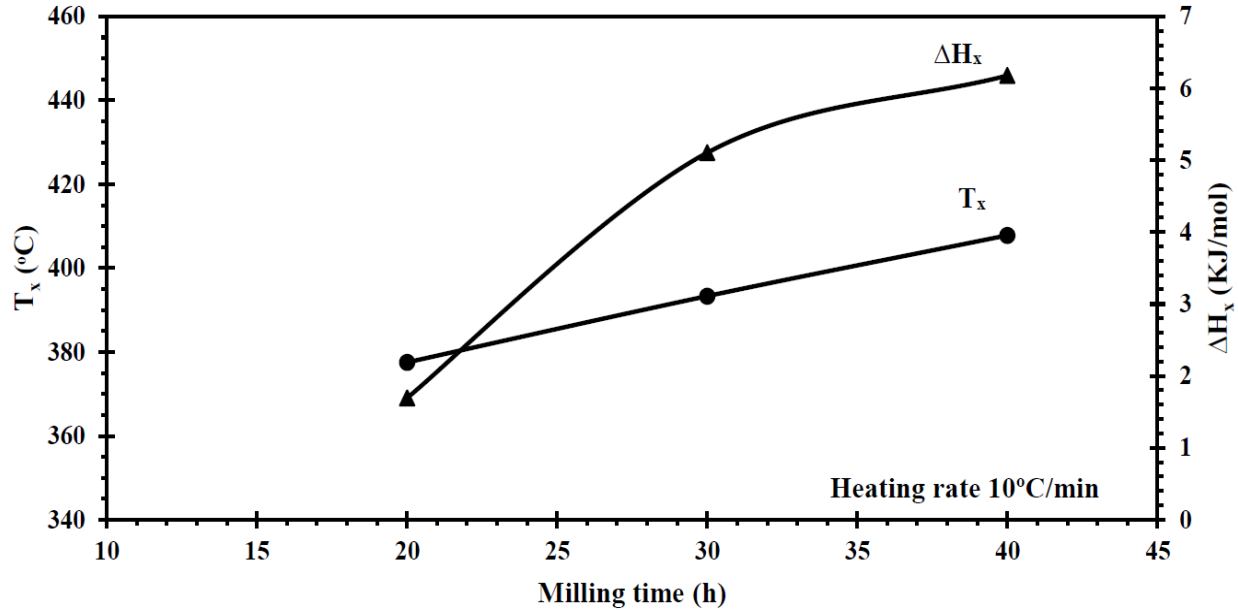


Figure 4.15: Effect of the milling time on the crystallization temperature, T_x and the enthalpy of crystallization, ΔH_x of mechanically alloyed $\text{Co}_{60}\text{C}_{40}$ in at. %.

Figure 4.16 shows the DSC curves of the mechanically alloyed powders of $\text{Co}_{70}\text{C}_{30}$ milled up to 40h, where they show a similar behavior to the powders of $\text{Co}_{60}\text{C}_{40}$, milled up to 40h. After 20h of milling, a shallow exothermic peak was released at 365°C , and as the milling time increased the exothermic peak slightly shifted to the higher temperature and became apparent after 40h of milling, as seen in Figure 4.16. However, as discussed and illustrated earlier in the composition of $\text{Co}_{60}\text{C}_{40}$, this exothermic peak is a precipitation of the crystalline cobalt in the amorphous carbon, which is predominantly a fcc phase, with a concomitant hcp phase. However, with increasing milling time, the T_x nearly reaches the saturation value by 382°C . On the other hand, the ΔH_x proceeds dramatically and monotonically to the saturation value, and saturates at a value of about 8.3 KJmol^{-1} , suggesting the formation of a single phase amorphous alloy. Furthermore, in the case of $\text{Co}_{70}\text{C}_{30}$ composition, the crystallization reaction exhibits the same concepts and mechanism behavior of crystallization reaction of $\text{Co}_{60}\text{C}_{40}$ composition, contrary to what happened with the co-sputtered $\text{Co}_{75}\text{C}_{25}$ amorphous alloy, reported by Konno et al. [1, 4]. However, the DSC results of co-sputtered $\text{Co}_{75}\text{C}_{25}$ amorphous alloy in Konno's work have showed two exothermic peaks,

which indicated that the crystallization reaction occurred during the two-stage of crystallization process. Konno et al. confirmed their results using the TEM analysis and explained that the first exothermic peak was due to the formation of metastable of Co_2C , while the second peak was due to the decomposition of Co_2C into hcp cobalt and graphite.

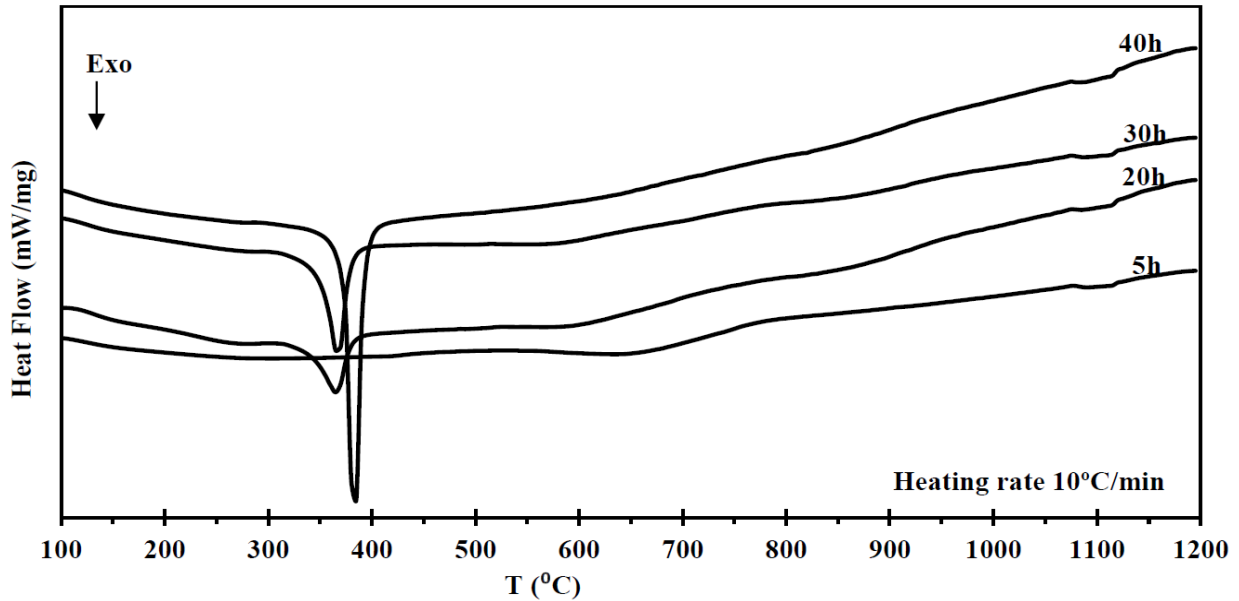


Figure 4.16: Differential scanning calorimetry curves of $\text{Co}_{70}\text{C}_{30}$ in at.%, milled for up to 40 hours at a heating rate of 10 °C/min.

However, the two-stage crystallization process was often seen in many other metal-metalloid systems, such as Pd-Si, Fe-C, Co-Si-B, Fe-Si-B alloys, etc. [38- 41], which were due to the formation of two metastable phases MS-I and MS-II [42- 46]. It is known that the metastable phase MS-II decomposes and ends up as a stable phase. According to Konno's postulate [1, 4], the distinction between the previously observed crystallization behavior in co-sputtered $\text{Co}_{75}\text{C}_{25}$ amorphous alloy and the behavior observed in the mechanically alloyed $\text{Co}_{70}\text{C}_{30}$ amorphous alloy in this study resulted from the excess of carbon atoms and the lack of interstitial sites. As a consequence, the carbon atoms accumulate at the Co_2C /matrix boundary, effectively stopping the Co_2C growth; therefore the crystallization process will occur in one step as a precipitation of the crystalline cobalt in the amorphous carbon, as previously discussed and illustrated. However, the huge distortion in the hcp structure of cobalt that occurred during the milling restricted the octahedral sites that the carbon atoms tried to occupy. Consequently, the excess of carbon atoms in the system and the unoccupied octahedral sites inaccessible that have been created make the

carbon atoms diffusion very difficult through the amorphous matrix at low temperatures [1]. In other words, under these circumstances many carbon atoms must be accommodated within the hcp-based Co_2C , and the diffusion of the excess carbon atoms through the amorphous matrix is too slow to allow the growth of the Co_2C phase [1]. In view of that, the carbide phase will not be formed and the amorphous carbon cannot transform to a stable phase, just by the path of graphite, diamond, or staying in an amorphous phase, as in our case here [1].

Figure 4.17 shows the DSC data for the composition of $\text{Co}_{80}\text{C}_{20}$ milled for up to 40h plotted prevalently for each milling time. However, the sample of 20h milling shows two exothermic peaks at 261 and 391°C, suggesting a two-stage crystallization process, as seen in Figure 4.17, while samples milled for 30 and 40h show one exothermic peak at 431 and 436°C, respectively, indicating a one-stage crystallization process. However, the results indicate that the crystallization reaction of $\text{Co}_{80}\text{C}_{20}$ milled for 20h is very different from the higher carbon compositions as well as the samples milled for a longer period, obviously depending on the chemical composition and milling time. In fact, the crystallization reaction of the composition $\text{Co}_{80}\text{C}_{20}$ milled for 20h occurred in two-stages of crystallization instead of one-stage, as was seen in the compositions of 30 and 40 at.% carbon that were also milled for 20h.

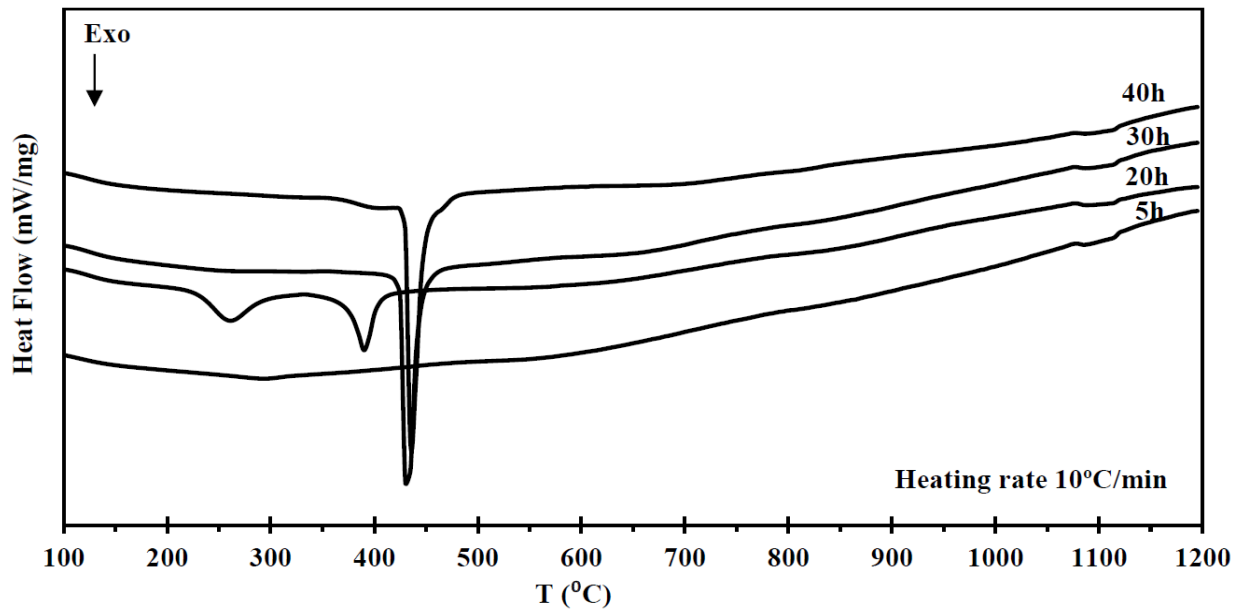


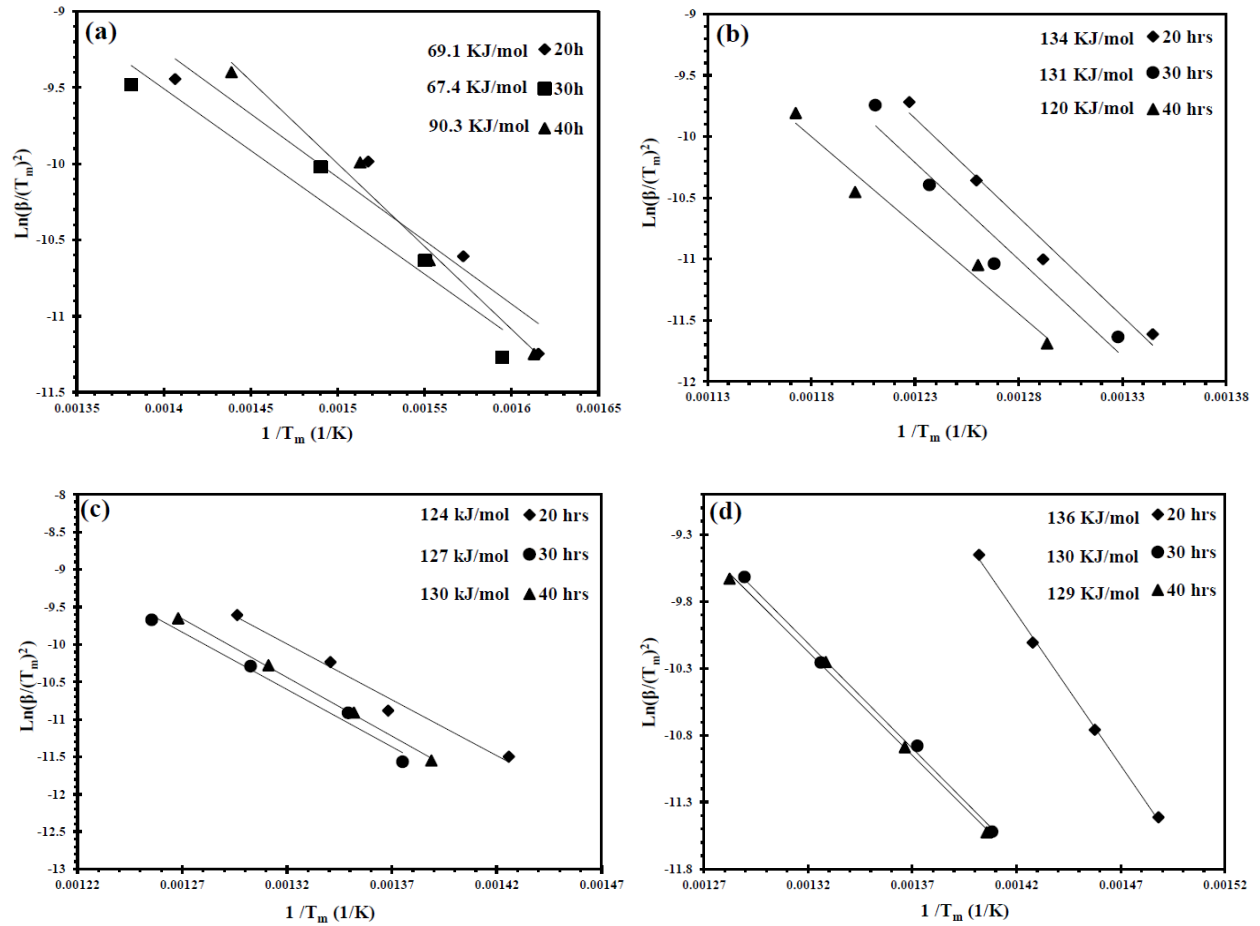
Figure 4.17: Differential scanning calorimetry curves of $\text{Co}_{80}\text{C}_{20}$ in at.%, milled for up to 40 hours at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

As Konno et al. [1] pointed out in their work on the composition of $\text{Co}_{82}\text{C}_{18}$ co-sputtered, the first exothermic peak is a formation of the metastable of Co_2C , whereas the second peak is due to the decomposition of Co_2C into hcp cobalt and graphite. The agreement between Konno's results and this work results is systematically good. Therefore, the first exothermic peak is the formation of the metastable phase of Co_2C , while the second peak is due to the decomposition of Co_2C and the crystallization of the remaining amorphous cobalt. However, the metastable Co_2C in this work mainly decomposed into a fcc cobalt with some concomitant hcp phase, as seen in Figure 4.22, and might be a graphite, instead of an amalgum of hcp cobalt and graphite, as stated in Konno's work. Despite the very good agreement between the peak temperature values and the released energies between Konno's results and this work, the high stacking fault structure and the grain size resulting from the process mechanism [31] (mechanical alloying) are responsible for these differences between Konno's results and the results of this work.

In contrast, from the investigation made by Carroll et al. [47] on the thermal behavior of the cobalt carbide phases, using elevated temperature X-ray diffraction (ETXRD), it has been shown that Co_2C decomposed to fcc cobalt phase and hcp cobalt at 275°C . Based on Carroll's study, we find that there is an excellent agreement between Carroll's results and the results of this work in terms of thermal decomposition of the metastable Co_2C phase. However, both studies, Carroll's the present one, show that the Co_2C decomposed to the fcc cobalt phase and some hcp cobalt phase at around $275^\circ\text{C} \pm 15^\circ\text{C}$. In the same context, Pola et al. [31] also stated that the metastable Co_2C phases that were generated from the laser-induced processes decomposed only to the fcc cobalt phase. In their study, they also illustrated that the processing method that was used to form the cobalt carbides played large role in the formation mechanism as well as in the decomposition. Therefore, we conclude that, although some studies showed that the metastable Co_2C phase mainly decomposes to a hcp cobalt phase, for $\text{Co}_{80}\text{C}_{20}$ powder milled for 20h the exothermic peak observed at 391°C mainly arises from the decomposition of Co_2C into fcc cobalt with some concomitant of the hcp phase and graphite, as well as from the crystallization of remaining cobalt amorphous, as seen in Figure 4.22.

Overall, this difference in the crystallization process between the 20 at.% of carbon and the higher carbon compositions that have all been milled for 20 hours is considered to be due to the effects of excess carbon atoms and the lack of the octahedral sites (interstitial sites) on the diffusion

of the carbon atoms in the amorphous matrix [1]. So, the excess of carbon atoms resulting from the higher carbon content and the lack in the octahedral sites make the carbon atoms diffusion too slow to allow for the Co_2C phase to form and grow [1]. Therefore, in this case, the quick reaction path for the system to reduce the excess free energy of the amorphous phase only occurs with abundant precipitation of very small crystalline cobalt phase particles in the amorphous carbon [1]. However, the increase of the activation energy of the crystallization reaction E_a that was observed when the carbon content increased above of 20 at.%, as seen in Figures 4.18 and 4.19, obviously confirms the rationale of this approach.



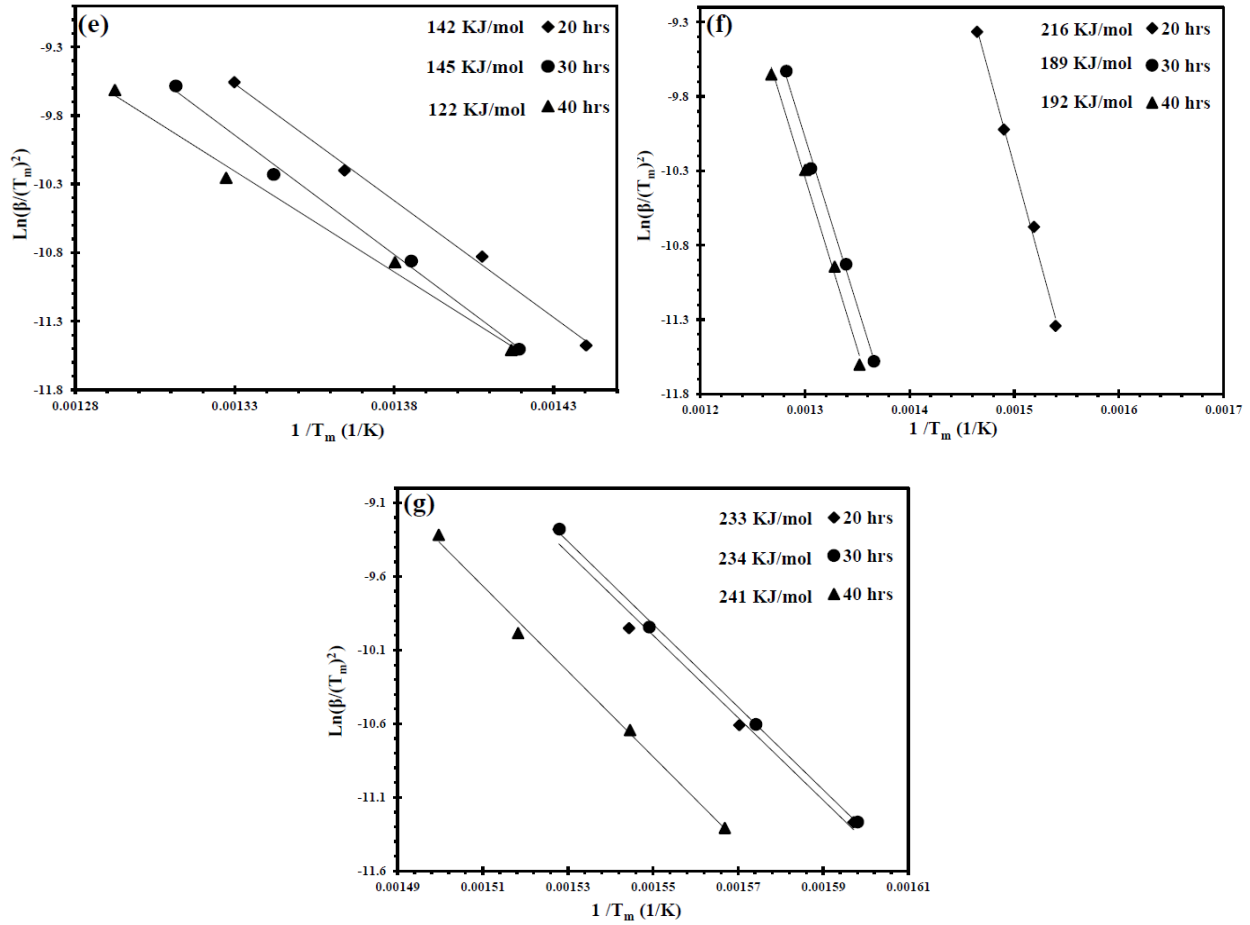


Figure 4.18: Kissinger's plots of the crystallization activation energy of the Co-at. % C, alloys milled up to 40h: (a) 2 at.%, (b) 5 at.%, (c) 10 at.%, (d) 15 at.%, (e) 20 at.%, (f) 30 at.% and (g) 40 at%.

Therefore and as Figures 4.18 and 4.19 indicate, the apparent activation energy of the crystallization reaction E_a in the compositions of 20 at.% carbon or less ($70\text{--}140\text{ kJ mol}^{-1}$) was substantially lower than for the higher carbon compositions ($189\text{--}241\text{ kJ mol}^{-1}$), and it gradually increased as the carbon content of the alloy increased. Indeed, these activation energies values are in good agreement with the activation energies of the C diffusion in Co [48 and 49] and the Co self-diffusion [50]. In view of these results as well as that of the higher carbon compositions (≥ 20 at.% carbon), the activation energy for carbon diffusion in cobalt ($145 \pm 5\text{ kJ mol}^{-1}$) [48, 49] was lower for the activation energy of the crystallization reaction of the system ($189\text{--}241\text{ kJ mol}^{-1}$). Since in this case the exponential factors were equal within a factor of 45, the activation energies were directly related to the crystallization reaction rates. This means that the reaction rate for the

carbon diffusion reaction was lower than the rate of the crystallization reaction for higher carbon compositions (≥ 20 at.% carbon). Because of that, during the stages of the crystallization reaction, the carbon underwent the difficult process of mobility, or slow diffusion state, in which the octahedral sites (interstitial sites) that the carbon used for the diffusion were scarce; thus the Co_2C formation reaction activity was low and mostly unavailable [1].

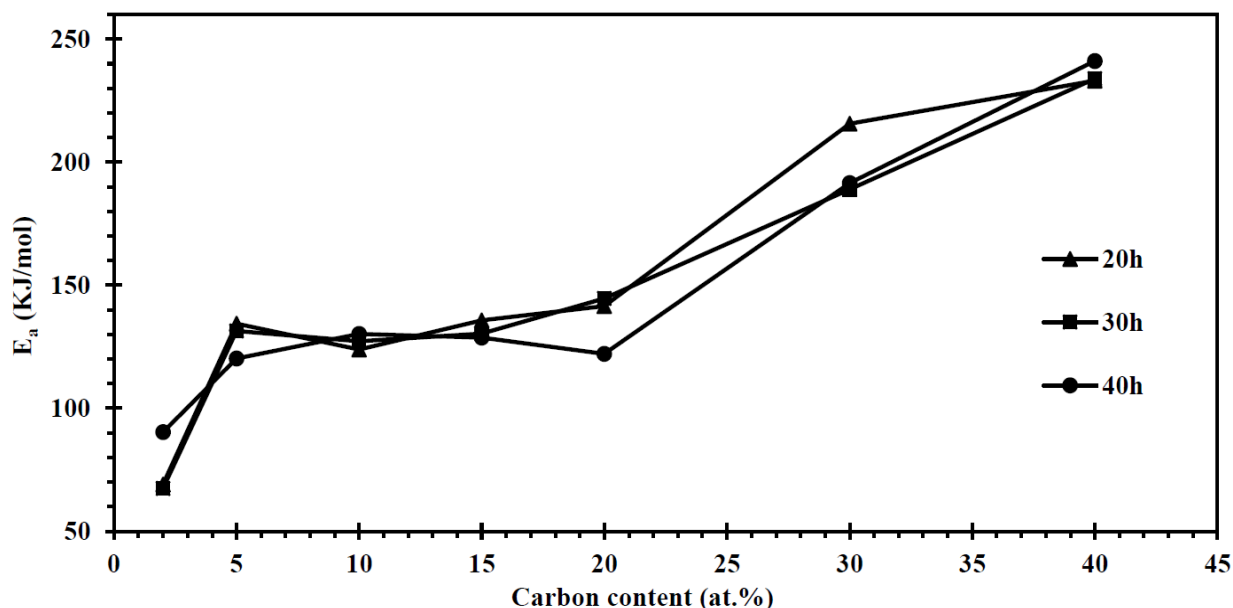


Figure 4.19: Activation energy of crystallization E_a for Co-at.% C with different milling times, as a function of at.% C contents.

Despite the lower carbon compositions (≤ 20 at.% carbon), the apparent activation energies of the crystallization reaction of the system were 70-140 kJ mol^{-1} , which is in line with the reported values for the activation energy of the formation reaction of the metastable Co_2C (67-125 kJ mol^{-1}) [51-54]. In this case the activation energy for the carbon diffusion in cobalt (145 kJ mol^{-1}) was higher than it was for the activation energy of the crystallization reaction of the system (70-140 kJ mol^{-1}); hence, the activation energies could be seen to be directly related to the crystallization reaction rates. Therefore, the carbon diffusion rate was high enough to form and grow Co_2C [1], as confirmed by the results of the DSC measurements through the emergence of the first exothermic peaks in the stages of the crystallization reaction.

Therefore, the DSC result of the $\text{Co}_{80}\text{C}_{20}$ milled for 20h, as shown in Figure 4.17, confirmed that the first exothermic peak at 261°C was the formation of the Co_2C metastable phase, whereas

the appreciably large second exothermic peak at 391°C was due to the decomposition of the Co_2C and the crystallization of the remaining amorphous cobalt. Consequently, the system ended up with a stable fcc cobalt with some concomitant hcp phase and graphite. Thus, it is obvious that the $\text{Co}_{80}\text{C}_{20}$ milled 20h released its excess free energy via a metastable phase formation and not by a Co-mediated crystallization of carbon phase. Further, the two exothermic peaks in the DSC results confirmed that the crystallization process in the composition of $\text{Co}_{80}\text{C}_{20}$ milled for 20h occurred in two-stage of crystallization instead of the one-stage, as had been clearly observed in the high carbon compositions.

In contrast, as shown in Figure 4.17, the crystallization reaction in the composition of $\text{Co}_{80}\text{C}_{20}$, milled for longer than 20h, occurred in a one-stage of crystallization process by precipitating the crystalline phase of fcc cobalt with some concomitant of hcp phase, and amorphous carbon. However, using the mechanical alloying process to amorphize the Co-C system in this work caused a lack in the octahedral sites (interstitial sites) that the carbon atoms needed for their diffusion through the cobalt during the crystallization process, as explained earlier. Therefore, in this case, the system was unable to follow the metal-mediated crystallization process to reduce its excess free energy by precipitating the crystalline phase of fcc cobalt with some concomitant of hcp phase and amorphous carbon.

Figure 4.20 and Figure 4.21 show the DSC results of the compositions of $\text{Co}_{85}\text{C}_{15}$ and $\text{Co}_{90}\text{C}_{10}$ in at.%, milled for up to 40h. These compositions present comparable results to the one found in the composition of $\text{Co}_{80}\text{C}_{20}$ milled 20h, as shown in Figure 4.17. However, the results in both Figures show two exothermic peaks. As explained earlier, these two exothermic peaks indicate that two stages of crystallization mechanism occurred during the crystallization of these compositions under the stated conditions. Consequently, the first exothermic peak was attributed to the Co_2C metastable phase formation; while, the second exothermic peak corresponded to the decomposition of the Co_2C and the crystallization of remaining amorphous cobalt, which ended up as a stable fcc cobalt with a concomitant of the hcp phase and graphite.

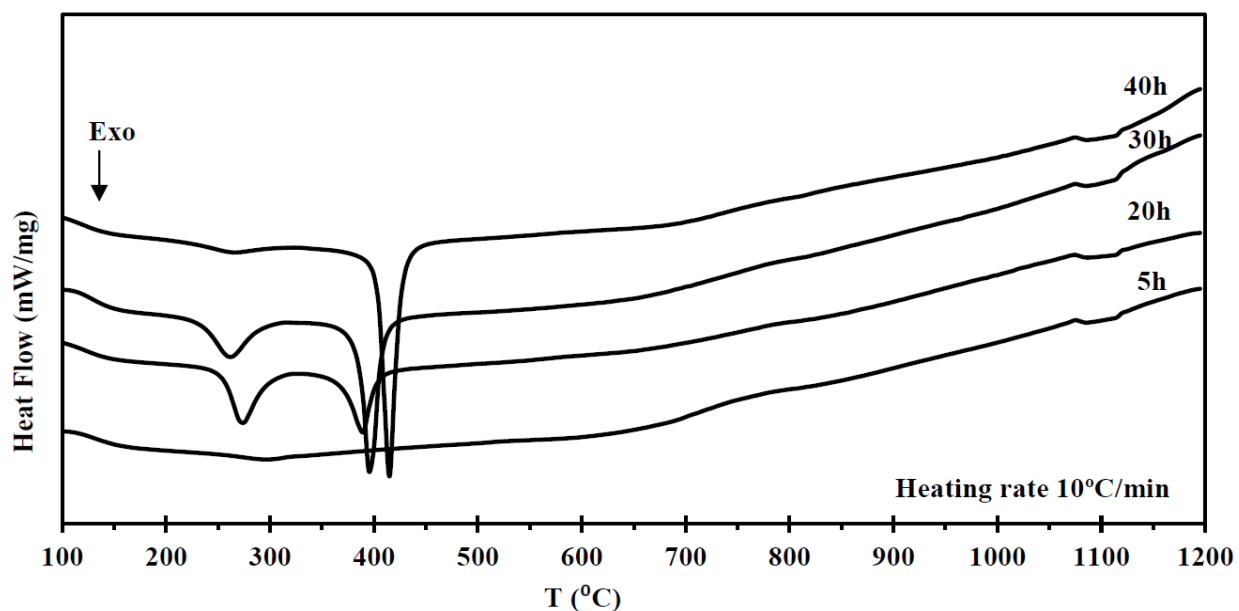


Figure 4.20: Differential scanning calorimetry curves of $\text{Co}_{85}\text{C}_{15}$ in at.%, milled for up to 40 hours at a heating rate of 10 °C/min.

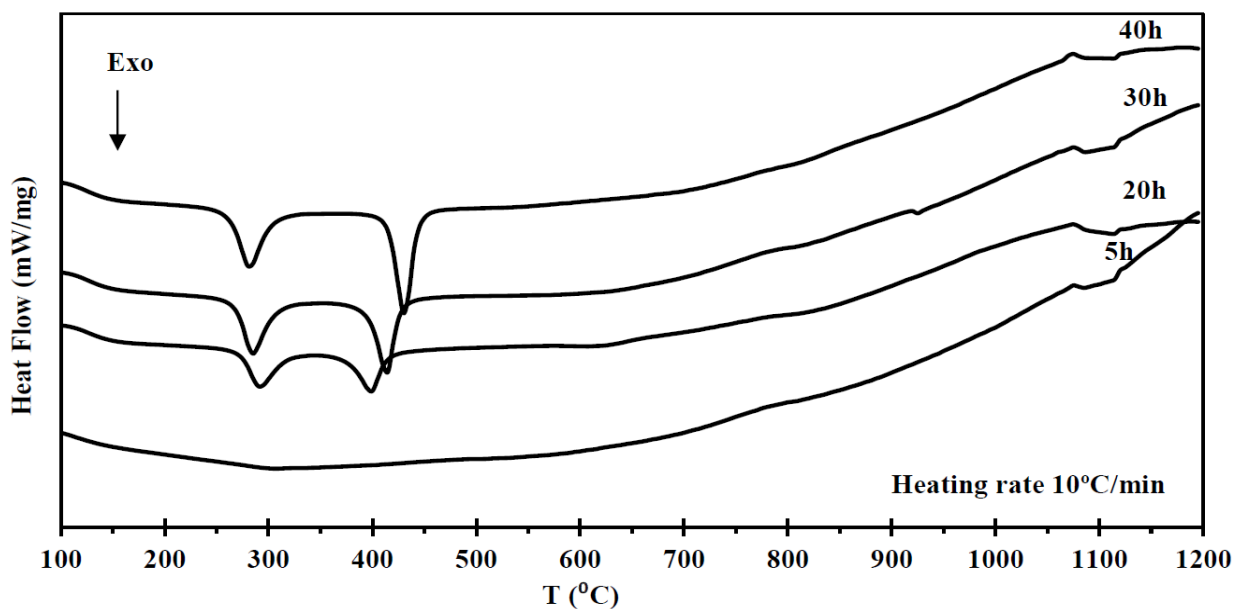


Figure 4.21: Differential scanning calorimetry curves of $\text{Co}_{90}\text{C}_{10}$ in at.%, milled for up to 40 hours at a heating rate of 10 °C/min.

In order to confirm these results, annealing experiments at 360°C and 520°C followed by XRD measurements were conducted to identify the phase structures of these DSC exothermic peaks. However, two specimens of $\text{Co}_{90}\text{C}_{10}$, milled for 40h, were heated in an argon atmosphere at 360°C

and 520°C, with a heating rate of 10 °C/min, and cooled to room temperature under the same conditions. After the annealing process, the XRD measurements were conducted for these specimens. Figure 4.22 depicts the XRD patterns for the Co₉₀C₁₀, milled for 40h, at each annealing temperature, compared with the milled specimen. In this XRD patterns, it was found that the phase structure at these temperatures were obviously a fcc cobalt structure, concomitant by some of the hcp cobalt and graphite. However, the 2θ position of the peaks and the d-spacing confirmed that the phases were mostly fcc cobalt with some hcp cobalt, and the broadening in the peaks indicated that there was either some amorphous phase leftover or very fine cobalt particles. Interestingly, the cobalt-carbide of (Co₂C) was not observed in the XRD profiles of the annealed specimens, as reported in some studies which found that the first exothermic peak in the DSC results were always related to the Co₂C formation [1 and 32]. Therefore, the absence of the Co₂C phase in the XRD profiles may have been due to the detector (PANalytical PW3015/20 X'Celetator) that was used in this work, i.e., that it was not sensitive enough to pick up this phase. Another possible reason was that the amount of the Co₂C was not large enough to be detected, owing to the size of the Co₂C particles being very fine [1 and 55] so that its broad peaks could be hidden in the background noise.

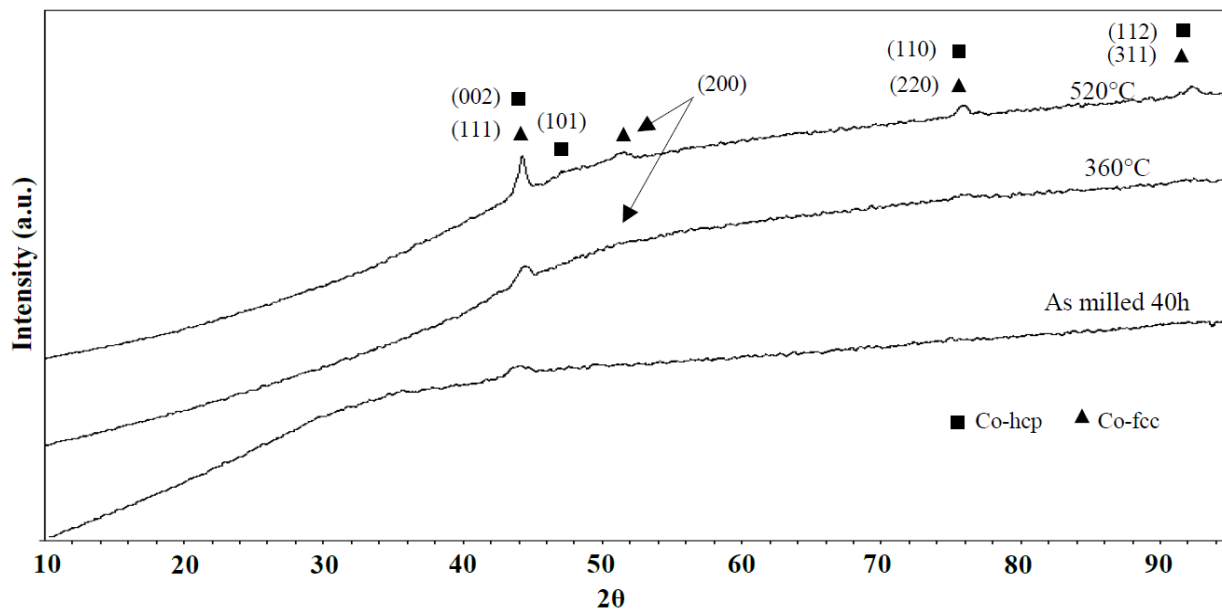


Figure 4.22: X-ray diffraction patterns for Co₉₀C₁₀ in at.%, milled for 40h and heated at different temperatures.

The DSC results for the Co_{95}C_5 milled for up to 40h are shown in Figure 4.23. These results showed that the samples have three exothermic peaks. The first peak occurred in the range of 300 to 315°C, resulting from the Co_3C metastable phase formation [56], as also confirmed by the XRD results in Figure 4.25, not from the Co_2C metastable phase, as supposed earlier. On the other hand, the second peak took place in the range of 408 to 438°C, originating from the Co_3C metastable phase decomposition reaction and the remaining cobalt amorphous crystallization reaction. In addition to these two exothermic peaks, a third shallow exothermic peak occurred in the range of 575 to 605°C. This shallow exothermic peak is related to the growth of the nanocrystallites [57-61]. Indeed, the same type of exothermal peak was observed for several other nanocrystalline cobalt-base alloys, and had been previously reported for nanocrystalline Co [62], Co-P [58], Ni [63-66], and Ni-P [67]. Therefore, this third peak shows that mechanically alloyed powders of Co_{95}C_5 are not a perfect amorphous phase, but rather a nanocrystalline structure embedded in an amorphous phase. In other words, this third exothermic peak has revealed the existence of some nanocrystalline structure in the mechanically alloyed powders of Co_{95}C_5 , as evidenced by SAED pattern in the TEM results.

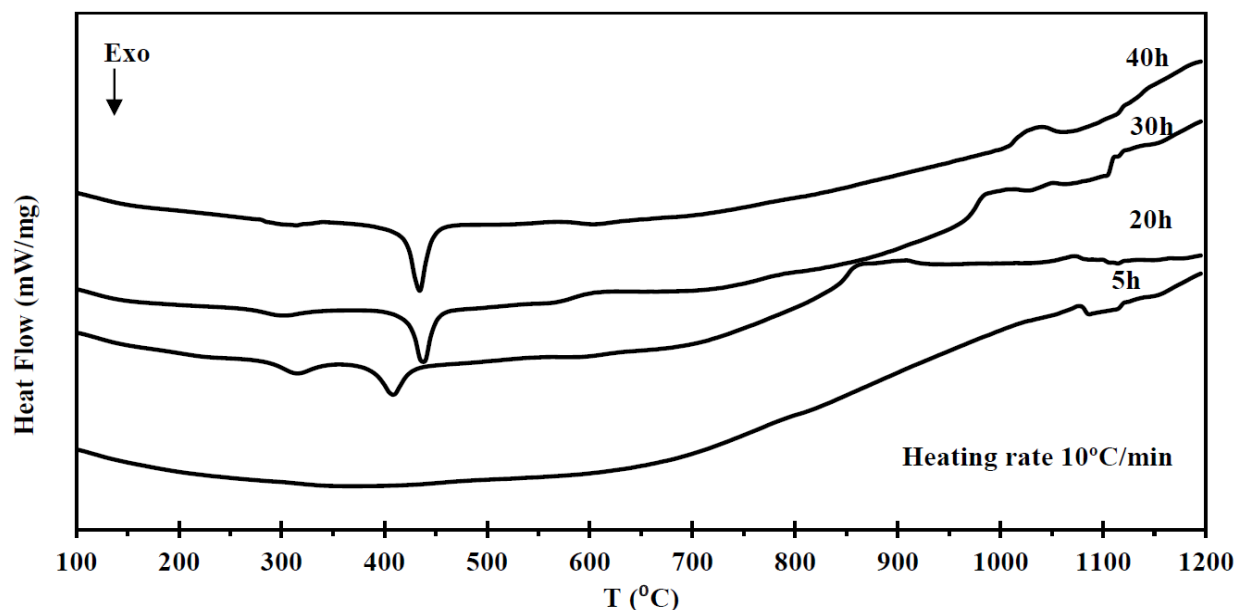


Figure 4.23: Differential scanning calorimetry curves of Co_{95}C_5 in at.%, milled for up to 40 hours at a heating rate of 10 °C/min.

In order to obtain as accurate and complete thermal behavior as possible for our system by DSC and also to investigate the phases evolution by XRD, an innovative procedure has been designed

to achieve this approach; heat the virgin sample (milled powder) in the DSC until the first phase (first exothermic peak) is formed; cool to room temperature, and then reheat until the next phase (second exothermic peak) is formed. Thereafter it is cooled to room temperature again, back and forth until the last cycle of the procedure reaches 1100°C and then cooled to room temperature, as seen in Figure 4.24. The Co_{95}C_5 powder which was milled for 20h was selected for these cycles of annealing.

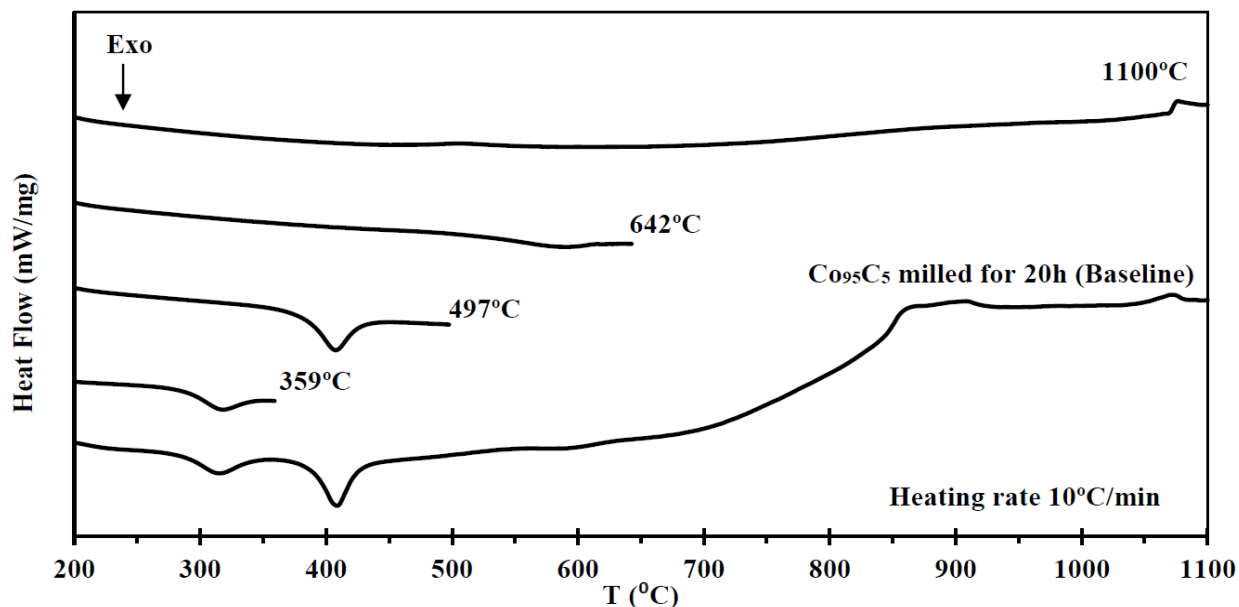


Figure 4.24: Differential scanning calorimetry traces of Co_{95}C_5 in at.% powder, mechanically alloyed for 20 hours, continuously heat-treated at a rate of 10 °C/min, compared with the DSC baseline of the Co_{95}C_5 powder milled for 20h. The DSC traces appeared after heating the sample to 359°C, cooled to room temperature, then reheated to 497°C. Thereafter it was cooled to room temperature again, back and forth in the same way until 1100°C.

Therefore, for the annealing cycles and temperatures, the DSC baseline of the Co_{95}C_5 powder was milled for 20h, as shown in Figure 4.23, with a heating rate of 10 °C/min. Moreover, another batch of samples was also annealed in the DSC, by using the same parameters that were used in the first batch, in order to investigate the evolution of the phases by XRD, as seen in Figure 4.25. Consequently, Figure 4.24 shows the DSC traces data of Co_{95}C_5 , milled for 20 hours plotted individually for each cycle. The DSC baseline for the Co_{95}C_5 powder milled for 20h showed three exothermic peaks. As explained earlier, the first exothermic peak at 315°C was a formation peak of the Co_3C metastable phase, and the second exothermic peak at 408°C was a combination for

the Co_3C metastable phase decomposition reaction and the remaining cobalt amorphous crystallization reaction. The shallow exothermic peak at 590°C was assigned to the growth of the nanocrystallites.

As shown in Figure 4.24, the trace denoted as 359°C was obtained from the first heating cycle by heating the Co_{95}C_5 powder, milled for 20h to 359°C and cooled to room temperature. As expected, it showed an exothermic peak at 315°C which was a formation peak of the Co_3C metastable phase, as stated earlier. The trace peaked by 497°C , represents the second cycle of the annealing procedure. However, after completing the first cycle and reaching room temperature, the sample started the second cycle after being reheated to 497°C and then cooled to the starting temperature. Figure 4.24 shows only one exothermic peak corresponding to the second exothermic peak in the baseline of Co_{95}C_5 milled powder, which is the Co_3C metastable phase decomposition reaction and the remaining cobalt amorphous crystallization reaction, as confirmed by the XRD results in Figure 4.25. Immediately after the second heating cycle was finished, the third heating cycle started after the sample was heated to 642°C and immediately cooled to room temperature. The trace of this cycle is defined as 642°C , as seen in Figure 4.24. In the third cycle of heating, only a shallow exothermic peak at about 590°C appeared, which was due to the growth of the nanocrystallites, as mentioned above and confirmed by the XRD results in Figure 4.25. The exothermic peak that showed up in the second cycle disappeared, confirming that this reaction is an irreversible reaction with no phase transformations occurring on cooling or immediate reheating. Finally, the trace labeled as 1100°C was obtained from the last cycle in the annealing procedure, which began immediately after the sample completed the third heating cycle. However, in this cycle, the sample was reheated to 1100°C and then it was cooled to room temperature. As expected, the shallow exothermic peak had disappeared and no other peaks showed up, confirming that there was no phase transformation during the cooling or immediate reheating. Therefore, such a heat effect over the shallow exothermic peak temperature range can be explained as the heat of irreversible growth of the nanocrystallites.

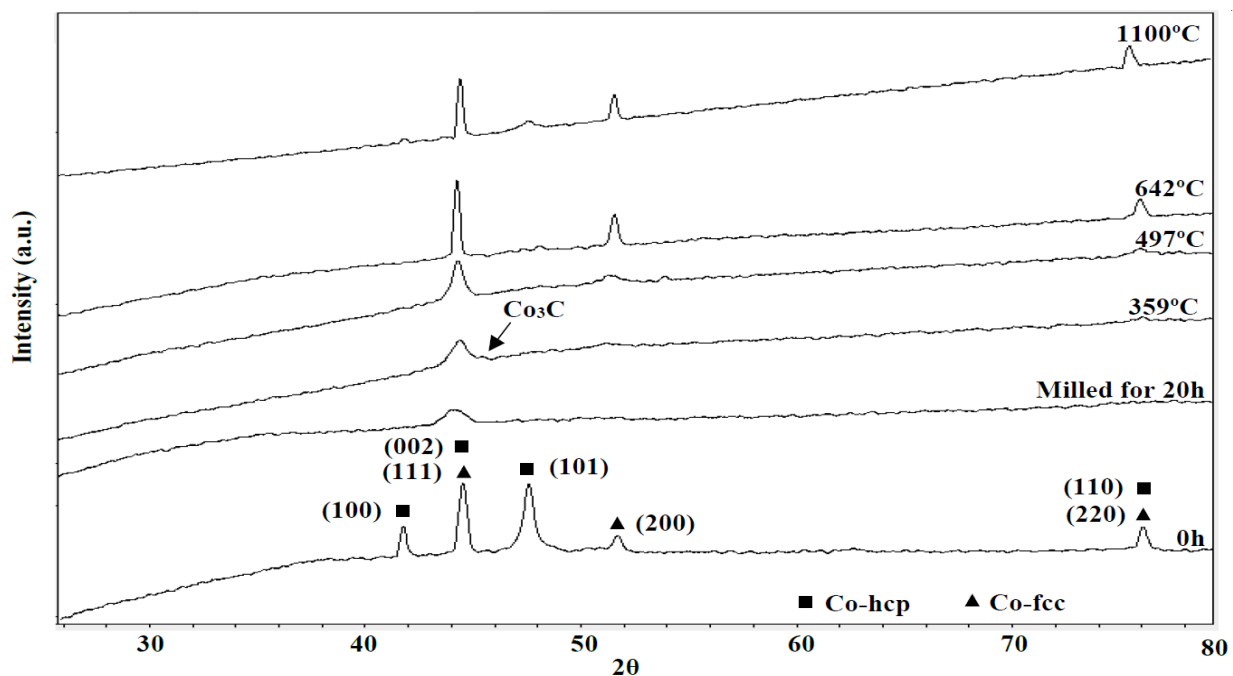


Figure 4.25: X-ray diffraction patterns for Co_{95}C_5 in at.%, milled for 20h and heated back and forth to different temperatures, compared with unmilled cobalt.

Figure 4.25 illustrates the XRD patterns of Co_{95}C_5 milled 20h, and continuously heat treated back and forth to 359, 497, 642 and 1100°C. For the milled sample, a single broad peak embodying the nanocrystallites and amorphous phase appeared. After the sample was heated to 359°C, a tiny peak at around $2\theta = 45.3^\circ$ appeared, which belonged to the Co_3C metastable phase, as marked by an arrow in Figure 4.25. However, the XRD pattern of this sample was indexed to the ICDD PDF reference powder diffraction file Co_3C (PDF#26-450) with orthorhombic and space group Pbnm (62) ($a=4.44 \text{ \AA}$, $b=4.99 \text{ \AA}$ and $c=6.7 \text{ \AA}$); also these lattice parameters are in good agreement with the other results of the Co_3C metastable carbide structural investigations [68]. However, these XRD results emphasized the existence of the Co_3C metastable phase in the system; therefore this confirms that the first exothermic peak that was observed in the DSC curves of the Co_{95}C_5 powder, milled 20 h, as shown in the Figures 4.23 and 4.24, reverted to the reaction of the Co_3C formation. This result brings us to the question of why the XRD detector can pick up the Co_3C metastable phase but cannot in the case of Co_2C . It is most likely because of the grain size, where is the grain size of Co_3C larger than Co_2C by several hundred $\text{\AA}$ [1, 55 and 69], and this difference in the grain size is due to the phase formation temperature [69]. As has been seen, the Co_2C phase for different compositions and milling times occurred between 260 to 290°C, whereas the Co_3C was 300 to

315°C. Therefore, the high formation temperature of Co_3C caused the Co_3C to have a larger grain size than Co_2C , and for this reason, the Co_3C phase was easier to be picked up by the XRD detector than the Co_2C phase.

As can be seen from Figure 4.25, since the sample was heated to 359°C, there was no major difference in the peak broadening, just an emergence of the little peak of the Co_3C metastable phase. The broad peak was still present and the breadth was about the same as for the as-milled sample. These observations suggested that an amorphous phase did not fully crystallize during this heat treatment, nor did the nanocrystallites grow at all. However, when the powder was heated up to 497°C and cooled, some new peaks appeared and the Co_3C peak disappeared, as shown in Figure 4.25. These new peaks were caused by the fcc cobalt, but they were slightly broad owing to the nanostructure. Alternatively, some carbon could still have been dissolved in the cobalt. However, the disappearance of the Co_3C peak and the disappearance of the fcc cobalt peaks suggested that the Co_3C metastable phase was decomposed into a fcc cobalt phase and graphite, but this result was contrary to what most other studies have reported.

However, many studies [56] reported that the Co_3C decomposed into a hcp cobalt phase and graphite instead of fcc cobalt, as reported in this study. As Nagakura claimed [55], for the decomposition of the cobalt carbides, the atomic arrangement of the cobalt in these carbides was responsible for the form of the decomposed phase. This atomic arrangement of cobalt in both cobalt carbides, Co_2C and Co_3C , is in good agreement with the atomic arrangement of hcp cobalt. Therefore, due to this congruence, Co_2C and Co_3C essentially decompose to hcp cobalt instead of to fcc cobalt, even though the decomposition temperature is higher than the cobalt allotropic phase transformation. Later on, Konno and Sinclair [1] explained that the Co_3C metastable phase decomposes firstly into a Co_2C metastable phase and then to the hcp cobalt. However, based on Konno's explanation and observations confirmed earlier about the Co_2C decomposition, it looks as if the Co_3C firstly decomposes into a Co_2C metastable phase, and then the Co_2C metastable phase decomposes to fcc cobalt with some concomitant of the hcp phase, as discussed earlier. Therefore, as can be seen in Figure 4.25, the fcc cobalt, with some concomitant hcp phase, became evident as the annealing temperature increased, which confirmed the validity of this approach. However, the Co_2C phase was not clearly shown during the decomposition of the Co_3C phase,

possibly due to the closeness of the decomposition temperatures for these phases. The short incubation time for the Co_2C phase that resulted made it difficult to capture it.

For the sample reheated to 642°C and cooled, the peaks of the fcc cobalt became sharper and more distinct, as shown in Figure 4.25. This observation indicates the presence of the hcp cobalt phase and the coarsening of the cobalt structure with increase in temperature, as evident in Figure 4.25. Moreover, the XRD scan from the specimen reheated to 1100°C showed that there was no phase transformation occurring in the cooling or immediate reheating, as seen in Figure 4.25. Therefore, the lack of phase transformation is evidence that the third exothermic peak reaction that was observed in the DSC curves do not lead to any structural and/or phase transformation, but it comes mainly from the growth of the cobalt nanocrystallites that have produced during the milling and from the relaxation of the powders that were strongly distorted during the milling process. However, in the absence or insufficiency of negative heat of mixing between the constituent elements to form the amorphous phase during the mechanical alloying, the heavy mechanical deformation during the ball-milling caused nanometer-scale crystallites to form [60]. Likewise, this is what happened with the mechanically alloyed powders of Co_{95}C_5 and Co_{98}C_2 in this work, where they showed the nanocrystallite phase because both of them have a very small negative heat of mixing, which were about -2.2 and -0.8 KJmol^{-1} , respectively, as related to the Miedema's model [30], as seen in Figure 4.9. Therefore, these values were not enough to be a driving force for the diffusion to form a fully amorphous phase in the system, responsible for the formation of nanocrystallites phase embedded in the amorphous phase. However, the atomic disorder and nanocrystallite boundaries were the main places of mechanical energy storage; consequently the quick reaction path to the system to reduce this stored energy was only possible by means of the atomic reordering and grain growth of the nanocrystallite [60]. So, the third exothermic peak that showed up in the mechanically alloyed powders of Co_{95}C_5 and Co_{98}C_2 were mainly due to the growth of nanocrystallites, as seen in both Figures 4.23 and 4.27. As can be seen from Figure 4.25, after the growth of the cobalt nanocrystallites by reheating the sample to 1100°C , the fcc cobalt phase peaks appeared sharper, while the hcp cobalt phase peaks showed up more clearly, but their coarsening into sharp peaks increased in volume fraction only at higher temperatures, as shown in 1100°C scan in Figure 4.25.

Thus, it can be concluded that, with respect to the Co_{95}C_5 powder mechanically alloyed for 20h, its crystallization process for the amorphous part occurred in two stages. Based on XRD analysis and DSC, the crystallization stages were characterized first as a Co_3C metastable phase formation, and secondly, as a Co_3C metastable phase decomposition reaction. The remaining cobalt amorphous crystallization reaction, which resulted in a stable fcc cobalt with some concomitant of the hcp phase and graphite. However, the lack of the graphite peaks in the XRD results were questionable, and so to verify the presence of the carbon in the alloy, an energy-dispersive X-ray spectroscopy (EDS) point analysis was performed on the Co_{95}C_5 sample, milled for 20h and annealed at 770°C , as seen in Figure 4.26. As can be seen from Figure 4.26, the EDS spectra clearly demonstrated that in addition to the strong peaks of the Co, there were obviously C peaks.

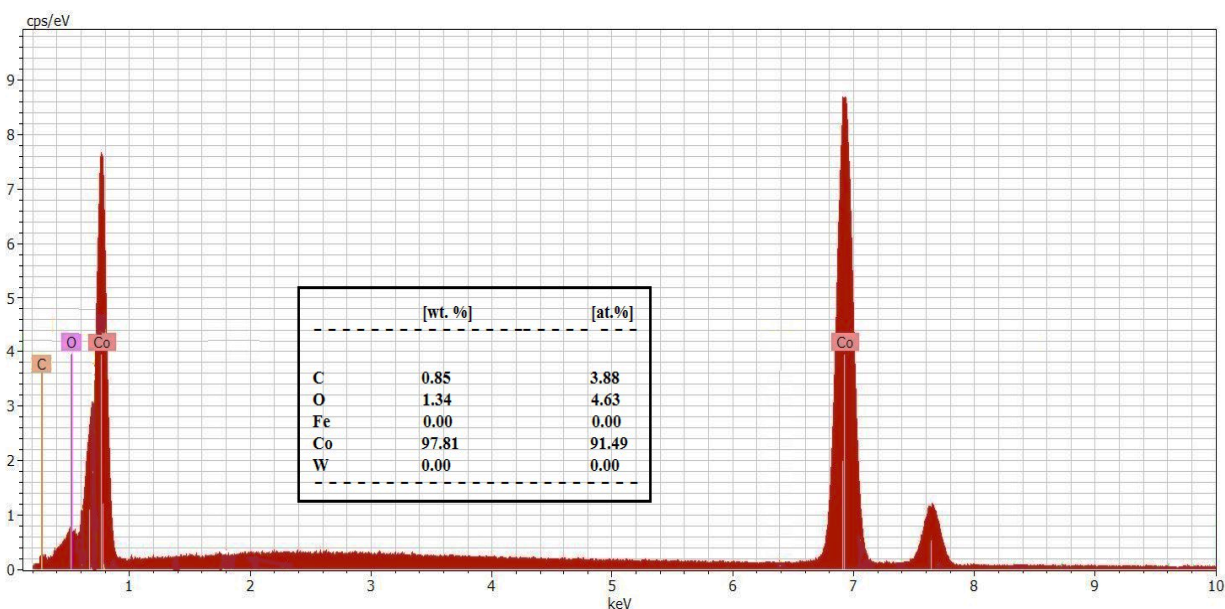


Figure 4.26: EDS spectra from the mechanically alloyed powder of Co_{95}C_5 , milled 20h and annealed at 770°C , shows intense cobalt peaks, a minor carbon peak and nothing else in more than a trace amount of oxygen.

Therefore, from this chemical analysis that shows up in the EDS data, it was found that the elemental composition for this data clearly and quantitatively corresponded to the pristine elemental composition of the sample (Co_{95}C_5), confirming the presence of the elements Co and C in the sample chemical composition. Moreover, in order to check the extent of the impurities in the system which may have transferred from the grinding media to the system, in addition to the carbon and cobalt chemical analysis, a chemical analysis was executed on the elements of oxygen,

iron and tungsten. However, besides the cobalt and carbon amounts that were found in the test result, as seen in Figure 4.26, a trace amount of oxygen was detected and may have existed during the preparation for the EDS test or as impurities in the starting powders.

Interestingly, the carbon phase was not observed in the XRD profiles of the annealed specimens as shown in Figure 4.25. However, the lack of detection of the carbon phase in the XRD profiles may be due to the detector (PANalytical PW3015/20 X'Celetator) that was used in this study because it is not sensitive enough to pick up the carbon phase, or the amount of the carbon is not large enough to be detected. Another possible reason is that the carbon structure could be have a very broad XRD profile due to the fine structure and its broadening peaks could be hidden in the background noise.

Figure 4.27 shows the DSC results of the compositions of Co_{92}C_2 in at.%, milled for up to 40h. This composition presents comparable results to those found in this study in the composition of Co_{95}C_5 milled for up to 40h, as shown in Figure 4.23. The results in both Figures show three exothermic peaks. As discussed earlier, the first and the second exothermic peaks indicate that the two-stage of crystallization mechanism occurred during the crystallization of these compositions under the stated conditions. Consequently, the first exothermic peak occurred around 365°C and contributed to the Co_3C metastable phase formation. In contrast, the second exothermic peak took place in the range of 438 to 470°C and points to the decomposition of the Co_3C and the crystallization of the remaining amorphous cobalt, which ended up as a stable fcc cobalt with some concomitant hcp phase and graphite, as seen in the composition of Co_{95}C_5 . In addition to these two exothermic peaks, a third exothermic peak occurred around 560°C . However, this third exothermic peak is related to the growth of the nanocrystallites [57-61], as seen in the composition of Co_{95}C_5 .

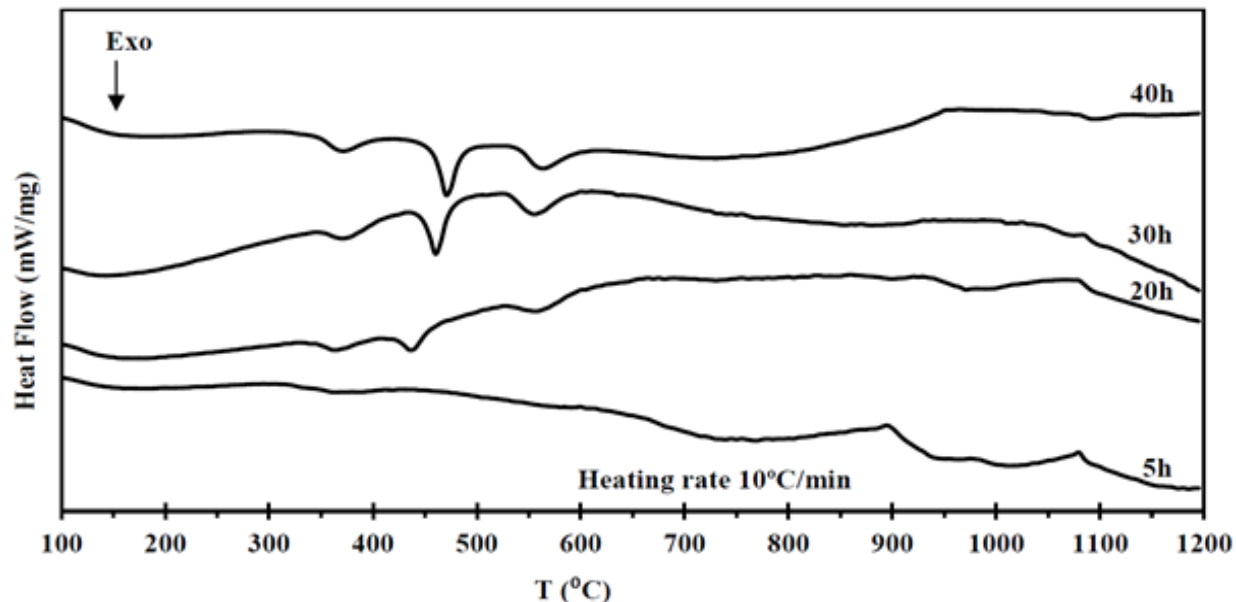


Figure 4.27: Differential scanning calorimetry curves of Co_{98}C_2 in at.%, milled for up to 40 hours at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$.

In order to investigate that the release of energy shown by exothermic peak is due to the growth of the cobalt nanocrystallites, pure cobalt powders were milled for 5, 20, 30 and 40h under the same conditions that were been used during the milling of the Co-C alloys. Moreover, the DSC measurements and XRD were conducted for these specimens in order to evaluate the thermal behavior and phases transformations. Figure 4.28 depicts the XRD patterns for the pure cobalt milled for up to 40h, compared with the unmilled specimen. As can be seen from Figure 4.28, the intensity of all diffraction peaks decreased gradually with the increasing milling time, whereas the width of the peaks increased with the milling time. After 20h of milling, some of the low-intensity diffraction peaks disappeared, and with further milling, the diffraction line intensities continued decreasing, whereas the width of the peaks kept increasing. After 40h of milling, more decreasing in the diffraction line intensities and more broadening for the peaks took place, but the pattern still had the features of the hcp cobalt structure.

Therefore, these observations suggest that the cobalt powder did not amorphize after all this milling time, which means that the amorphization was not likely to take place. As a result, the peak broadening and absence of some diffraction peaks that were observed were due to the mechanical milling. However, during the ball milling the milled material was exposed to cold work deformation, causing a reduction in the crystallite size (coherent domains) and inducing strains

and distortions within the crystallites [70 and 71]. Accordingly, the absence of some diffraction peaks strongly indicates that an atomic disorder was generated in the cobalt powder by means of mechanical milling, so the pure cobalt after 40 h of milling turned nanocrystalline, as seen in Figure 4.28.

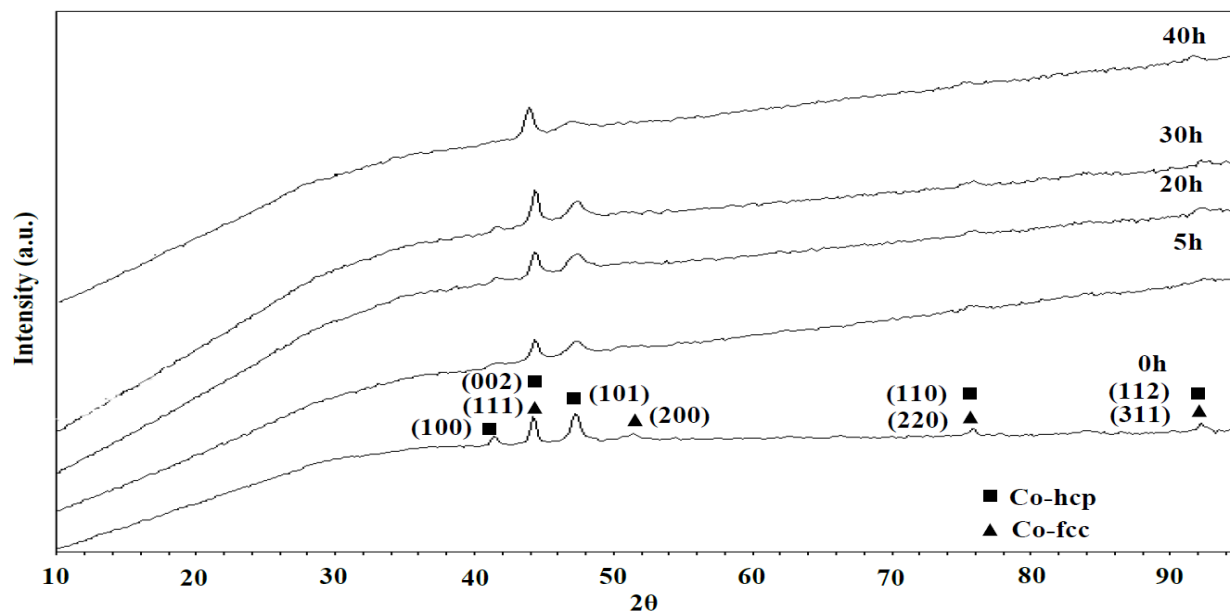


Figure 4.28: X-ray diffraction patterns for pure cobalt powders milled for up to 40 hours, compared with unmilled cobalt powder.

The thermal behavior of the pure cobalt milled powders was analyzed by the DSC, as seen in Figure 4.29. As can also be seen from Figure 4.29, for all the samples except the one milled for 5h, one exothermic peak in the range of 540 to 571°C was evident. This exothermic peak became much more pronounced with the increase in the milling time, by releasing more energy, suggesting that the change in the powder structure was highly intense as the milling time increased. The DSC trace of powder mechanically alloyed for 5h, on the other hand, didn't show much difference from the unmilled sample, as seen Figure 4.29, indicating that there wasn't much change in the sample structure. However, as the milling time increased, the atomic disorder and nanocrystallite increased because they were the main places of mechanical energy storage. Therefore, the quick reaction path to the system to reduce this stored energy was only by atomic reordering and grain growth of the nanocrystallite [60]. However, in terms of the peak temperature and the heat release, the pure cobalt milled for up to 40h exhibited comparable results to the third exothermic peak in the composition of Co_{98}C_2 and Co_{95}C_5 , also milled for up to 40h, as shown in Figure 4.23 and 4.27.

Indeed, this observation suggests that exothermic peak is a result of the growth of the cobalt nanocrystallites.

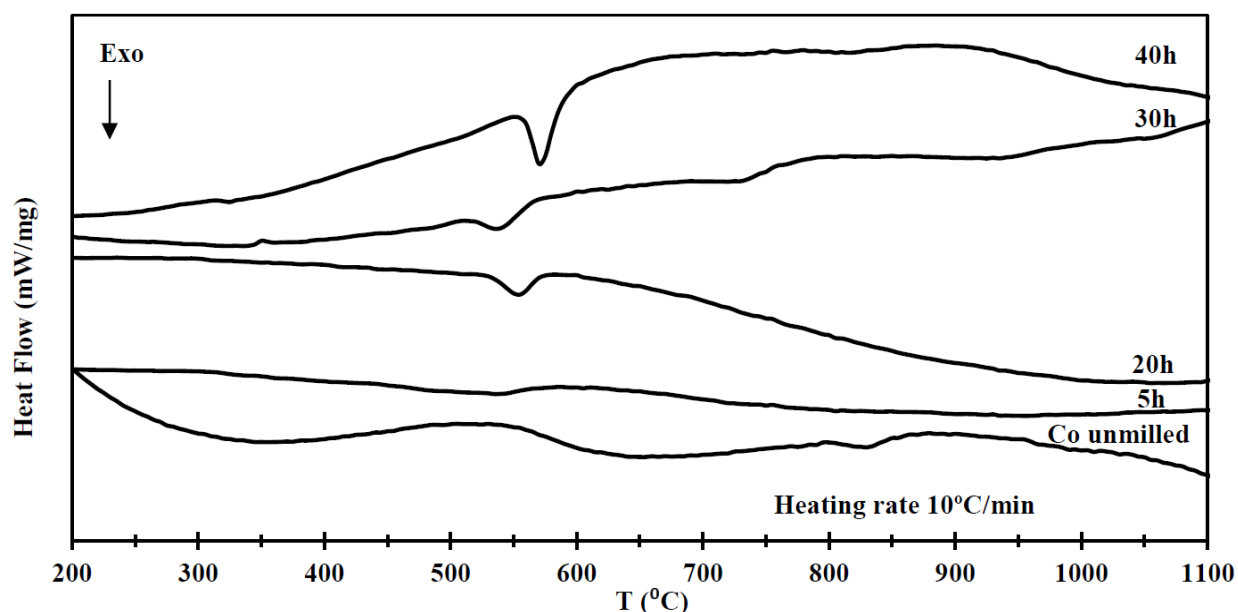


Figure 4.29: Differential scanning calorimetry curves of pure cobalt, milled for up to 40 hours at a heating rate of 10 °C/min.

In order to improve the accuracy of the experiments, an annealing experiment at 650°C, followed by XRD measurement, was conducted to identify the phase structure of this DSC exothermic peak. Thus, a specimen of pure cobalt milled for 40h was heated in an argon atmosphere at 650°C, with a heating rate of 10 °C/min, and cooled to room temperature under the same conditions. After the annealing process, the XRD measurement was conducted for this specimen. Figure 4.30 depicts the XRD patterns for the pure cobalt milled for 40h at the annealing temperature, compared with the milled specimen and unmilled pure cobalt specimen. In this XRD patterns, it was found that the phase structure at this temperature was obviously a fcc cobalt structure, concomitant with some of the hcp cobalt. However, the 2θ position of the peaks and the d-spacing confirmed that the phases that we obtained were mostly fcc cobalt with some hcp cobalt, as seen in Figure 4.30. These observations suggested that there were no new phases formed during this heat treatment except for the growth of the cobalt nanocrystallites; hence solid-state amorphization or phase transformations was not likely to take place.

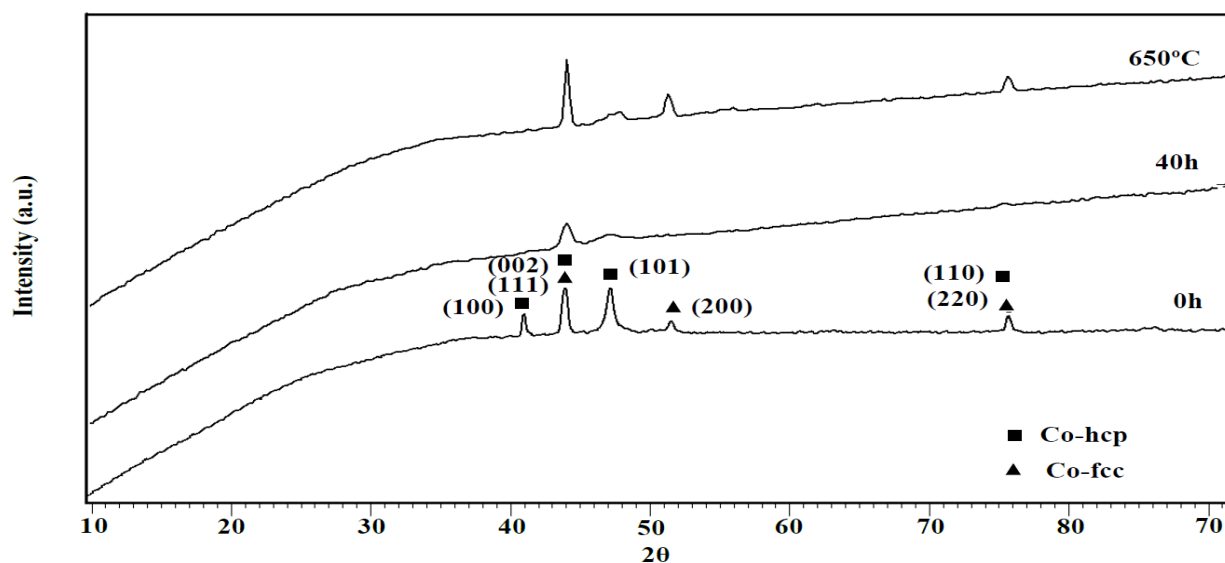


Figure 4.30: X-ray diffraction patterns for pure cobalt milled for 40h and annealed at 650°C.

As has been noted, the exothermic peak of the milled pure cobalt powders and the third peak of the mechanically alloyed powders of the Co_{98}C_2 clearly show that the mechanically alloyed powders of Co_{98}C_2 were not a perfectly amorphous phase, as discussed earlier in the composition of Co_{95}C_5 , but rather a nanocrystalline structure embedded in an amorphous phase. In other words, this third exothermic peak in the mechanically alloyed powders of the Co_{98}C_2 and Co_{95}C_5 revealed the existence of some nanocrystalline structure in the mechanically alloyed powders of Co_{98}C_2 and Co_{95}C_5 , as evidenced by the SAED pattern in the TEM results.

Consequently, the DSC trace data of Co_{95}C_5 and Co_{98}C_2 , both milled for up to 40h, as seen in Figures 4.23 and 4.27, also indicated that the crystallization process for the amorphous part of the alloy occurred during the two-stage mechanism. Evidently, the dependence of the two-stage mechanism of crystallization was primarily due to the carbon content more than the milling time itself. Nevertheless, this two-stage mechanism of crystallization was achieved when the ratio between cobalt and carbon atoms was close to the stoichiometric composition of the cobalt carbides Co_2C and Co_3C [1, 72]. Therefore, in the presence of this stoichiometry of the C/Co ratio, the crystallization process began with forming a metastable phase of Co_2C or Co_3C as a first step, which materialized in the first exothermic peak on the DSC curves. Then, in the second step in the crystallization process, the Co_2C or Co_3C metastable phases decomposed with the crystallization of the remaining amorphous cobalt. This step was considered a second step in the crystallization process, with the reaction showing up as a second exothermic peak on the DSC curves.

Thus, as observed in the all of DSC results, the two-stage mechanism of crystallization takes place when the carbon content is less than 20 at.%. But, during the crystallization process, if the carbon content deviates from the stoichiometric composition of the cobalt carbides Co_2C and Co_3C phase, which is beyond the available of the octahedral sites (interstitial sites), another phase will appear. With excess of carbon, consequently, the Co-C amorphous system will follow the one step of crystallization by forming a crystalline phase of fcc cobalt, with some concomitant hcp phase, and amorphous carbon, whereas in the absence of carbon, the quick reaction path to the system of reduce the excess free energy of the amorphous phase only occurs in the presence of an abundant formation of Co_2C or Co_3C as first step in the crystallization process, thereby decomposing them with the crystallization of the remaining amorphous as a second step.

The reaction characteristics of the cobalt carbides formation (Co_2C and Co_3C) are indexed by the enthalpy of reaction, $\Delta H_{\text{cobalt carbide formation}}$ (the total area under the first exothermic reaction peak), and the reaction temperature, $T_{\text{cobalt carbide formation}}$ (the temperature of the first exothermic reaction peak); these are presented as a function of the carbon content (at.%) and milling time (h) in Figures 4.31-4.34. It is clear in Figures 4.31-4.34 that the reaction enthalpy $\Delta H_{\text{cobalt carbide formation}}$ of the cobalt carbides formation (Co_2C and Co_3C) takes place during the intermediate stages of milling (20 and 30h), where this reaction can be carried out only when the carbon content is in the range of 2 to 20 at.%, increasing dramatically as the carbon content increased in the above range. However, at a very low carbon content (2 and 5 at.% carbon), the system is forced to form the metastable phase of cobalt carbide Co_3C , whereas the metastable phase of the cobalt carbide Co_2C is formed when the carbon content in the system is in the range of 5 to 20 at.%. As the carbon content reaches the 20 at.%, the Co-C amorphous system will lose the ability to form the cobalt carbide (Co_2C) because of the excess of carbon atoms and the lack of octahedral sites; the absence of the first exothermic reaction peak on the DSC curves of higher carbon compositions (≥ 20 at.% carbon) confirms that conclusion. Thus, the excess of carbon atoms that results from the high carbon content in the system and the lack in the octahedral sites make the quick reaction path to the system reduce its excess free energy only because of the abundant precipitation of very small particles of the crystalline cobalt phase in the amorphous carbon, as mentioned earlier. In the case of 40h of milling, the reaction enthalpy increases dramatically as the carbon content increased and takes the high place just when the carbon content reaches 10 at.%, as shown in Figures 4.32 and 4.33.

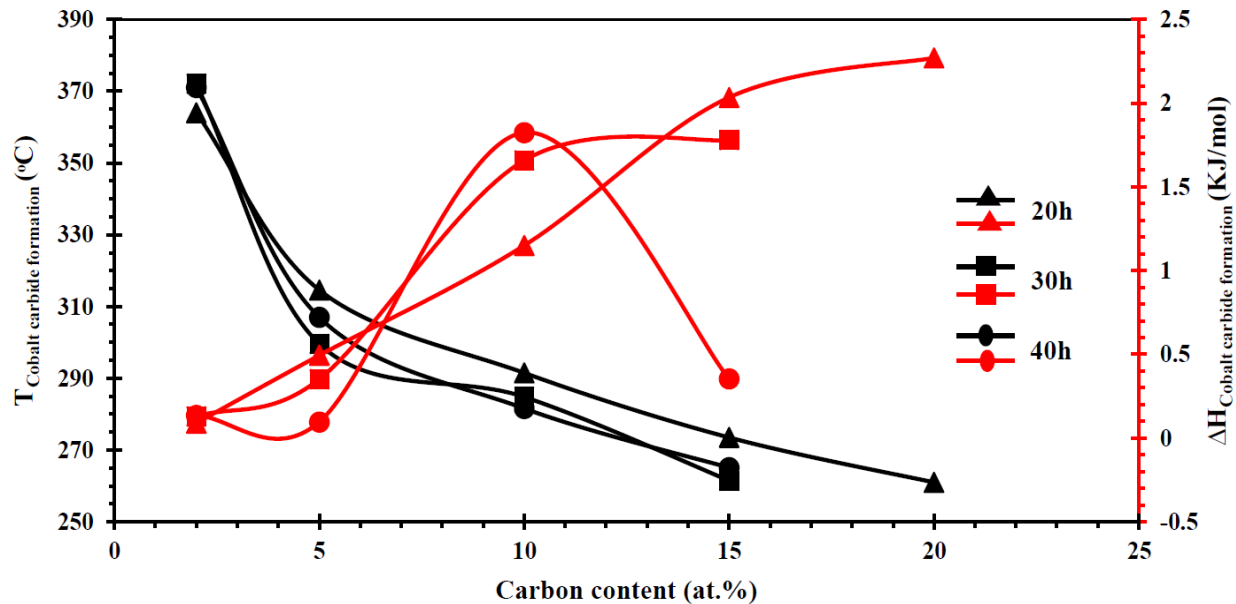


Figure 4.31: Effect of the carbon content (at.%) on the reaction temperature of the cobalt carbides, $T_{\text{cobalt carbide formation}}$ and the enthalpy of the reaction, $\Delta H_{\text{cobalt carbide formation}}$ of mechanically alloyed Co-C system.

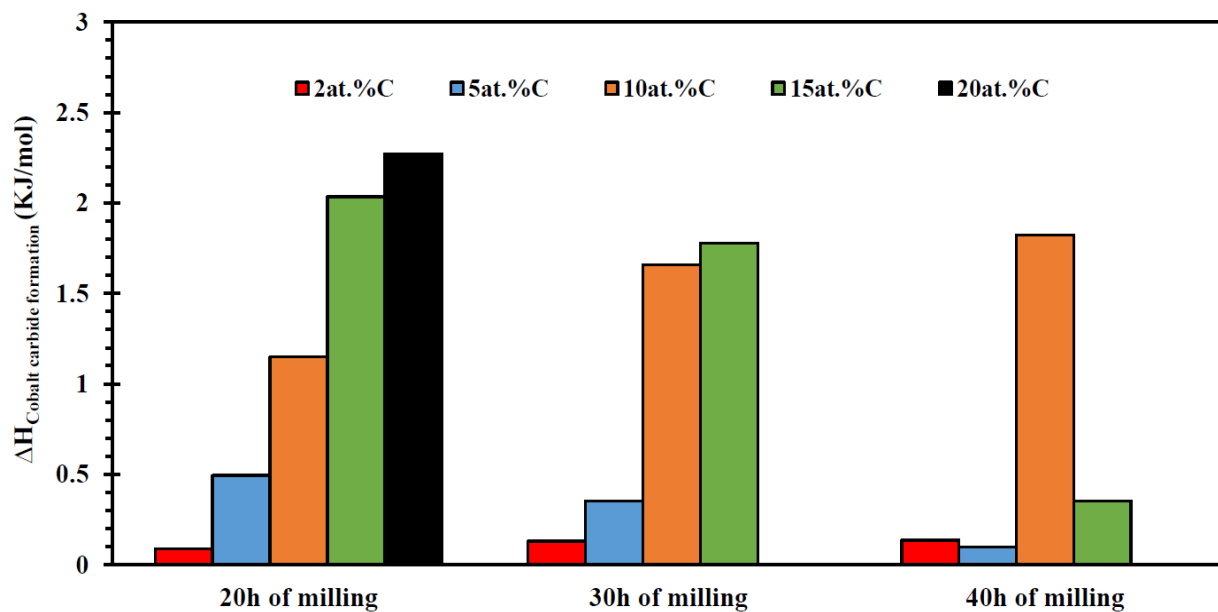


Figure 4.32: Comparison of enthalpy of crystallization, $\Delta H_{\text{cobalt carbide formation}}$ produced by different carbon contents on three different milling times.

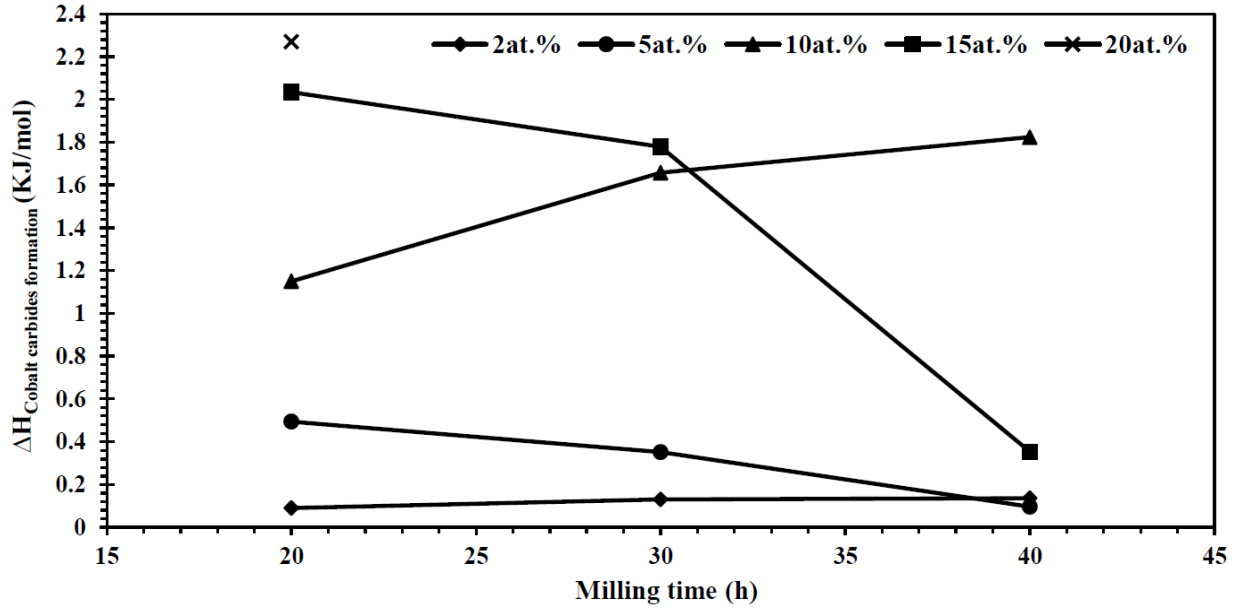


Figure 4.33: Effect of the milling time (h) on the enthalpy of the reaction, $\Delta H_{\text{cobalt carbide formation}}$ of mechanically alloyed Co-C system.

Once the carbon content reached 15 at.%, it steeply decreases, suggesting that the increase of the carbon content in the system is not suitable for the cobalt carbides to form. After the 15 at.% carbon, the system loses the ability to form the carbide because of the excess of carbon atoms and the lack of octahedral sites. The diffusion of the excess carbon atoms through the amorphous matrix will be too slow to allow the carbide phase to form or grow. However, this steep increase in the reaction enthalpy values is attributed to the limitation of the octahedral sites that the carbon atoms try to occupy, where this limitation is due to the huge distortion of the hcp structure of the cobalt during the long milling process.

In contrast, in the case of less than 10 at.% carbon, the Co_2C phase also becomes unable to form, and is superseded by the Co_3C phase, as shown in Figures 4.23 and 4.25. To restate, due to the massive distortion on the hcp structure of cobalt that has occurred during the milling, the Co_2C has lost its ability to form and grow. However, the carbon at some point during the milling process acts as a lubricant to reduce the effect of the excessive plastic deformation and fracture by maintaining the balance between the cold welding and the fracturing of powder particles [12, 29, 73, 74], but when the amount of carbon goes down, as in the case of Co_{95}C_5 , the state of the lubricant in the system will also go down. The plastic deformation and fracture on the cobalt structure for the low carbon content samples will thereby be much heavy than those with higher

carbon content, leading to the severe lack in the octahedral sites. As a result, the system will lose its ability to form the Co_2C . Indeed, the thermal behavior observations for the low carbon content alloys suggest that the increase in the temperature values of the cobalt carbides formation reaction ($T_{\text{cobalt carbide formation}}$) may be associated with the decrease in the carbon content, as shown in Figure 4.31 and 4.34. Consequently, since the milled powders are severe lacking in the octahedral sites after the milling, the high temperature values of $T_{\text{cobalt carbide formation}}$ could be attributed to the difficulty of the carbon atoms diffusion through the cobalt at a low temperature. The increase in the reaction temperature $T_{\text{cobalt carbide formation}}$ is accordingly steeper in the low carbon content alloys, becoming bigger as the carbon content is decreased, as seen in Figures 4.31 and 4.34.

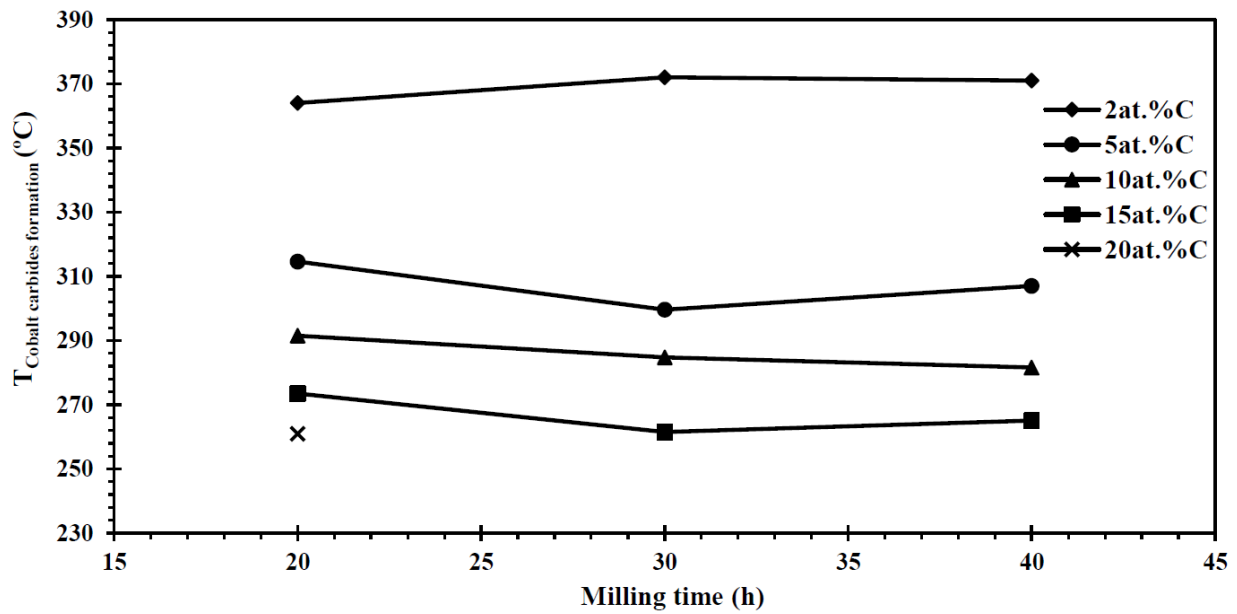


Figure 4.34: Effect of the milling time (h) on the reaction temperature of the Co_2C , $T_{\text{cobalt carbide formation}}$ of mechanically alloyed Co-C system.

In fact, with the decreasing carbon content, the system suffers more and more from the lack of the octahedral sites, which makes it at some point unable to form the Co_2C phase, even if the temperature goes up. However, at 5 at.% carbon, the cobalt carbide of the Co_2C cannot be formed even if heat is supplied to it because the carbon atoms cannot find a fast path to diffuse through the cobalt to meet the requirement of the Co_2C phase formation reaction in the absence the octahedral sites. Therefore, in this case and with the large surface areas of the cobalt, only by forming the cobalt carbide phase of Co_3C can the quick reaction path for the system reduce the excess free energy.

As has been explained above, the crystallization process of the Co-C amorphous system mechanically alloyed depends on the carbon content as well as milling time. However, the deficiency of carbon in the system leads to the formation of metastable phase Co_2C carbide, whereas an excess of carbon leads to the precipitation of very small particles of a crystalline cobalt phase in carbon amorphous, as mentioned earlier. Therefore, the upper boundary for the Co_2C composition to be formed is normally a stoichiometric composition between the carbon and cobalt, where all octahedral interstitial sites of the cobalt crystal are filled with carbon atoms [1, 72]. According to Konno et al. [1], the C/Co ratio should be less than 0.5 for the Co_2C reaction to start. In the present thesis, it was found that this ratio was lower than that value by half, i.e., around 0.25. This stoichiometry discrepancy between these studies probably was due to the preparation processes, as stoichiometry is a direct function of the structure or of the changes of the lattice parameter. However, the mechanism of the preparation process of the Co-C amorphous alloy is reflected in the structure of the resulting alloy. Therefore, in the case of Co-C mechanically alloyed system, the intense deformation with large defect densities, especially at the grain boundaries, are generated by using the mechanical alloying technique, creating a huge distortion in the crystal structure of cobalt. This distortion is due to a lack in the octahedral sites that carbon atoms try to occupy as interstitial sites, and in this case, the stoichiometry of C/Co ratio shrinks as the number of the octahedral sites go down. Thus, these results show that, for the Co-C amorphous crystallization at any carbon content and milling rate, the stoichiometry of C/Co ratio plays an important role in the mechanism of the crystallization and the phases to be reached.

In view of that, the cobalt carbides formation in different phases is another point of investigation in this work, and this point needs some clarification to retain the objectivity of this study. However, Konno et al. [1] in their work on the Co-C system co-sputtered pointed out that the metastable phase of Co_3C phase was formed in the composition of $\text{Co}_{89}\text{C}_{11}$, whereas the Co_2C phase was formed in the higher carbon compositions, thereby confirming the DSC and the TEM results. By looking to the work by Konno et al. [1], we find that the Co_3C phase was formed in the compositions of low carbon content, i.e., in the cobalt rich compositions. These results suggest that the cobalt carbides were likely to form a Co_3C phase more than Co_2C in the case of cobalt rich compositions such as Co_{98}C_2 and Co_{95}C_5 in this work. Therefore, we believe the cobalt carbide forming mechanism is behind this. However, the formation mechanism of the Co_3C is similar to the formation mechanism of Fe_3C [1, 55, 69 and 72] and Ni_3C [32, 55 and 75], which is based on

the nucleation and growth. Consequently, the Co_3C formation was initiated by the formation of a nuclei of the Co_3C carbide crystal on the cobalt crystal surface and grew up gradually [55]. In contrast to this formation mechanism, the formation mechanism of the Co_2C is based on the principle of the carbon atoms occupying the octahedral sites (interstitial sites) of the cobalt by diffusing the carbon active atoms into the octahedral sites (interstitial sites) of the cobalt [1, 55 and 72]. According to Nagakura's conception [55], on the other hand, this occupation of carbon atoms for the octahedral sites of the cobalt crystals and moving through them causes a lattice expanded in the cobalt crystals, leading to a distortion in the cobalt crystals. Therefore, this distortion of the cobalt crystals has become as a new atomic arrangement between the cobalt and carbon atoms, which is the Co_2C crystal structure. Meanwhile, since the size of these new crystallites (Co_2C) is very close to that of the cobalt, the cobalt crystal transforms to Co_2C crystal without crystal growth. As has been explained, the Co_3C carbide phase clearly relies on the cobalt surfaces to complete its formation, whereas the Co_2C depends on the octahedral sites (interstitial sites) of the cobalt. Accordingly, as seen earlier, the lower carbon content alloys (Co_{98}C_2 and Co_{95}C_5) have lost their ability to form the Co_2C phase, but instead have replaced it with the Co_3C phase, suggesting a lack of the octahedral sites. However, during the milling, the milled powder (cobalt rich) is exposed to a massive deformation leading to a distortion in the cobalt crystals. At the same time, the carbon at some point during the milling works as lubricant to reduce the effect of the excess of the plastic deformation and fracture by maintaining the balance between the cold welding and fracturing of powder particles [12, 29, 73, 74]. When the carbon amount goes down, as in the case of Co_{98}C_2 and Co_{95}C_5 , the lubricant condition goes down too. The plastic deformation and fracture on the cobalt structure will thus be much heavier than those with higher carbon content, leading to a severe lack in the octahedral sites. As a result, this severe lack of the octahedral sites makes the carbon atoms diffusion very difficult through the system matrix, or too slow to allow the Co_2C phase to form and grow [1]. Thus, the system will lose its ability to form the Co_2C phase, and this explains why the Co_2C phase in the cases Co_{98}C_2 and Co_{95}C_5 does not form. On the other hand, the cobalt rich powders after the milling will show a large surface area for the cobalt, which makes it a suitable place for the Co_3C phase to nucleate and grow. However, any system during the crystallization reaction will look for a mechanism that provides the fastest reaction pathway to reduce its excess free energy, by modifying the activation-energy barriers of the nucleation, growth, and phase transformation. In view of that, for the low carbon compositions,

such as our case of Co_{98}C_2 and Co_{95}C_5 , the favorable crystallization mechanism and the fastest reaction path for the system to reduce its excess of the free energy, under the severe lack of the octahedral sites, and losing the ability to form the Co_2C phase is only through the formation of the metastable phase of Co_3C , where the Co_3C phase nucleates its nucleuses on the cobalt crystals surfaces and these nucleuses grow up gradually to form the Co_3C phase, as has been discussed earlier.

4.3.3 Transmission Electron Microscopy (TEM) Analysis

Transmission Electron Microscopy (TEM) was used in this work to characterize the microstructure of the milled powders. A typical bright field micrograph (BF) and corresponding selected area electron diffraction (SAED) pattern for mechanically alloyed powder of Co-40 at.% C, milled for 40h, are shown in Figures 4.35 and 4.36. Figure 4.35a shows particles amorphous of an $\text{Co}_{60}\text{C}_{40}$ sample, milled for 40h, whereas Figure 4.35b shows a selecting amorphous particle for the SAED pattern analysis by focusing on the particle edges. For a high-resolution TEM image, Figure 4.36a presents a high-resolution bright field micrograph obtained from the mechanically alloyed powder of $\text{Co}_{60}\text{C}_{40}$ milled for 40h.

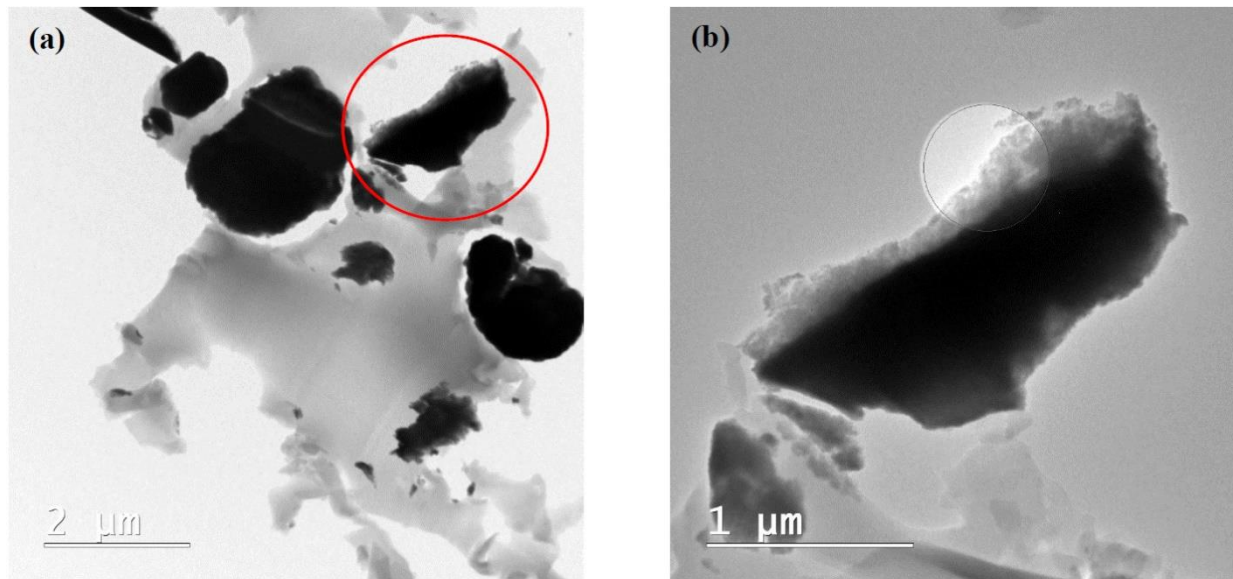


Figure 4.35: A typical bright filed micrograph of mechanically alloyed powder of Co- 40 at.% C, milled for 40h: (a) $\text{Co}_{60}\text{C}_{40}$ amorphous particles, (b) selecting amorphous particle for the SAED pattern analysis.

The microstructure appears to be uniformly amorphous. There is no clear evidence of microcrystallinity or nanocrystallinity which means that no lattice fringe was found in either the cobalt or the carbon, and this has been confirmed by the SAED patterns, as shown in Figure 4.36b. However, Figure 4.36b shows the corresponding SAED patterns of the bright field micrograph that was showed in Figure 4.36a. As can be seen from Figure 4.36b, no diffracted rings were found in either the cobalt or the carbon on the SAED patterns, suggesting that it was completely amorphous. However, in the case of the completely amorphous phase, the feature of concentric rings in the pattern disappeared and a halo was left around the bright center spot, which shows that the electrons were scattered randomly by the amorphous structure of the specimen, as shown in Figure 4.36b. Consequently, it can be concluded that the mechanically alloyed powder of $\text{Co}_{60}\text{C}_{40}$ milled for 40h is a completely amorphous structure. Indeed, the TEM characterization seen here qualitatively verifies the data found by XRD and DSC of mechanically alloyed powder of $\text{Co}_{60}\text{C}_{40}$ milled for 40h, which is a completely amorphous phase.

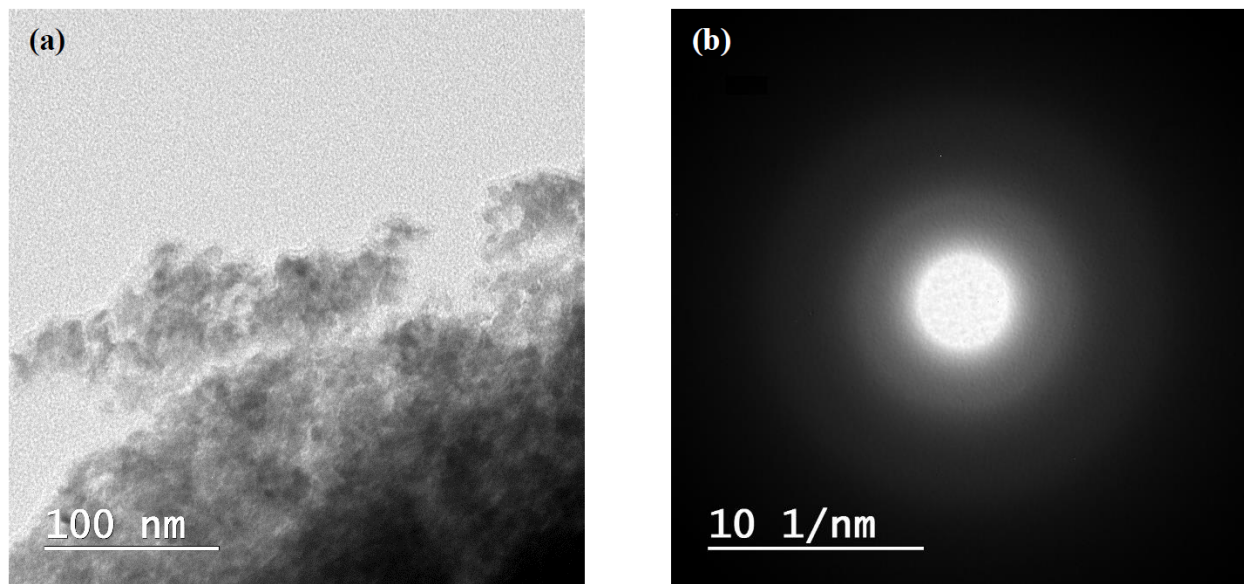


Figure 4.36: TEM characterization of mechanically alloyed powder of Co- 40 at.% C, milled for 40h: (a) Bright filed micrograph, (b) SAED pattern. The bright filed micrograph shows an amorphous microstructure. While in the SAED pattern, the feature of concentric rings in the pattern disappears and a halo is left around the bright center spot, which confirms that the structure is a completely amorphous phase.

Additionally, in order to determine the accuracy of the selected zone composition, a dispersive X-ray spectroscopy (EDS) mapping analysis was conducted to confirm that the selected zone is related to the $\text{Co}_{60}\text{C}_{40}$ system, as shown in Figure 4.37. As can be seen from Figure 4.37, the EDS spectra and EDS mapping analysis for the elemental chemical analysis provided evidenced that the selected zone is related to the $\text{Co}_{60}\text{C}_{40}$ system, confirming the presence of respective elements (Co and C) in the sample chemical composition. Moreover, in addition to the carbon and cobalt chemical analysis, a chemical analysis was carried out on the elements of oxygen, iron and tungsten, in order to determine the extent of the impurities in the system which may have transferred from the grinding media to the system. However, besides the cobalt and carbon amounts that were found in the test result as shown in Figure 4.37, a trace amount of oxygen was detected and may have existed during the sample preparation for the test or as impurities in the starting powders.

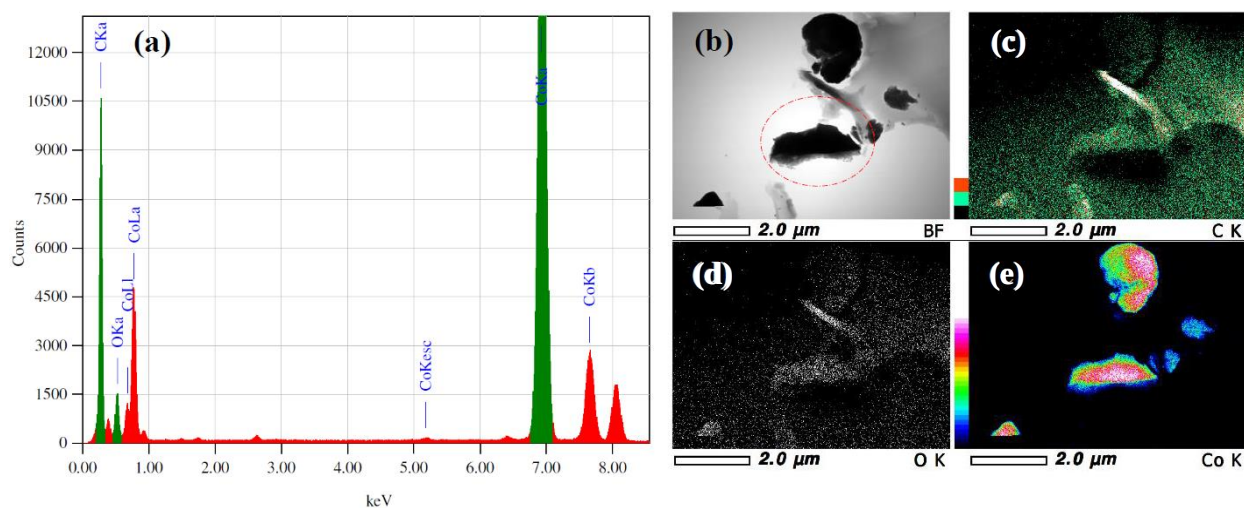


Figure 4.37: EDS spectra and EDS mapping analysis from the mechanically alloyed powder of $\text{Co}_{60}\text{C}_{40}$ that was milled 40h: (a) EDS spectra of the elements analysis, (b) bright filed micrograph, (c) EDS mapping of the C and a combination of morphology with its distribution, (d) EDS mapping of element the O, (e) EDS mapping of the Co and a combination of morphology with its distribution. The EDS spectra and EDS mapping analysis shows intense cobalt peaks, a minor carbon peak, but nothing else except a trace of oxygen.

Figure 4.38 shows the EDS spectra of the analyzed elements and the TEM characterization for the mechanically alloyed powder of Co- 10 at.% C, milled for 40h. Figure 4.38a presents the EDS

spectra of the analyzed elements for the $\text{Co}_{90}\text{C}_{10}$ milled for 40h, it shows intense cobalt peaks, a minor carbon peak and nothing than a trace amount of oxygen. Therefore, the analysis demonstrates the presence of the respective elements (Co and C) in the sample chemical composition, which confirms that the selected zone is related to the $\text{Co}_{90}\text{C}_{10}$ system. The corresponding SAED patterns in Figure 4.38b shows that $\text{Co}_{90}\text{C}_{10}$ mechanically alloyed powder, milled for 40h, also does not show the cobalt and carbon diffracted rings, suggesting that it is completely amorphous as well. However, it exhibits a similar SAED pattern to the $\text{Co}_{60}\text{C}_{40}$ mechanically alloyed powder milled for 40h, as seen in Figure 4.36b, in spite of the fact that the central halo is a little smaller here compared to that of $\text{Co}_{60}\text{C}_{40}$, due to the higher C content of the former [76].

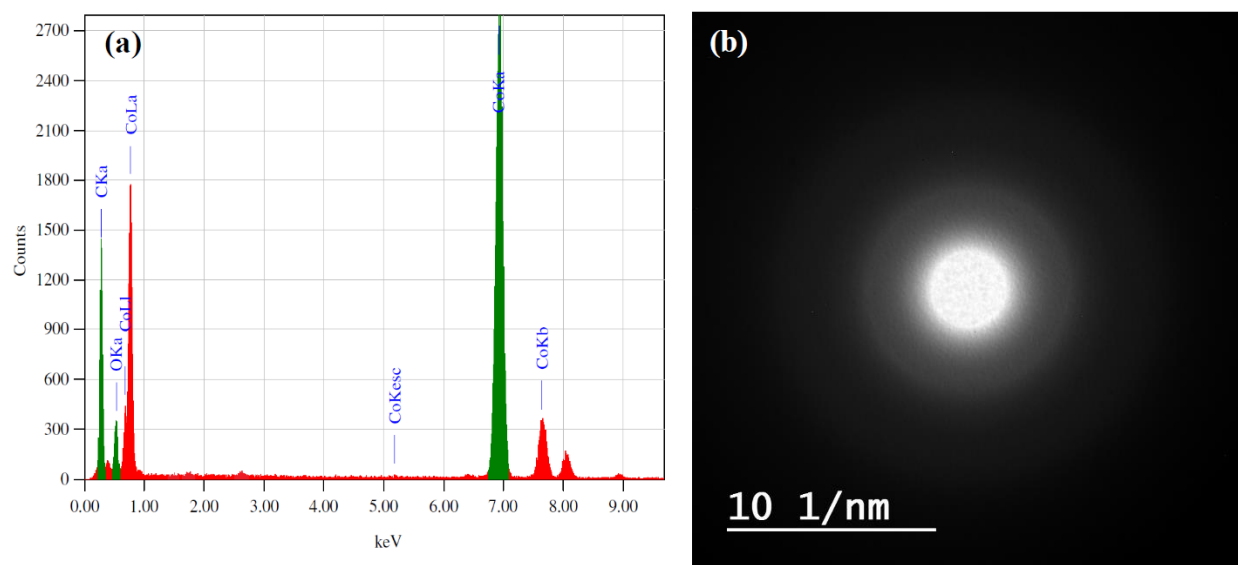


Figure 4.38: TEM characterization of mechanically alloyed powder of Co- 10 at.% C, milled for 40h: (a) EDS spectra of the element analysis, (b) a SAED pattern. However, in the SAED pattern, the feature of concentric rings disappears and a halo is left around the bright center spot, which confirms that the structure is a completely amorphous phase.

Similar to the results of the TEM characterization of the mechanically alloyed powders of Co- 10 and 40 at.% C, milled for 40h, the compositions of 10 up to 40 at.% C, after being milled for 40 h, should have a complete amorphous phase transformation. However, if the composition of $\text{Co}_{90}\text{C}_{10}$ after 40h of milling has exhibited a complete amorphous phase transformation, according to the solid-state amorphization reaction requirement, the compositions with a higher carbon content

should have a complete amorphous phase transformation as well. The present evidence suggests that as the carbon content increases, the amorphous forming ability increases, exhibiting a higher degree of amorphization. Therefore, our conclusion is that a complete amorphous phase transformation has occurred in the compositions of 10 up 40 at.% C, after being milled for 40h.

Figure 4.39 shows the EDS spectra of the element analysis and TEM characterization for the mechanically alloyed powder of Co- 5 at.% C, milled for 40h. In this Figure, the EDS spectra of the element analysis emphasizes the presence of respective elements (Co and C) in the sample chemical composition, which confirms that the selected zone is related to the Co_{95}C_5 system, as seen in Figure 4.39a. Figure 4.39b shows a bright field micrograph for the areas that are selected for the SAED pattern analysis by focusing on the particle edges. In contrast, Figure 4.40 shows the typical corresponding SAED patterns of Co_{95}C_5 mechanically alloyed powder milled for 40h. However, according to the XRD and DSC results of the mechanically alloyed powder of Co_{95}C_5 , milled for 40h, the mechanically alloyed powder is composed of nanocrystals embedded in an amorphous matrix. In order to confirm these results and to obtain more accuracy in the experiments results, different areas were selected to conduct the SAED pattern analysis to identify the phase structure of Co_{95}C_5 powder milled for 40 h, as seen in Figure 4.39b. However, a typical example of the corresponding SAED pattern analysis for one of these areas is shown Figure 4.40a.

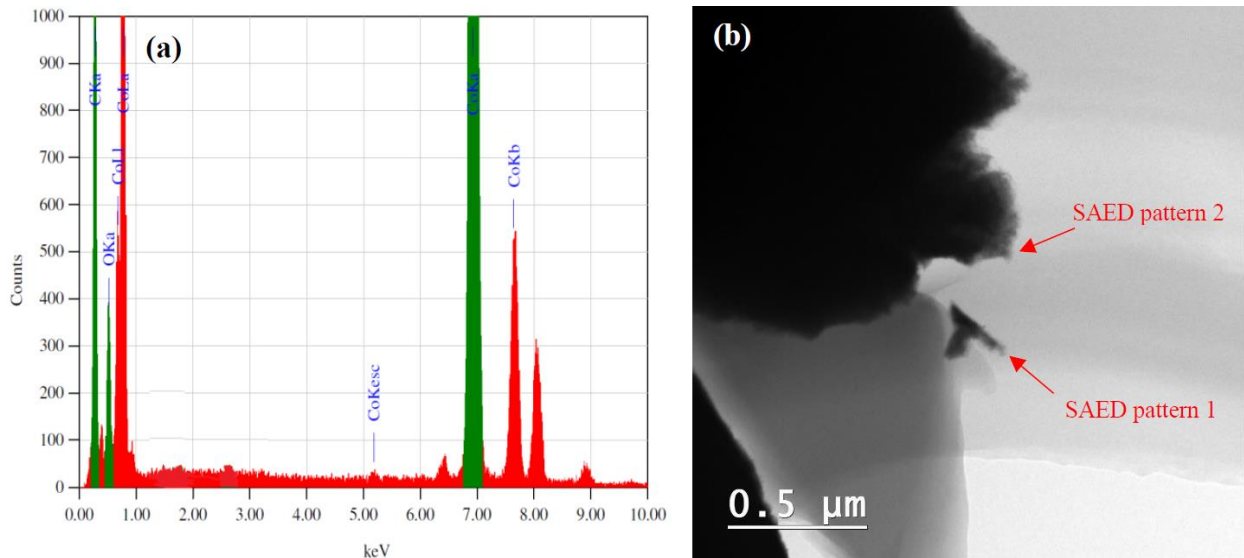


Figure 4.39: TEM characterization of mechanically alloyed powder of Co- 5 at.% C, milled for 40h: (a) EDS spectra of the element analysis, (b) bright filed micrograph shows the selected areas.

The SAED patterns analysis of this area depicts a halo, but no clear diffracted rings were found for either the cobalt or the carbon on the SAED patterns, suggesting that it may be a fully amorphous or a very high degree of the amorphous phase. On the other hand, Figure 4.40b offers another example of the corresponding SAED pattern analysis for another area, where it exhibits a halo as well as a diffracted spotty ring, suggesting that this region is composed of nanocrystals embedded in an amorphous matrix. Therefore, these results show that the amorphous phase produced is not fully amorphous and that it also contains nanocrystals, where these results correspond well with the DSC analysis, which also showed a mixture of nanocrystals and amorphous matter.

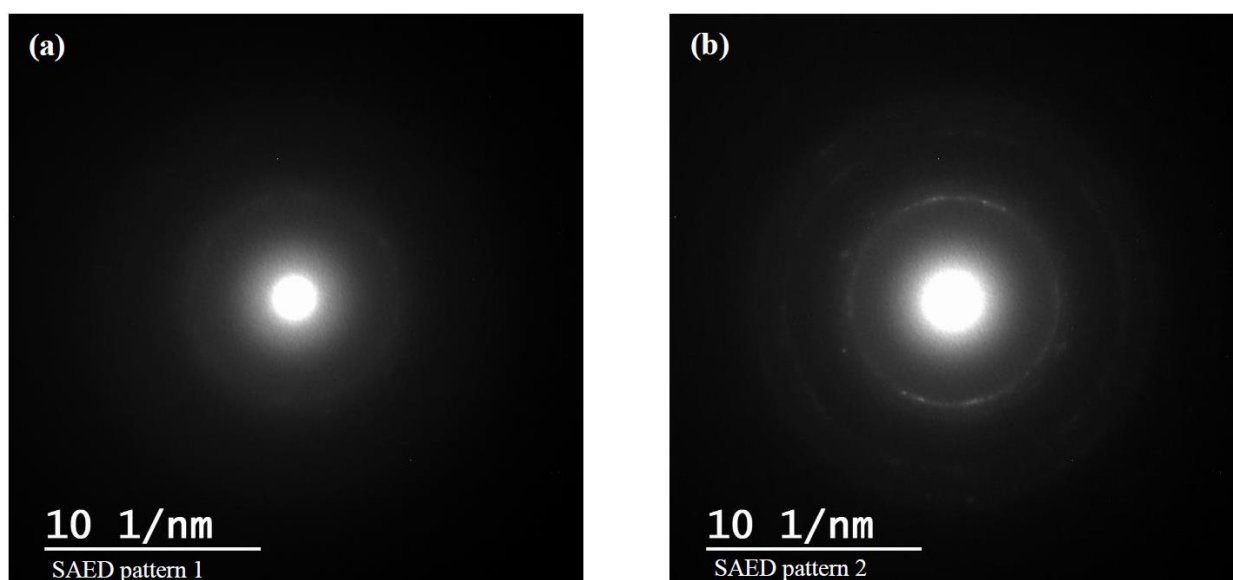


Figure 4.40: TEM characterization of mechanically alloyed powder of Co- 5 at.% C, milled for 40h: (a) SAED pattern 1, (b) SAED pattern 2. A halo from this analysis as well as diffracted spotty rings, indicates that this region is composed of nanocrystals embedded in an amorphous matrix.

Figure 4.41 shows the EDS spectra of the elements analysis and a typical bright field micrograph of the selected area of the mechanically alloyed powder of Co- 2 at.% C, milled for 40h. As can be seen from Figure 4.41a, the EDS spectra of the element analysis confirms the presence of the respective elements (Co and C) in the sample chemical composition, which proves that the selected zone is related to the Co_{98}C_2 system, whereas Figure 4.41b depicts the selected area for the EDS analysis as well as the SAED pattern analysis. As for the corresponding SAED patterns, Figure 4.42 demonstrates the SAED patterns of Co_{98}C_2 mechanically alloyed powder,

milled for 40h. As expected, it shows a composition of nanocrystals embedded in an amorphous matrix; however, a halo as well as a diffracted spotty ring can be seen in the corresponding SAED patterns, confirming the DSC results which also indicate that the amorphous phase produced is not fully amorphous and that it also contains nanocrystals. However, it exhibits a similar SAED patterns to the Co_{95}C_5 mechanically alloyed powder milled for 40h, as seen in Figure 4.40, in spite of the diffracted spotty rings being clearer here compared to those of Co_{95}C_5 , due to the higher carbon content of the former. Therefore, the present evidence suggests that as the carbon content decreases, the cobalt nanocrystals phase amount increases, exhibiting a higher nanocrystal phase. In other words, as the carbon content increases, the amount of the cobalt nanocrystal phase decreases, offering a higher degree of amorphization. From this result of the TEM characterization, it can be concluded that the amorphous phase did occur during milling; however, this mechanically alloyed powder of Co- 2 at.% C, milled for 40h, did not become fully amorphous.

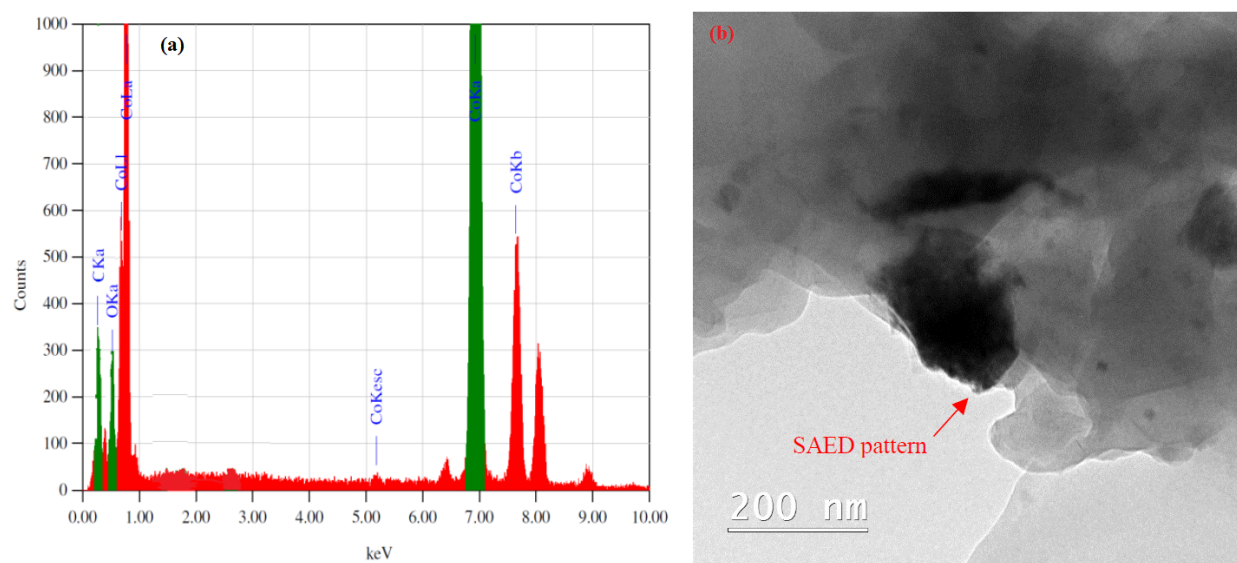


Figure 4.41: TEM characterization of mechanically alloyed powder of Co- 2 at.% C, milled for 40h: (a) EDS spectra of the elements analysis, (b) bright filed micrograph shows the selected area.

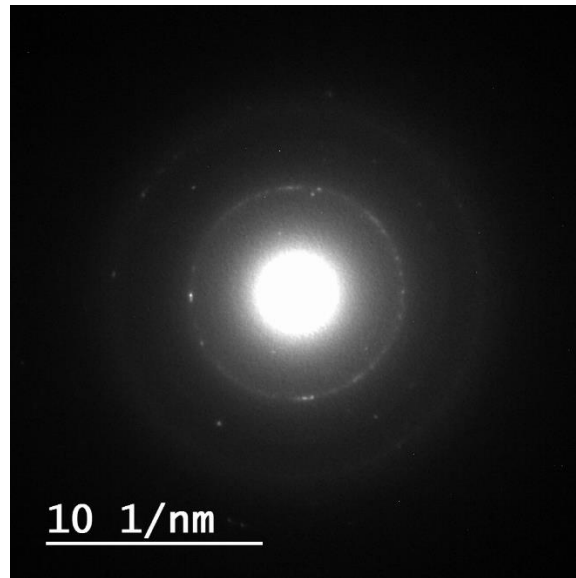


Figure 4.42: TEM characterization of mechanically alloyed powder of Co- 2 at.% C, milled for 40h, shows the SAED pattern. A halo as well as diffracted spotty rings, indicates that this region is composed of nanocrystals embedded in an amorphous matrix.

Thus, the TEM characterization and EDS analysis show that an amorphous phase forms in all the compositions of 2 to 40 at.% of carbon after milling for 40h, whereas the complete amorphous phase transformation can only be obtained where the concentration of carbon is approximately more than 10 at.%. Otherwise, in the compositions of less than 10 at.% of carbon, the nanocrystals phase will take place, and the structure of the sample will be as a composition of nanocrystals embedded in an amorphous matrix.

4.4 Discussion

It is clear from the above discussion that the crystallization reaction of the mechanically alloyed amorphous Co-C system is strongly dependent on the chemical composition and milling time. As was previously stated and as summarized in Figure 4.43, in the lower carbon compositions (≤ 20 at.% carbon), the crystallization reaction takes place in two-stages of crystallization: (1) by forming the metastable phase of cobalt carbides in the amorphous matrix; and (2) by decomposing this metastable phase into stable phases, as shown in Figure 4.43. On the other hand, the higher carbon compositions (≥ 20 at.% carbon) follow the one-stage of crystallization mechanism by precipitating very small crystalline cobalt phase particles in the carbon amorphous phase, as shown

in Figure 4.43. In fact, most crystallization reactions follow a kinetic pathway, which is inherently difficult to describe with theoretical models and, of course, to predict outcomes with any certainty.

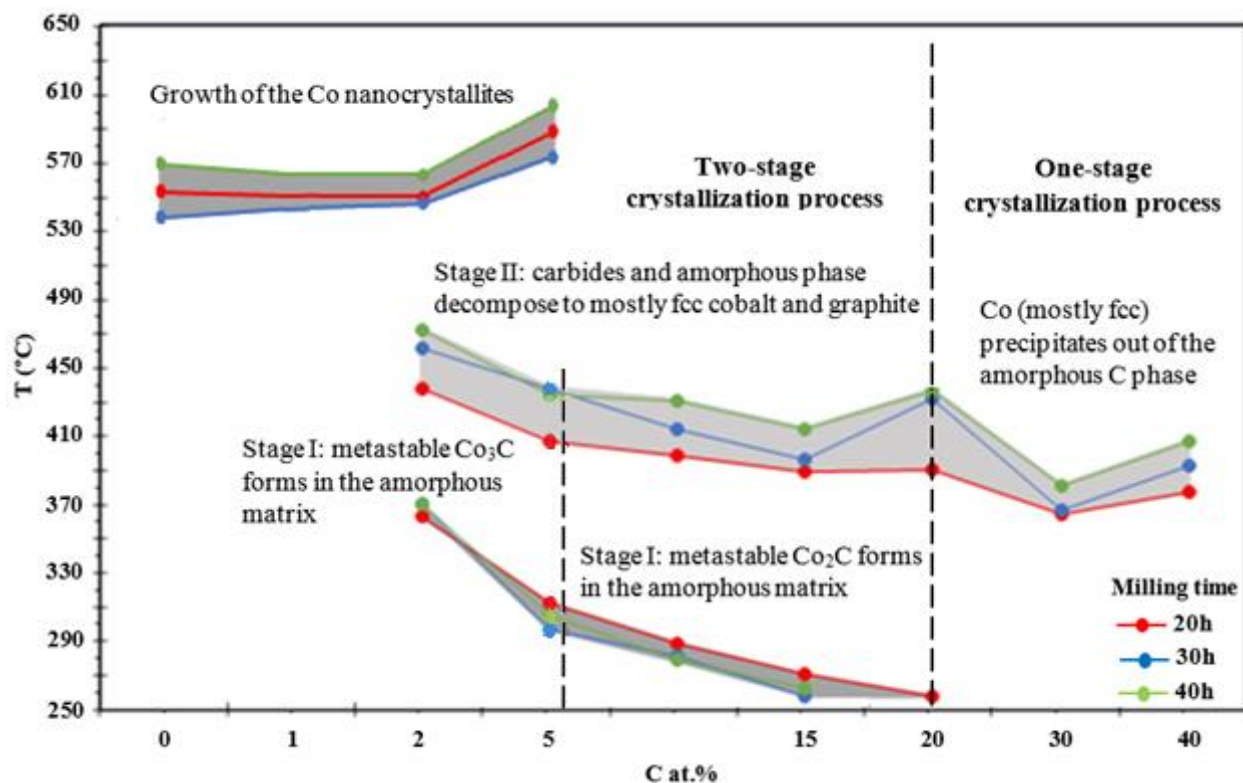


Figure 4.43: A temperature-composition map exhibiting how the crystallization of the milled powders depend on carbon composition. For concentrations of up to 15 at.% C (all milling times) and 20 at.% C (20-h milling), a low temperature partial reaction produces a metastable carbide (Co₃C or Co₂C) before the remaining amorphous phase and the carbide transform to crystalline cobalt (fcc) and graphite. For longer milling times for the 20 at.% C (30 and 40 h), and 30 at.% C and 40 at.% C alloys, only one reaction is observed and its products are Co (fcc) and amorphous carbon.

However, generally speaking, crystallization is a process of arranging atoms or molecules so as to form a rigid and well-defined crystalline network in order to minimize their energy state, following a specific mechanism imposed by the constraints of the system. Thus, the crystallization mechanism that the system is following provides the fastest reaction pathway for the system to reduce its excess free energy, by modifying the activation-energy barriers of nucleation, growth, and phase transformation. Thermodynamically, the least dense phase is formed first and is transformed to the next dense phase until, finally, the densest, and usually the most stable, phase

is formed, as seen in the lower carbon compositions (≤ 20 at.% carbon) cases in this work. But in some other cases, a compound or phase is formed directly even though it is thermodynamically unfavorable, such this crystallization mechanism, which we find in the higher carbon compositions (≥ 20 at.% carbon) cases, where there is a very small particle precipitate crystalline cobalt phase in the carbon amorphous phase. Indeed, this style of crystallization mechanism is essentially identical to that in the metal-mediated crystallization reactions such as Al-Si [77-79], Ag-Si [80 and 81], Ag-Ge [81 and 82], Al-Ge [83-89], etc. It is therefore deemed as an one-step crystallization reaction.

With respect to the amorphous phase crystallization processes, it is known that the transformation mechanism from the amorphous phase to its inherently more stable crystalline counterpart, generally requires a thermally assisted kinetic process involving nucleation and growth. However, in the metal-mediated crystallization process, the reaction mechanism adopts a different approach, where the reaction relies on a mechanism that involves the dissolution of the amorphous element in the metal crystalline phase, thereby supersaturating it with respect to the crystalline phase [1, 80-82]. In view of that, this precipitation inside the metal provides an atomic diffusion path from the amorphous phase to the crystalline phase, and by this mechanism the entire system can crystallize without forming metastable phases [1, 80-82]. However, our Co-C amorphous system at the higher carbon compositions (≥ 20 at.% carbon), has likewise followed the metal-mediated crystallization reaction because this mechanism has provided the fastest reaction path to the system to reduce its excess free energy [1], by precipitating very small crystalline cobalt phase particles in the carbon amorphous phase. Otherwise, in low carbon compositions, such as 20% or less, the most favorable crystallization mechanism and the fastest reaction path of the system to reduce its excess free energy is only through the formation of the metastable phase of Co_2C or Co_3C [1, 55, 90, 91], where the carbon atoms diffuse through cobalt atoms in the case of Co_2C , or nucleation and growth in case of Co_3C , instead of the metal-mediated crystallization of the metalloid crystalline phase, as discussed earlier. However, the metastable phase, Co_2C , forms and grows as long as the carbon atoms diffuse through the cobalt, and this diffusion can occur only if the number of the octahedral sites in the host cobalt lattice during the crystallization reaction is appropriate to accommodate the mobile carbon atoms. Therefore, through this mechanism, carbon atoms do not need a long-range diffusion process to form and grow a Co_2C phase, but it will take place by diffusing the carbon atoms through the cobalt. As has

been discussed earlier, the compatibility between the activation energy of the C diffusion in Co and the activation energy of the metastable Co_2C formation support this line of argument. On the other hand, the formation mechanism of the Co_3C is based on the nucleation and gradual growth of the Co_3C carbide nucleus on the cobalt crystal surface. Moreover, the DSC results of the low carbon compositions (≤ 20 at.% carbon) as shown in Figures 4.17, 4.20, 4.21, 4.23, and 4.27, confirm that the first exothermic peaks are the formation of the Co_2C or Co_3C metastable phase, whereas the appreciably larger second exothermic peaks are due to the decomposition of the Co_2C or Co_3C and the crystallization of the remaining cobalt amorphous.

4.5 Summary

Cobalt-carbon amorphous powder alloys with various cobalt and carbon concentrations were successfully synthesized using a mechanical alloying process. However, the Co-C powders with high carbon contents (≥ 10 at.% carbon), after milling for 40h, exhibited a complete amorphous phase transformation, while the low carbon compositions (≤ 5 at.% carbon) showed a composition of nanocrystals embedded in an amorphous matrix. The crystallization reaction of the mechanically alloyed amorphous Co-C system was shown to be strongly dependent on the chemical composition and milling time. However, in the low carbon compositions (≤ 20 at.% carbon), the crystallization reaction took place in two-stages. The first exothermic peak in the DSC traces corresponded to the formation of the metastable phase of cobalt carbides; therefore, it was considered as the first stage of the crystallization. On the other hand, the second stage of the crystallization was represented in the second exothermic peak, which corresponded to the decomposition of the metastable phase of the cobalt carbides, which crystallized the remaining amorphous cobalt. Consequently, the process ended up with the formation of fcc cobalt with a concomitant some of hcp phase and graphite. In contrast, the high carbon compositions (≥ 20 at.% carbon) followed the one-stage crystallization mechanism by precipitating very small crystalline particles of the fcc cobalt phase with some concomitant hcp phase, and amorphous carbon. Lastly, the formation of the metastable phases of cobalt carbides was shown to strongly depend on the amount of the carbon content. However, according to the cobalt carbide formation mechanism, at a very low cobalt content (≤ 5 at.% carbon), the metastable phase of cobalt carbide Co_3C would most likely form, whereas by increasing the cobalt content (> 5 to 20 at.% carbon), the metastable phase of Co_2C became most likely to form.

4.6 Acknowledgements

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5. Magnetic Properties of Amorphous Co-C Alloys Prepared by Mechanical Alloying

5.1 Introduction

In the past three decades, metallic amorphous alloys have received much attention in magnetic applications due to their useful magnetic properties for high performance electrical, electromagnetic and electromechanical devices, such as electromagnets, electric motors, generators, transformers, and magnetic storage such as tape recorders, hard disks and others [1-6]. Metallic amorphous alloys can be obtained by various methods and techniques, such as mechanical alloying, melt-spinning, thermal decomposition, sputtering and chemical reduction [7-15]. Compared to other methods and techniques, amorphization by mechanical alloying since 1983 has created widespread research interest, owing to its advantages compared with other methods. For example, its ability to produce a large amount of amorphous material with equiatomic compositions have made it an effective amorphous material producer. The mechanical alloying technique can produce a large amount of amorphous metal powders, which can be compacted and sintered in the desired sizes, shapes and dimensions for practical applications, using a rapid sintering technique such as spark plasma sintering (SPS) [16]. Meanwhile, this isn't the only advantage that is recommended for using the mechanical alloying to produce metallic amorphous alloys. Indeed, the metallic amorphous alloys that are produced by the mechanical alloying technique have wider composition ranges of the amorphous phases compared with the rapid solidification technique [17]. To give an illustration, the mechanical alloying technique generally produces amorphous phases around the equiatomic composition, while the rapid solidification technique is usually around deep eutectic compositions [18]. Therefore, the mechanical alloying amorphization is a solid state amorphization reaction, which is a technique capable of amorphizing materials below their crystallization temperature, using interdiffusion mechanisms. [7, 19 and 20]. Moreover, amorphization by mechanical alloying has a wider glass forming composition range in many binary alloy system; therefore equiatomic compositions are most favorable for amorphization by mechanical alloying [21, 22]. On the other hand, in the rapid quenching technique, amorphization is restricted to the compositions near the eutectic, due to kinetic restraints

[21]. This unique capability of mechanical alloying is reason for choosing mechanical alloying as a processing technique for this work.

Amongst the metallic amorphous alloys that are prepared by means of mechanical alloying are the Co-based amorphous alloys, which are of considerable interest because of their magnetic and mechanical properties. The Co-based amorphous alloys exhibit excellent soft magnetic properties such as low coercivity, high permeability and low hysteresis losses, and these soft magnetic properties result from their near zero magnetostriction and magnetocrystalline anisotropy [23- 26]. Consequently, mechanical alloying has been successfully utilized as a technique to produce Co-based amorphous powders of several binary, ternary, quaternary and multi component systems, and a proven effective technique to obtain Co-based amorphous powders [27, 28].

In many special applications, the requirements for low core losses come together with that of a multi-use magnetic behavior. Therefore, these requirements may be satisfied by the based-cobalt metallic amorphous alloys even though they have lower saturation flux densities than the iron-based alloys. Consequently, depending on the alloy composition, the cobalt-based metallic amorphous alloys are characterized as having soft magnetic properties because their magnetostriction is very small or almost zero. In view of this, at low frequency applications, the magnetic values of cobalt-based metallic amorphous alloys are comparable to or better than those of Permalloys. While at high frequency applications, the cobalt-based metallic amorphous alloys are superior to ferrites. These materials are therefore highly suited for high frequency applications [29]. However, the main drawback with the cobalt-based metallic amorphous alloys is the relatively high manufacturing cost resulting from their high cobalt contents and the restricted to small batches by the mechanically alloying method. So the choice remains a matter of economic optimality.

Indeed, cobalt-based metallic amorphous alloys exhibit exceptional performances with respect to high permeability, low coercivity, and negligible magnetostriction, but they suffer from a low polarization saturation. On the other hand, iron-based metallic amorphous alloys exhibit a higher saturation, but at the cost of permeability and coercivity. Therefore, the combination of higher saturation, higher permeability and lower coercivity facilitates good designing, such as the alloy composition and processing. For example, the addition of about 20% of cobalt to iron-based alloy can lead to a desirable combination of high saturation and permeability but low coercivity [30],

while the design of a nanocrystalline soft magnetic material from an amorphous alloy is an example of appropriate processing of a soft magnetic material [31-34].

This present work investigates the amorphous forming ability in a Co-C system at high Co contents, in order to improve the magnetic and mechanical properties by using the criterion described. Therefore, the detailed composition and processing can vary widely, which allows for the coverage of a large spectrum of soft magnetic properties according to the demands of the applications.

In this work reports on magnetic measurements results regarding to $\text{Co}_{100-x}\text{C}_x$ (2, 5, 10, 15, 20, 30 and 40 at.%) amorphous powders prepared by mechanical alloying. An investigative study of their magnetic properties has been performed in order to understand their magnetic characteristics. The interest for this alloy compositions is due to its desirable magnetostriction, permeability and power loss properties.

5.2 Experimental procedure

Elemental powders of cobalt (99.5% purity, 57 μm) supplied by Alfa Aesar and carbon powder (99.999% purity, 74 μm) supplied by Strem Chemicals Inc. were reduced under flowing pure hydrogen gas (20 mL/min) at 250°C for 2h, then formulated such that cobalt comprised 2, 5, 10, 15, 20, 30 and 40 at.% of the mixture under argon atmosphere. A tungsten carbide vial (5.7 cm x 6.35 cm with volume of ≈ 648.15 ml) was loaded and sealed in an argon-filled glove box with two 1/2" (12.7mm) diameter ultra-hard tungsten carbide balls and the powder mixture in a 2.5:1 charge ratio (i.e. ratio of grinding media mass to powder mass). Milling was carried out in a SPEX 8000M Mixer/Mill® operating at about 1,200 Hz for up to 40 hours.

X-ray diffraction of as-milled powder samples was performed using a PANalytical X'Pert Pro PW 3040 diffractometer. The thermal behavior of mechanically alloyed amorphous powders was determined by differential scanning calorimetry (DSC). The DSC measurements were performed under argon atmosphere and a heating rate of 10 °C/min by a Netzsch STA 449 C Jupiter TG-DSC. The as-milled powder samples were then examined by transmission electron microscopy (TEM) to validate the amorphous phase formation. TEM was performed on a JEOL 2100 TEM operating at 120 kV. As-milled powders samples were annealed in a Lindberg/Blue M tube furnace at 200°C for 2h under flowing pure hydrogen gas (20 mL/min), and the magnetic properties (saturation magnetization, coercivity, remanent magnetization and remanent-to-saturation ratio)

were measured at room temperature using a Princeton Measurements Corporation vibrating sample magnetometer (VSM Model 3900). Moreover, the particle size distribution of the mechanically alloyed powders was determined using a laser particle size analyzer (Horiba LA-960).

5.3 Results and Data Analysis

5.3.1 X-ray Diffraction Analysis

In Chapter 4, the X-ray diffraction patterns of the mechanically alloyed powders of 60 to 90 at.% Co showed that the amorphous phase was initially detected after about 20h of milling, as evidenced by the presence of a broad diffuse peak at the position of the (002 and 111) Co peak (Figures 4.1- 4.5). Therefore, this broad diffuse peak continued to expand and through the 40h of milling, suggesting that the amorphous phase produced was fully amorphous and quite stable, as seen and discussed in Chapter 4. However, during the early stages of milling (about 5h of milling), the X-ray diffraction patterns clearly showed evidence of creation of the atomic disorder in the milled Co-C powders, through the disappearing of the sharp peaks and appearing the broad diffuse peak (Figures 4.1- 4.5). Indeed, the amorphization has not yet occurred during this period of milling, but rather this is mainly the result of dissolution of carbon atoms into the cobalt which forms a supersaturated solid solution, as well as a grain refinement. While the cobalt-rich samples of mechanically alloyed powders of Co_{95}C_5 and Co_{98}C_2 also showed the broad diffuse peak in their X-ray diffraction patterns (Figures 4.7 and 4.8), but these were not considered to represent the perfectly amorphous phase. However, these broad diffuse peaks belonged to an amorphous phase and a nanocrystalline structure, as demonstrated by the DSC and TEM results in Chapter 4.

5.3.2 Thermal behavior and Differential Scanning Calorimetry (DSC) Analysis

The DSC traces of the powders mechanically alloyed for various milling times (Figures 4.10- 4.34) showed exothermic peaks after 20h of milling, suggesting that the amorphous phase was created during the milling. As seen and discussed in Chapter 4, the crystallization reaction of the mechanically alloyed amorphous powder of Co-C is strongly dependent on the chemical composition as well as the milling time. However, the crystallization reaction of the mechanically alloyed amorphous powders that have ≥ 20 at.% carbon has occurred in a one-stage mechanism, by precipitating very small crystalline cobalt phase particles in the amorphous carbon. While, at low carbon contents (≤ 20 at.% carbon), the crystallization reaction has happened in two-stages of crystallization: by (a) forming the metastable phase of cobalt carbides in the amorphous matrix

and (b) by decomposing this metastable phase and crystallizing the remaining cobalt amorphous. Moreover, the DSC results of the cobalt-rich samples of the mechanically alloyed powders of Co_{95}C_5 and Co_{98}C_2 have revealed the existence of some nanocrystalline structure in the mechanically alloyed powders of Co_{98}C_2 and Co_{95}C_5 , as evidenced by SAED pattern in the TEM results (Figures 4.40 and 4.42).

5.3.3 Transmission Electron Microscopy (TEM) Analysis

In Chapter 4, the TEM characterization of the mechanically alloyed powders for Co-C (Figures 4.35- 4.42) demonstrated that the amorphous phase was initiated in the compositions of 2 to 40 at.% C after 40h of milling. However, for a complete amorphous phase transformation to form the carbon concentration needed to be equal or more than 10 at.%. For compositions less than 10 at.% of carbon such as 2 and 5 at.% the amorphous phase was a partial phase transformation mixed with the nanocrystals phase. Therefore, the structure of milled powders consisted of nanocrystals cobalt embedded in an amorphous matrix.

5.3.4 Particle Size Analysis

Particle size analysis of the synthesized amorphous powders was also performed to evaluate the particle size distribution as a function of milling time and carbon content, using a Horiba laser light scattering particle size distribution analyzer. The mean particle size of the Co-C mechanically alloyed powders values are summarized in Table 5.1. Additionally, the mean particle size values are also plotted in Figure 5.1 as a function of milling time and as a function of carbon content in Figure 5.2. As shown in Table 5.1 and Figures 5.1 and 5.2 that the milling process reduces the mixed powder (Co-C) particle size about 5 times with the lower carbon content, while the particle size reduction with the higher carbon content is (10 to 12 times) higher. However, as it is known in the high energy ball milling process, the impacts between the balls and the powder that is trapped between them or with the vial walls induces a continuous deformation, fracturing, cold welding, and rewelding [13 and 16]; thus, this milling process causes massive deformation to the powder particles, leading to reduction in the particles size and work hardening [13 and 16]. As a consequence, the powder particle size will decrease dramatically, reaching a small value of a few micrometers only after a short period of milling and will continue to decrease with increasing milling time until the steady state particle size is achieved [16], as shown in Figures 5.1.

Table 5.1: The mean particle size of the Co- at.% C of the mechanically alloyed powders (μ).

Milling time (h)	The mean particle size of the Co- at.% C of the mechanically alloyed powders (μ)							
	Pure Co	2 at.% C	5 at.% C	10 at.% C	15 at.% C	20 at.% C	30 at.% C	40 at.% C
0	57							
5	14.86	12.68	32.98	9.49	6.91	7.99	6.36	5.44
20	23.33	48.30	30.94	9.46	6.33	5.00	5.02	3.36
30	24.82	51.34	39.72	8.74	5.90	4.60	3.88	3.31
40	37.71	80.07	16.17	10.26	7.02	4.73	3.68	3.45

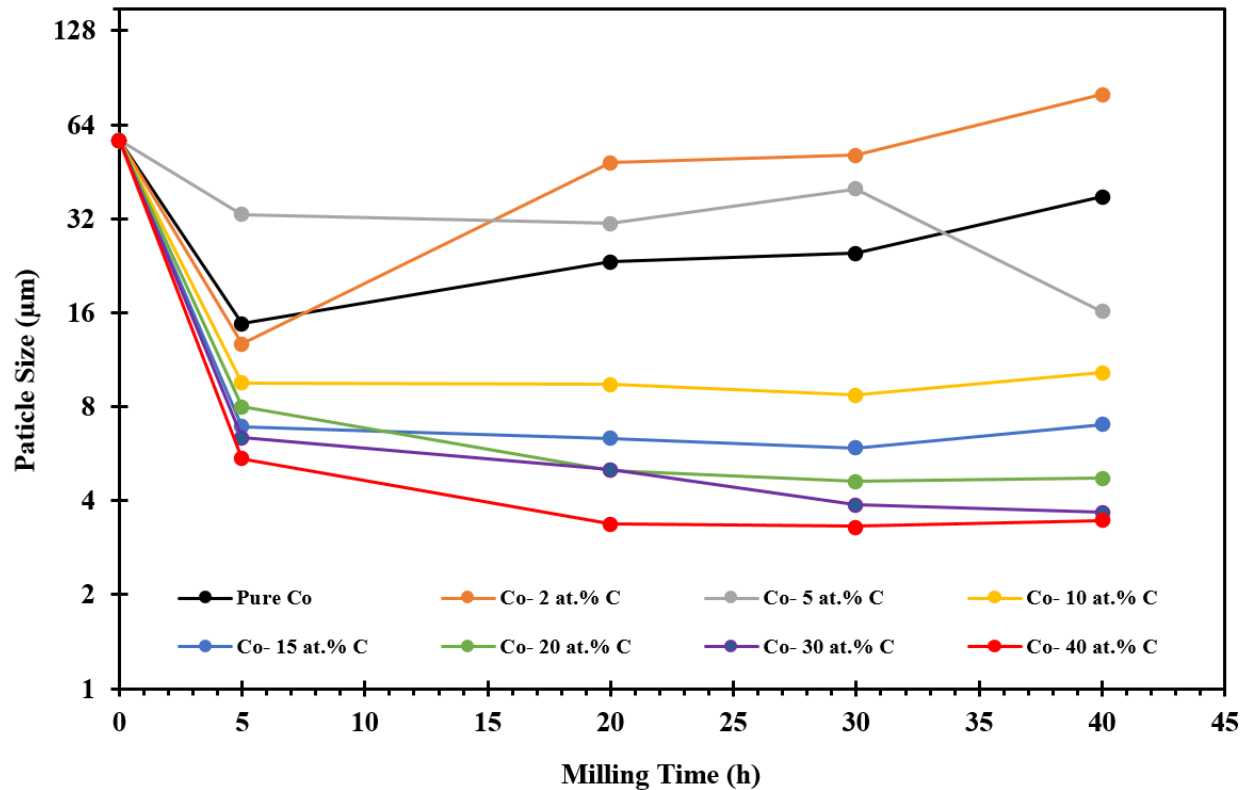


Figure 5.1: The effect of milling time on the particle size of the pure cobalt and Co-C mechanically alloyed powders for various carbon contents.

As shown in Figure 5.1, the particle size of Co-C powders decreased after 5h of milling. So the particle size reduction reached a steady state after 5h of milling. However, in the high carbon compositions (≥ 10 at.% C) of mechanically alloyed samples, the particle size decreased rapidly at the initial stage of the milling (5h), and remains steady (between 10 to 3 μm) to the end of 40h

milling. While in the pure and Co-rich (< 10 at.% C), the particle size initially decreased after the 5h of milling, and then as the milling times increased to 40h, the particle size increased because of particle agglomeration, reaching a steady state values, as seen in Figure 5.1. However, as the milling times increased, the powders deformation continuously is increased, resulting an increasing the surface free energy of the powders, thereby the powders would be re-agglomeration by cold welding to reduce this surface energy [16]. Over time, the steady state of the particle size is gradually achieved by obtaining a balance between the fracturing and cold welding of the particles, and eventually the particle size reached the steady state.

Taking into consideration the fact that a chemical composition of the powder has an impact on the particle size of the powder, thereby this relationship is shown in Figure 5.2. The particle size of the milled powder gradually decreases as the carbon content increase in the elemental composition. However, at lower carbon concentrations the particle size of the milled powders possesses a higher mean size compared with the higher carbon concentrations that continuously decrease with rising carbon content up to 40 at.%. The large particle size observed on the lower carbon concentrations could be due to the high ductility of the system [16]; consequently, in the presence of milling, an excessive cold welding will be occurring between the powder particles, which leads to the formation of larger particles, due to a re-agglomeration process [16], as shown in Figure 5.3. However, the morphologies of the 5 and 10 at.% C powder milled 40h are shown in Figure 5.3. As can be seen from Figure 5.3, the mechanically alloyed powders show an agglomerated particle contains smaller particles, confirming that the particles of the cobalt-rich powders increase in their size through agglomeration by excessive cold welding.

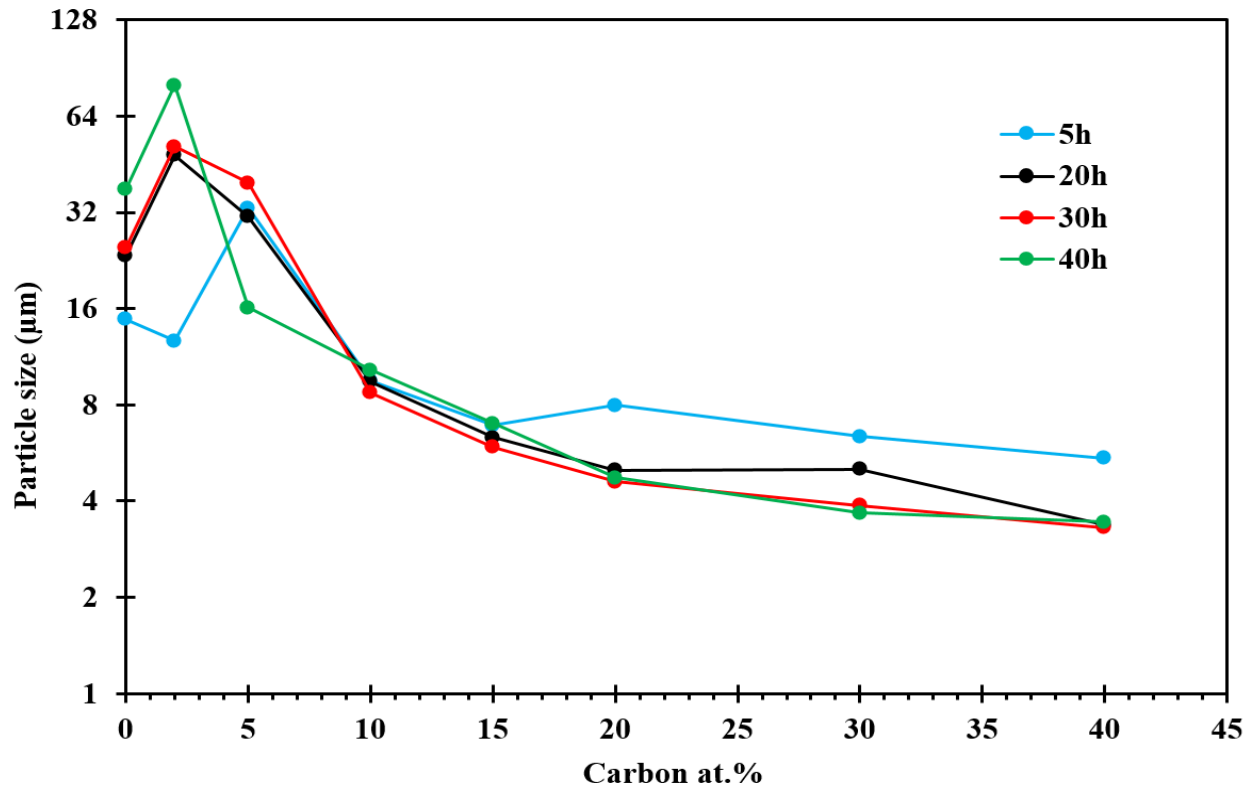


Figure 5.2: The effect of carbon content on the particle size of the pure cobalt and Co-C mechanically alloyed powders for various milling times.

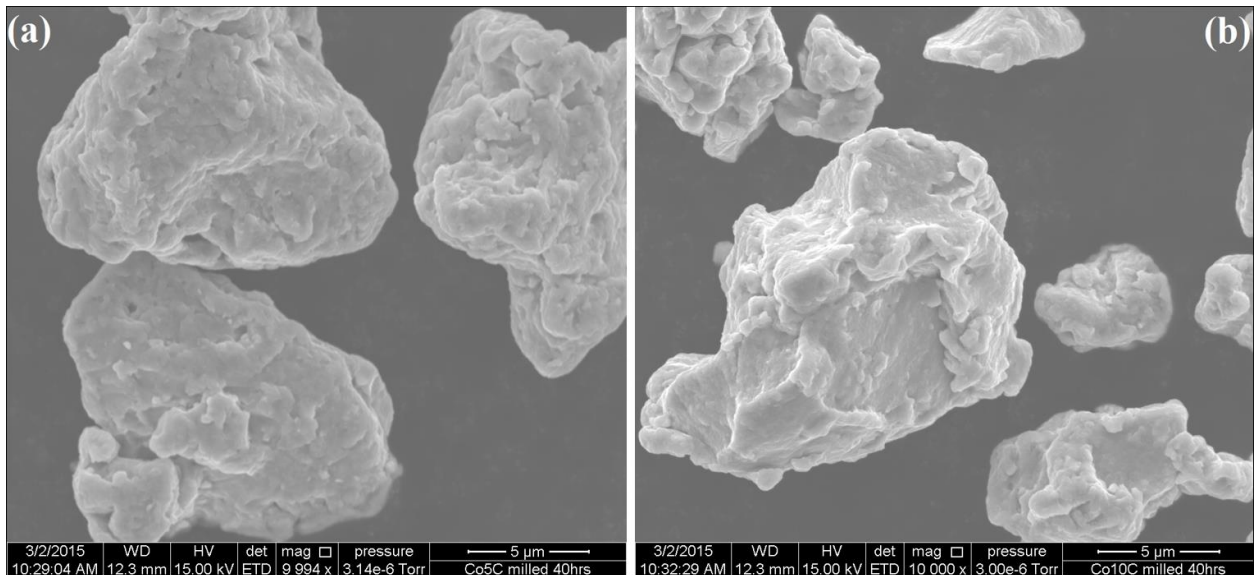
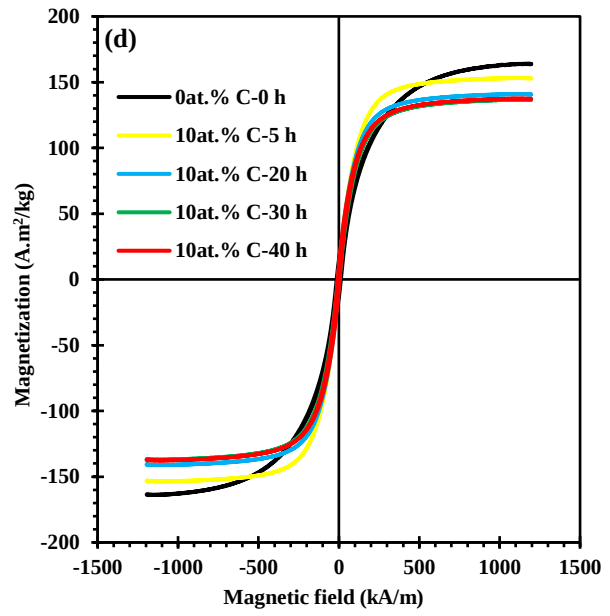
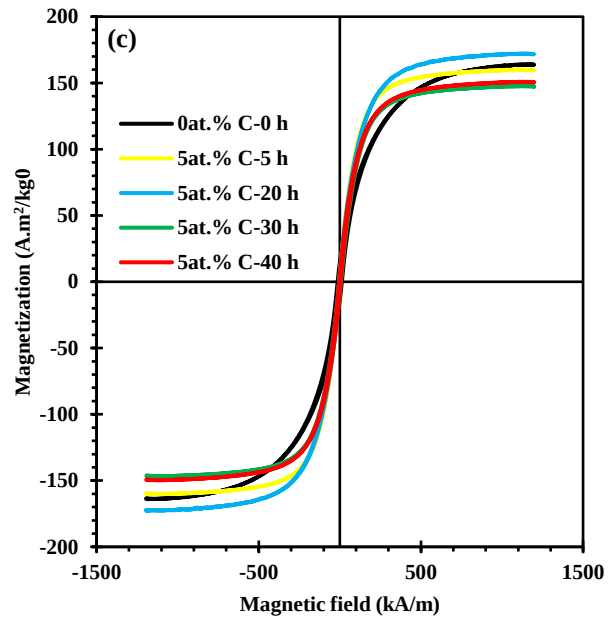
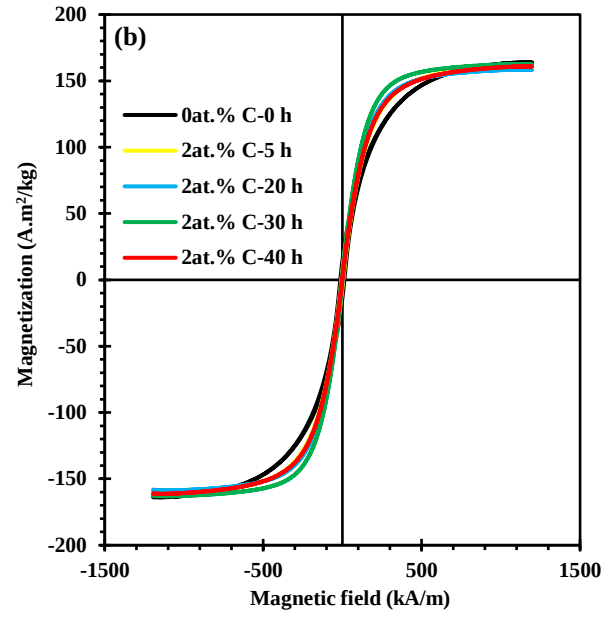
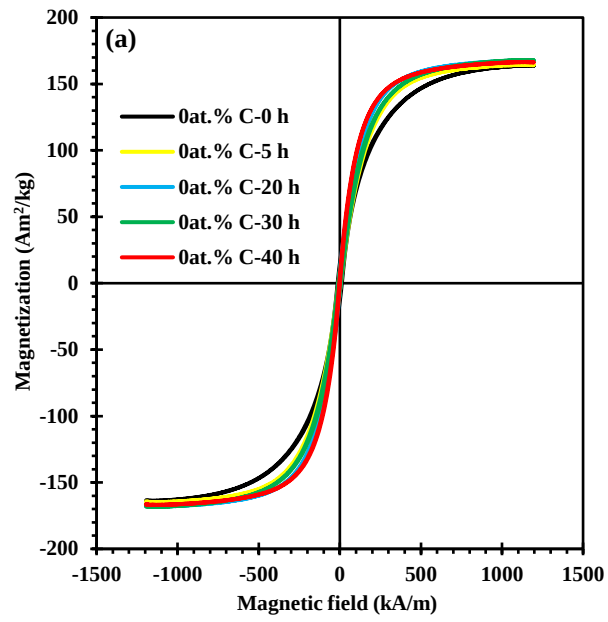


Figure 5.3: Morphology of the Co-C mechanically alloyed powder particles milled for 40h: (a) Co- 5 at.% C, (b) Co- 10 at.% C. The micrographs present typical individual agglomerated particles for the lower carbon concentrations.

On the other hand, the higher concentration of carbon (≥ 10 at.%) in the mechanically alloyed powders leads to a significant decrease in the mean particle size, as seen in Figures 5.2. However, this behavior was attributed to a reduction in the ductility of the system while increasing the concentration of the inherently brittle carbon, which in turn led to a decrease in the ductility of the system. Consequently, in this case, the presence of carbon acts as a process control agent (PCA) during the milling procedure, resulting in a reduction of the excessive cold welding and causing a balance between fracturing and cold welding of the particles. However, with continued milling, the cobalt and carbon powders continue deforming, fracturing and cold welding as well as hardening. Thus the tendency of the mechanically alloyed particles to fracture predominates over the cold welding as well as over the strong agglomerating forces, and the decline in the particle size becomes more predominant with increasing carbon content. Therefore, the decrease in the particle size that was observed with an increase in the carbon content in Figure 5.2, is an evidence of the above argument.

5.3.5 Magnetic Properties

Magnetic hysteresis loops of the pure cobalt and Co-C mechanically alloyed powders for various milling times after a prior anneal at 200°C for 2h under flowing hydrogen are shown in Figure 5.4. These hysteresis loops were measured at 300K, and they are typical of soft magnetic materials. The saturation magnetization, M_s , however decreases with increase of the carbon content as well as the milling time, as seen in Figure 5.4. It can be seen in Figure 5.5 that the M_s values decrease gradually in the Co-C mechanically alloyed powders with increasing the carbon content. The lower values of M_s are due to the presence of the non-magnetic carbon atoms that have been dissolved into the microstructure of the powders. The presence of the metalloid elements by > 20 at.% in the ferromagnetic alloys is generally known to reduce the magnetization of these ferromagnetic alloys [35-37], and this was corroborated in the present alloys by the results reported in Figure 5.5, which shows that the sharp decrease of magnetization occurred, when the carbon content reached to 20 at.%. Consequently, the presence of nonferromagnetic elements such as carbon in the chemical composition of the alloy reduces the ratio of cobalt atoms, and thus reduces the density of the magnetic atom interactions. As a result, the interchange interaction between the magnetic atoms is reduced and in the meanwhile the saturation magnetization decreases.



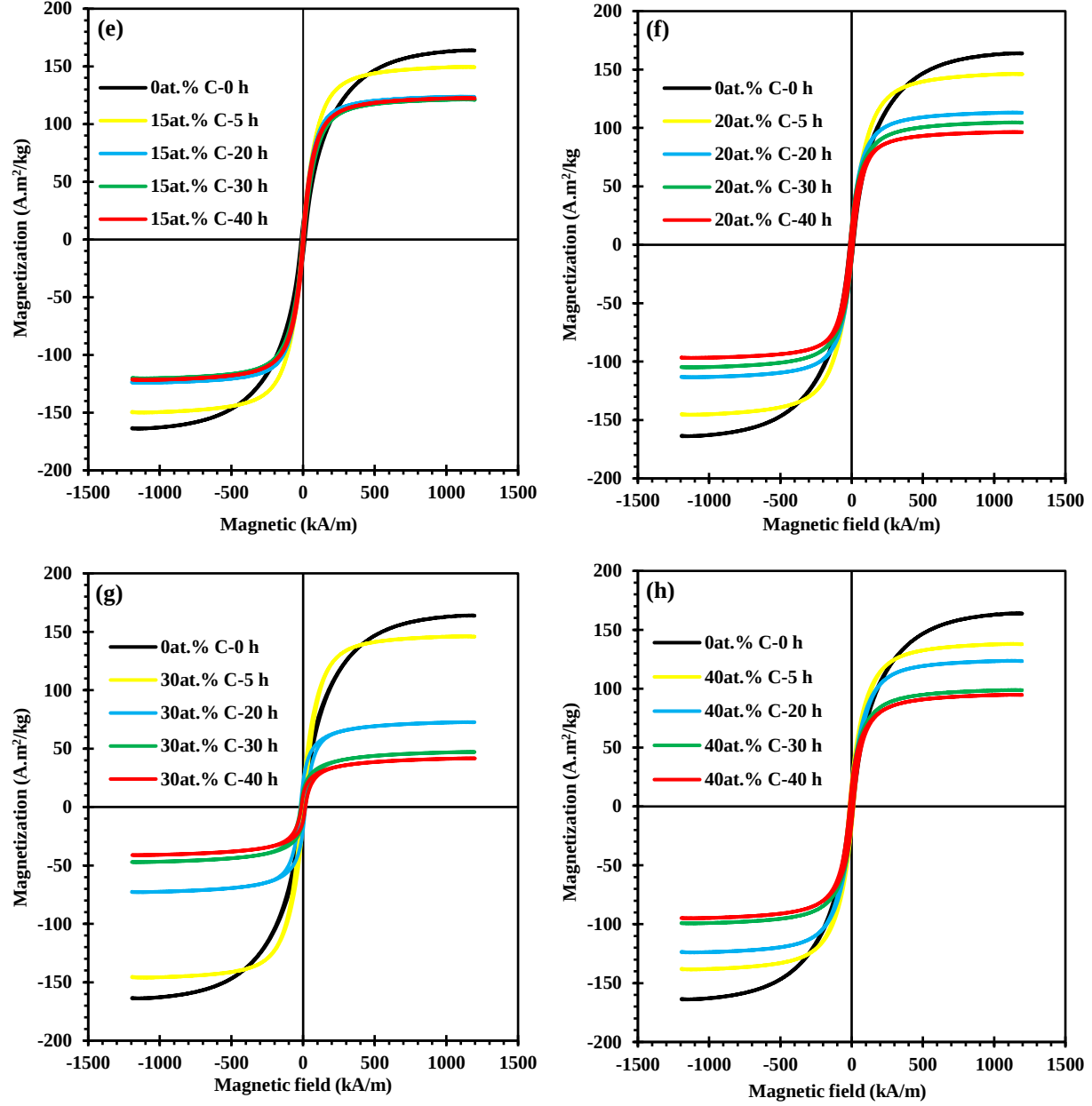


Figure 5.4: The hysteresis loops of the Co- at% C alloys milled up to 40h: (a) pure Co, (b) 2 at.%, (c) 5 at.%, (d) 10 at.%, (e) 15 at.%, (f) 20 at.%, (g) 30 at.% and (h) 40 at%.

According to Friedel's virtual-bound-state (**VBS**) model [38-40], the presence of the nonferromagnetic carbon in the present alloys introduces a strong perturbing and highly localized potential to the dipole moment. Therefore, when the perturbation due to alloying is strong enough, a bound state will be subtracted from the full d-band majority spin and moved to higher energies. When the **VBS** lies below the Fermi energy, the moment of the alloy will change slowly with

concentration. As the **VBS** moves above the Fermi level, however, a dramatic change in the magnetic moment is predicted to take place as electrons in the **VBS** empty into previously empty minority spin states. At this point for every additional solute atom added, a fivefold degenerate majority spin 3d **VBS** will empty into five unoccupied minority spin 3d states. This effect could suppress the magnetic moment of cobalt atoms through P-d hybridization [36, 39 and 41] and consequently decrease the M_s of the powders, as seen in Figure 5.5. In fact, in these current alloys, the strong p-d bonding between non-magnetic carbon and cobalt, greatly increases the **VBS** energy much higher than the Fermi energy and leads up to the transfer of an additional charge to the d-bands of magnetic atoms [36, 39 and 41]. In view of that, the 3p electrons of P or 2p electrons of carbon fill the d shell of cobalt through p-d hybridization and restrain the magnetic moment of cobalt, and consequently decrease the M_s [36, 39 and 41], as seen in Figure 5.5.

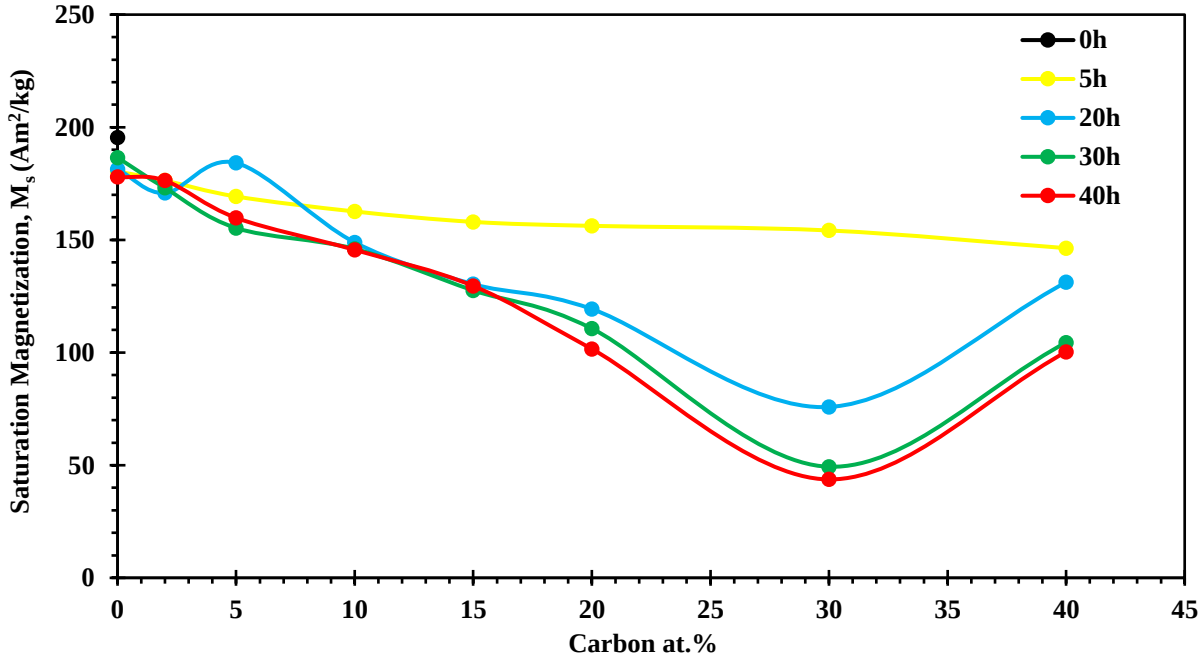


Figure 5.5: Plot of saturation magnetization, M_s , of Co-C mechanically alloyed powders for various milling times at room temperature against carbon content.

In addition to the aforementioned aspects of the negative effect on the saturation magnetization, the milling time also has a negative effect on the saturation magnetization, M_s . Figure 5.6 shows the evolution of the room temperature saturation magnetization, as a function of milling time. Overall, the total saturation magnetization of the pure cobalt and Co-C samples decreased

significantly at the end of 40h milling from the original un-milled state, from 195 Am²/kg for the un-milled pure cobalt to between 178 and 44 Am²/kg. A key observation was that the saturation magnetization decrease was steeper in the Co-C mechanically alloyed samples, getting bigger as the amount of carbon increased as shown in Figure 5.6. However, the magnetization decreased rapidly at the initial stage of mechanical alloying (5h of milling), and then reached a stable state value in the pure and rich-Co (<15 at.% C) mechanically alloyed samples to the end of 40h milling. While the high carbon content samples (≥15 at.% C) showed that the saturation magnetization decreased continuously as the milling times increased until around 30h of milling and then reaches a steady state value, as seen in Figure 5.6. Consequently, the decrease of the saturation magnetization indicates the introduction of large atomic disorder by the milling process to the alloys [42-45], where this disorder was clearly shown in the results of X-ray diffraction as disordered solid solution structure, as described in the previous chapter. Also these steady states in the saturation magnetization values are an evidence for the formation of a saturated solid solution in the mechanically alloyed samples. [46].

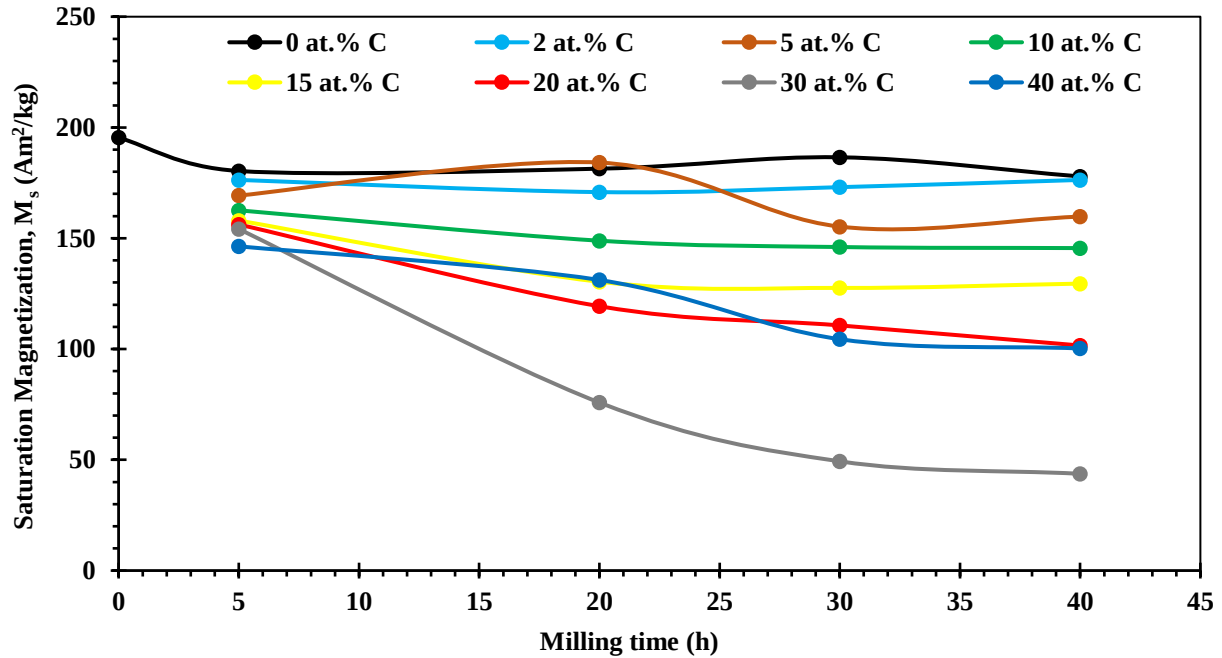


Figure 5.6: The effect of milling time on the saturation magnetization, M_s , of the pure cobalt and Co-C mechanically alloyed powders for various carbon contents at room temperature.

A key point to remember with respect to the mechanical alloying process, is that it results in a structural evolution on the milled alloy such as refinement of crystallite size and increases of the fraction of grain boundaries, amorphization, internal strain and the formation of defects; therefore this structural evolution will notably contribute to the saturation magnetization reduction [47-49] as seen in Figure 5.6. Consequently, the less dense structure of grain boundaries and amorphous phase increases the average inter-atomic distances between the neighboring atoms, weakens their exchange interaction, and consequently decreases the saturation magnetization [50, 51].

In these present alloys, the heavy plastic deformation of the cobalt powder particles which was followed by repeated fracturing and cold welding, leads to their particle size refinement and introduction of a high density of defects, particularly dislocations. However, such defects could cause a volume expansion [52-54], thus resulting in a change of the geometry of the atomic arrangement and the interatomic distances [52-54]; which results in a suppression of the exchange interaction between the magnetic (Co) atoms. In addition to the aforementioned aspects during the mechanical alloying, the exchange interaction among the Co atoms becomes weaker due to inter-diffusion of Co and C atoms, as discussed and illustrated earlier (Figure 5.5). Since the magnetization is induced by the domain wall movement and spin rotation, therefore these structural defects and the restrain in the exchange interaction between the magnetic atoms will contribute to the restrict of the domain wall movement and the spin rotation, which in turn can lead to lowering the saturation magnetization of the powders, seen in Figure 5.6.

In addition, the coercivity, H_C , which is another important magnetic parameter in determining the magnetic properties, extrapolated from the hysteresis loops, depended strongly on the carbon content and the milling times. Figure 5.7 shows the variations of the room temperature coercivity, H_C , of the pure cobalt and the Co-C mechanically alloyed powders for various milling times as a function of carbon content. It was noted that the coercivity rapidly decreased at the beginning when the carbon content was less than 15 at.% and then gradually increased as the amount of carbon increased. Overall, the coercivity decreased from the original un-milled state, from 12.7 kA/m for the un-milled pure cobalt to between 7.5 and 1.3 kA/m when the carbon content was between 0 and 15 at.%, and through this range, the reduction in coercivity was evident for all of the milling times. This reduction in the coercivity for Co-rich milled powders was related to the decrease in magnetocrystalline anisotropy, which was promoted by the reduction of the crystalline size, and

microstrain, which was promoted by the mechanical energy generated by the high-energy ball milling. The decrease in the coercivity with the increase in the milling time can be clearly observed through the Figures 5.7 and 5.8. Therefore, this behavior was attributed to the reduction in the magnetocrystalline anisotropy due to the diminution in crystallite size, which leads to an easier rotation of the domain walls [24, 55], reducing the directional dependence of a material's magnetic properties. In addition, according to Shokrollahi [56], a reduction in crystallite size promotes the averaging effect of magnetization over randomly oriented nano-size grains, which explains the reduction in the magnetocrystalline anisotropy.

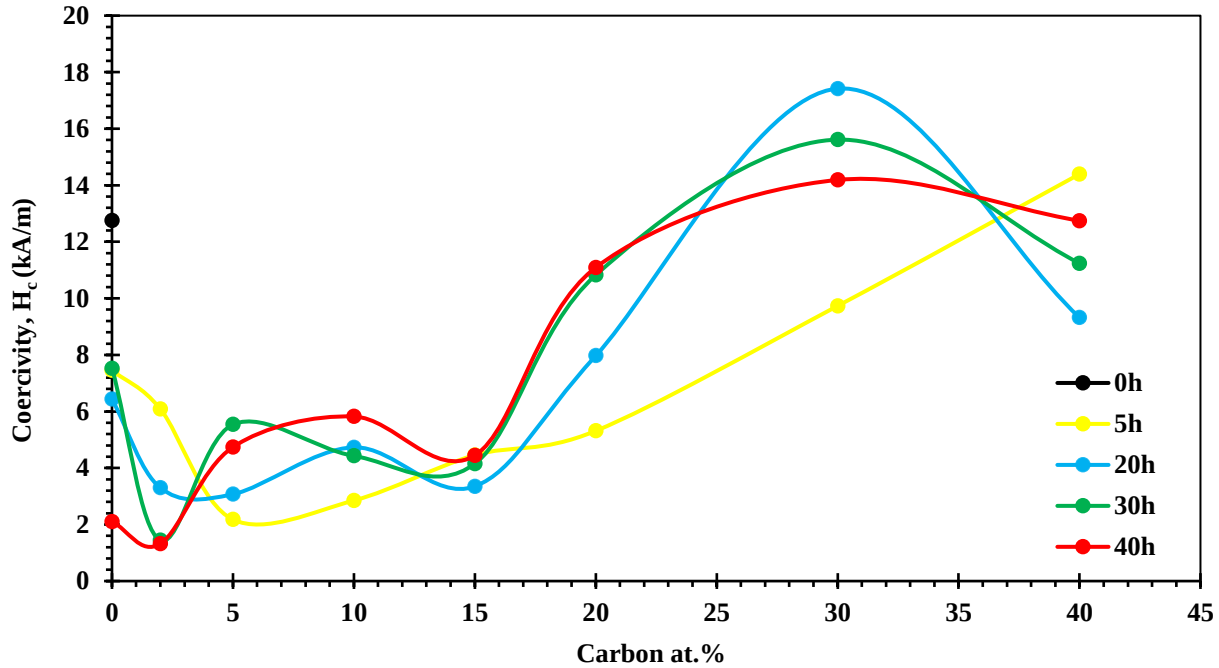


Figure 5.7: Variations of the room temperature coercivity, H_C , with carbon content for the pure cobalt and the Co-C mechanically alloyed powders for various milling times.

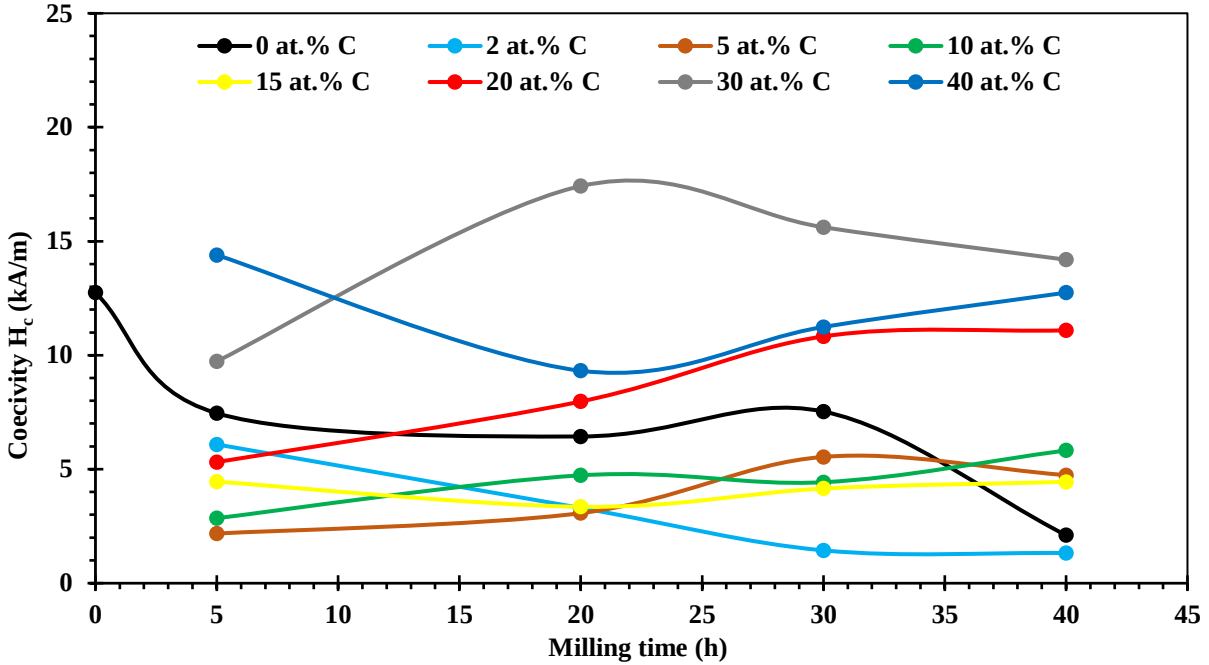


Figure 5.8: The effect of milling time on the coercivity, H_C , of the pure cobalt and Co-C mechanically alloyed powders for various carbon contents at room temperature.

On the other hand, the higher concentration of carbon in the mechanically alloyed powders lead to a significant increase in coercivity, as seen in Figures 5.7 and 5.8. However, it was considered that the atomic interactions in the amorphous structure may be between any magnetic-magnetic (Co-Co), magnetic-nonmagnetic (Co-C), or nonmagnetic-nonmagnetic (C-C) atoms, all of which were distributed randomly. A magnetic-magnetic (Co-Co) interaction would lead to a higher net magnetic moment compared to a magnetic-nonmagnetic interaction [57, 58], as seen in the Co-rich samples. Therefore, addition of nonmagnetic alloying elements (C) reduces the net dipole moment of an alloy [57], this behavior is attributed to the exchange interaction among the Co atoms becomes weaker due to inter-diffusion of Co and C atoms during mechanical alloying, as seen in the higher carbon content samples. Thus, the resulting structure would consist of isolated magnetic Co atoms surrounded by non-magnetic atoms (C) or weakly magnetic boundaries [59]. Such microstructural formations will increase the energy barrier for magnetic realignment of the domains and also with the absence enough net magnetic moment, the realignment of the domains will become somewhat more difficult and thereby increase the overall coercivity of the samples, making them magnetically hard. Therefore, the increase in the coercivity and the decrease in the saturation magnetization that was clearly observed with the increase in the carbon content, is an

evidence to confirm this argument. In conclusion, it must be pointed out that the values of the coercivity obtained in the current study were less than the values reported for the widely investigated mechanically alloyed and co-sputtered cobalt-based alloys. In fact, these present alloys exhibit a good soft magnetic property in comparison with other similar alloys such as cobalt-rich systems of Co-Zr, Co-Nb and Co-Ti (≈ 2 kA/m) [60], Co-M-Ti-B (M=Fe, Nb) (≈ 2.5 kA/m) [61], Co-C (≈ 16 kA/m), (≈ 32 kA/m), (≈ 30 kA/m), (≈ 64 kA/m), (≈ 37 kA/m) and (≈ 2.9 kA/m) [62-67], $\text{Co}_{40}\text{Fe}_{10}\text{Zr}_{10}\text{B}_{40}$ (≈ 21 kA/m) [68].

The remanent magnetization, M_r , is also affected by the evolution of the alloy microstructure. The effect of carbon content on the remanent magnetization, M_r , of the Co-C mechanically alloyed powders is shown in Figure 5.9. The remanent magnetization dropped from the original un-milled state, from $13.9 \text{ Am}^2/\text{kg}$ for the un-milled pure cobalt to between 8 and $1.3 \text{ Am}^2/\text{kg}$ when the carbon content was between 0 and 15 at.%, and through this range, the reduction in remanent magnetization was evident for all of the milling times. This reduction in the remanent magnetization values was attributed to the particle size refinement, which was promoted by the mechanical energy generated by the high-energy ball milling. In view of that the decrease in the remanent with the increase in the milling time can be clearly observed through the Figures 5.9 and 5.10. In contrast, by increasing the carbon content more than 15 at.%, the remanent increases significantly at a faster rate, as seen in Figure 5.9. Therefore, this behavior was attributed to the exchange interaction among the Co atoms becoming weaker due to inter-diffusion of Co and C atoms during mechanical alloying. Thus, the resulting structure consisted of isolated magnetic Co atoms surrounded by non-magnetic atoms (C) or weakly magnetic boundaries [59]. Such microstructural formations will increase the energy barrier for magnetic realignment of the domains and also with the absence enough net magnetic moment, the realignment of the domains will become somewhat more difficult and thereby increase the overall coercivity of the samples, making them magnetically hard.

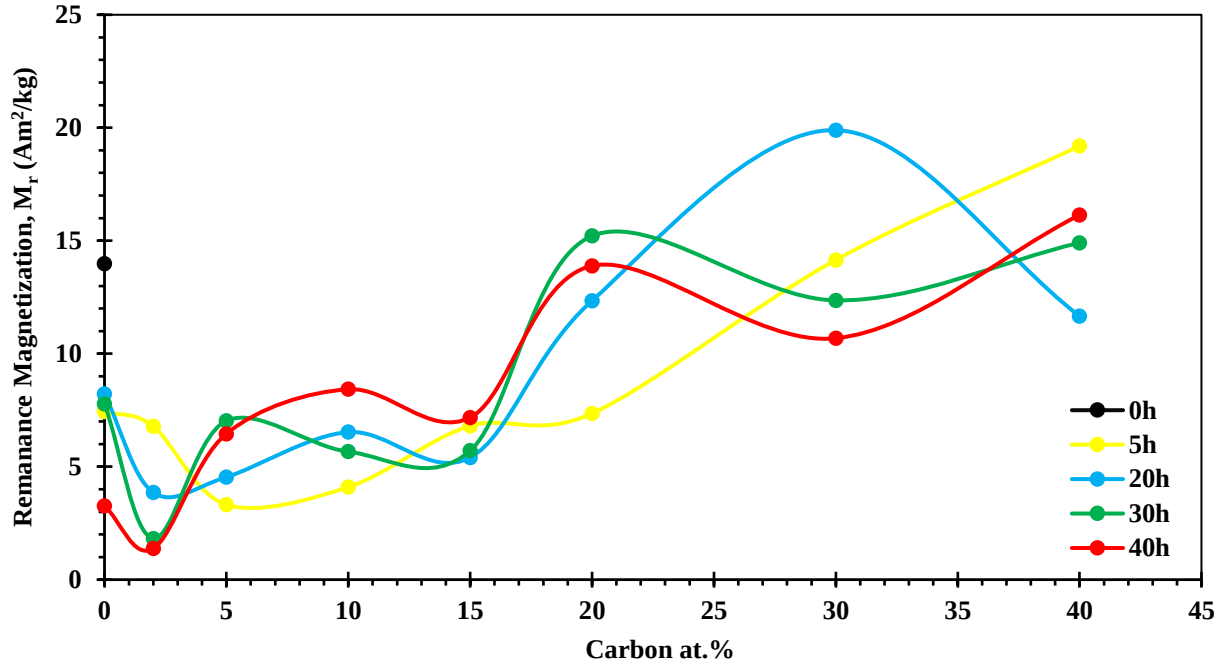


Figure 5.9: Variations of the room temperature remanent magnetization, M_r , with carbon content for the pure cobalt and the Co-C mechanically alloyed powders for various milling times.

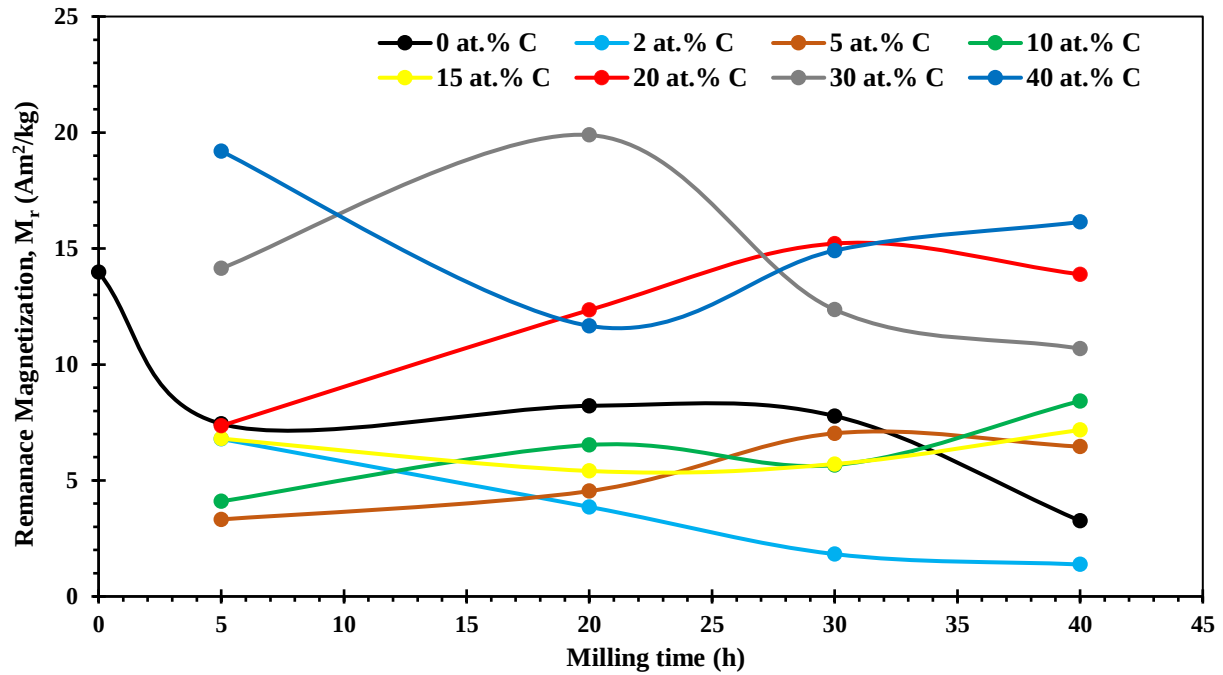


Figure 5.10: The effect of milling time on the remanent magnetization, M_r , of the pure cobalt and Co-C mechanically alloyed powders for various carbon contents at room temperature.

Figure 5.11 shows the effect of carbon content on the remanent-to-saturation ratio, M_r/M_s , which is an important magnetic parameter in determining the magnetic energy. Overall, the trend of the remanent-to-saturation ratio with carbon content was very similar to that observed for the coercivity (Figure 5.7). As inferred from Figure 5.11, the remanent-to-saturation ratio values dropped from the original un-milled state, from 0.07 for the un-milled pure cobalt to between 0.0078 and 0.05 when the carbon content was between 0 and 15 at.%, and through this range, the reduction in remanent-to-saturation ratio was evident in all of the milling times as shown in Figure 5.12. Such lower values of remanent-to-saturation ratio indicated that the small magnetic particles were typically single domain [69-71] and this was corroborated by the results of coercivity, as seen earlier in Figure 5.7.

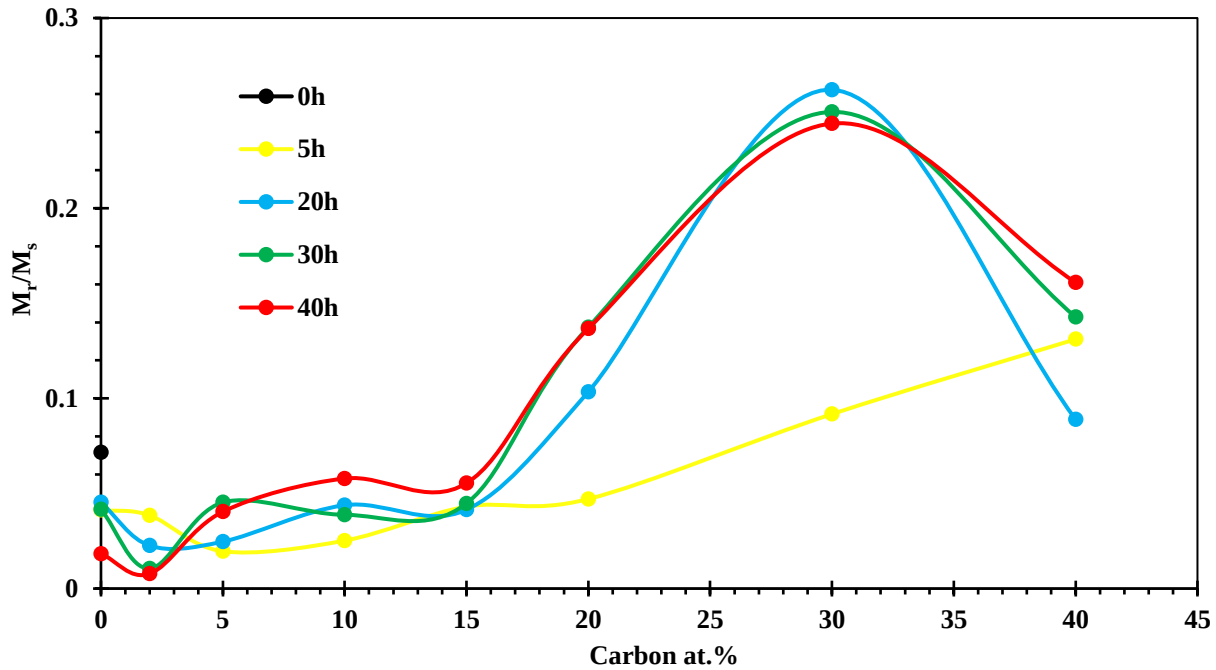


Figure 5.11: The effect of carbon content on the remanent-to-saturation ratio, M_r/M_s .

On the other hand, the higher concentration of carbon (≥ 20 at.%) leads to a significant increase in remanent-to-saturation ratio, as seen in Figures 5.11 and 5.12. However, this behavior was attributed to the exchange interaction among the Co atoms becoming weaker due to inter-diffusion of Co and C atoms during mechanical alloying. Consequently, the resulting structure consisted of isolated magnetic Co atoms surrounded by non-magnetic atoms (C) or weakly magnetic boundaries [59] as explained earlier. Therefore, such microstructural formations would increase

the energy barrier for magnetic realignment of the domains and also with the absence of enough net magnetic moment, the realignment of the domains becomes somewhat more difficult and thereby increase the overall coercivity of the samples, making them magnetically hard.

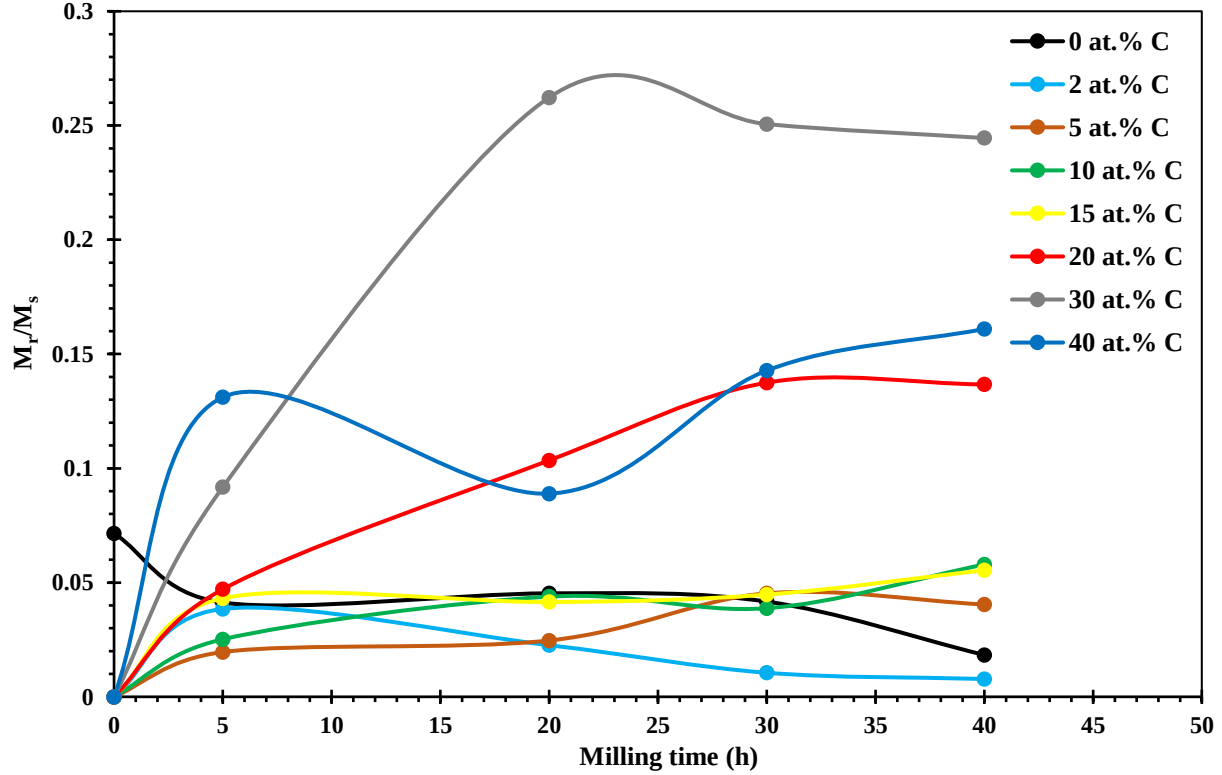


Figure 5.12: The remanent-to-saturation ratio M_r/M_s , as a function of milling time.

5.4 Summary

The magnetic properties of $\text{Co}_{100-x}\text{C}_x$ (2, 5, 10, 15, 20, 30 and 40 at.%) amorphous powders prepared by the mechanical alloying were studied. These mechanically alloyed powders of Co-C were carried out in a SPEX 8000M Mixer/Mill® operating as a function of carbon contents and milling time periods under different milling conditions over a wide range of compositions. The saturation magnetization decreases with increase the carbon content as well the milling time. However, the saturation magnetization of the milled powders decreases significantly at the end of 40h milling from the original un-milled state, from 195 Am^2/kg for the un-milled pure cobalt to between 178 and 44 Am^2/kg . Based on the VBS model, the suppression of magnetization during milling can be ascribed to the incorporation of non-magnetic carbon as well as to grain refinement and amorphization. The coercivity of the milled powders strongly depend on the carbon content

and the milling times. However, the milled powders exhibit a reduction in the coercivity values from the original un-milled state, from 12.7 kA/m for the un-milled pure cobalt to between 7.5 and 1.3 kA/m when the carbon content is less than 15 at.%, and then gradually increases as the amount of carbon increases. The evolution of the coercivity can be illustrated based on different parameters, such as residual stresses, grain refinement, amorphous phase formation, surface anisotropy and particles surface irregularities. Overall, the remanent-to-saturation ratio Co-C mechanically alloyed powders exhibits very small values, especially the low carbon compositions, where these low values are related to the demagnetization effects as well as to the presence of fine, single-domain particles. Although similar correlation between structure and magnetic properties has been observed in powders of all alloy compositions, the structural and magnetic parameters have been found to be strongly dependent on the composition of the alloys.

5.5 Acknowledgements

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6. Processing and Properties of Amorphous Co-C Reinforced Co Matrix Composite

6.1 Introduction

Metal matrix composites (MMCs) comprise a relatively wide range of materials defined by the metal matrix, reinforcement type, and reinforcement geometry. In the area of the matrix, most metallic systems have been explored for use in metal matrix composites, including Al, Be, Mg, Ti, Fe, Ni, Co, and Ag. From a reinforcement perspective, the materials used are typically ceramics since they provide a very desirable combination of stiffness, strength, and relatively low density. Candidate reinforcement materials include SiC, Al₂O₃, B₄C, TiC, TiB₂, graphite, and a number of other ceramics.

The morphology of the reinforcement material is another variable of importance in metal matrix composites. The three major classes of reinforcement morphology are continuous fiber, chopped fiber or whisker, and particulate. Typically selection of the reinforcement morphology is determined by the desired property/cost combination. Generally, continuous fiber reinforced MMCs provide the highest properties in the direction of the fiber orientation but are the most expensive. Chopped fiber and whisker reinforced materials can produce significant property improvements in the plane or direction of their orientation, at somewhat lower cost. Particulates provide a comparatively more moderate but isotropic increase in properties and are typically available at the lowest cost.

By adding to the three variables of metallic matrix, reinforcement material, and reinforcement morphology, the further options of reinforcement volume fraction, orientation, and matrix alloy composition, it is apparent that there is a very wide range of available material combinations and resultant properties.

This arrangement of the metal matrix composite variables could give a good combination of mechanical properties, however, there are problems with this close mixing of radically different materials (metallic matrix and reinforcement material). Moreover, the common problem with MMCs is the difficulty in creating a strong matrix/reinforcement interface without suffering extensive dissolution, debonding, or chemical reactions [1-3]. A possible solution to these

problems could be a crystalline metal reinforced by the amorphous phase of the same metal, thus both of them (metallic matrix and reinforcement material) will have similar chemical and physical properties. In other words, a metal matrix reinforced by an amorphous phase of the matrix; and as proposed in this work, Co-C amorphous particles were used to enhance the cobalt matrix, which should have a chemical similarity to the crystalline cobalt matrix.

In detail, the strengthening and structural units in the composites in general and, in particular, the particulate reinforced composite is due to the effective bonding at the interface of the matrix and reinforcement, which is either a mechanical bonding or chemical bonding [4]. From the scientific and the practical points of view, the expression “bonding at the interface in composite materials” refers to a bounding surface between the reinforcement and the matrix which is an interfacial region with a finite thickness [4]. However, the interface is the zone where the different materials (reinforcement and matrix) in a composite coincide, and, due to the differences in the chemical and physical properties such as the crystal structure, atomic registry, elastic modulus, density, coefficient of thermal expansion and thermodynamic properties (including chemical potential), the interface between the reinforcements and matrices in the composites is a very important and critical region [4, 5].

Therefore, the compatibility in the chemical and physical properties in the reinforcements and matrices help to create a strong interface bonding. In order to create a successful applicable composite, it must form an interface that is strong and favorable towards maximum compatibility between the reinforcement and the matrix. In view of that, and specifically in the particulate reinforced composites, the interface has a very significant effect on the strengthening, stiffening and toughness [6]. However, due to the difference of the properties of the composite phase components as mentioned earlier, the interface or interphase between the particles and matrices, a complex stress state appears during the loading. In view of that, a crack blunting effect and a significant drop in fracture ductility mostly occur during the weak bonding between the ductile matrix and the hard particles, where this bond is not adequate to execute the reinforcement in this composite system [7]. Therefore, in this case, a good bonding between the particles and matrices is very important in the reinforcement of the composites in terms of yield strength but not fracture strength, ductility, or strain hardening exponents at large strains [8].

Thus, the interface between the reinforcement and matrix in metal matrix particulate reinforced composites plays a crucial role in the properties of the composite, especially in its mechanical properties. As has been stated above, it is clear that a weak reinforcement/matrix interface will lead to a failure of the composite material under use. Therefore, the interfacial failure in the composite is one of the most important issues in composite materials and a great deal of attention should be paid to it, especially when it leads to a structural fracture in the composite. Therefore, a good interface is imperative for composite materials to perform well in their desired applications and survive under the stresses and other different circumstances.

In addition to the importance of the mechanical properties of metallic matrix composites, the magnetic properties of metallic matrix composites made up of magnetic materials are also very important properties and are of great interest. Therefore, these magnetic metallic matrix composites are used in many different applications of the electronic devices and biotechnologies fields, such as microwave devices, permanent magnets, high-density magnetic, recording media, storage devices, transformers, magnetic resonance imaging contrast, biomedical applications, and multilayer chip inductor [9-17]. However, the composite materials of magnetically two-phase (hard and soft) are excellent candidates for high performance permanent magnets [18-24]. In fact, magnetic properties of the two-phase permanent magnet composite materials depend on the microstructural features of the composite, such as the hard and soft magnetic phase distribution, grain size, particle shape, and grain boundary type. In composite materials with permanent magnets, the soft magnetic grains are bound to provide a high magnetization, while the hard magnetic grains are bound to create a large coercivity on the condition that these grains are of small sizes, uniform grain structure and strong exchange coupled [23-26]. However, this precondition for a small size and uniform grain structure for both hard and soft phases is in order to enable exchange interactions across the interfaces between the two phases to be effective [25 and 26]. In other words, when the two grains (hard and soft) are in direct contact with each other, the magnetic moments at the interface of these two grains create exchange coupling interactions between these two grains. However, with the presence of this interaction, the spontaneous magnetization may have to deviate from its easy axis. Thus, the resulting magnetization may increase in the direction of the applied field, which in turn enhances the remanent magnetization. Moreover, the effect of the exchange coupling interaction can be further enhanced by reducing the grain size. Therefore, when the average of the grain size decreases to the nanoscale size, the

magnetic properties of this material will change dramatically. So due to these exchange coupling interactions between the soft and hard grains, the product of nanocomposite magnet can acquire the magnetic behavior of both the soft and hard phases. However, could have both the high coercivity of the hard phase and the high saturation magnetization of the soft phase simultaneously, and thus have a high energy product [26]. Therefore, the characteristics of the high magnetization and large coercivity in the two-phase permanent magnet composite materials lead to remanent enhancement which are expected to improve the maximum energy product of permanent magnets dramatically [27 and 28].

Accordingly, a cobalt matrix and cobalt amorphous particles reinforcement have been used here to better understand the behavior of metallic particles enhancing metal matrices created by using the mechanical alloying (MA) method. An analysis of the composite materials with cobalt/cobalt amorphous particles processed by MA will be discussed in this chapter.

This work reports on the microstructure and mechanical and magnetic properties analysis regarding to $\text{Co}_{100-X}(\text{Co}/\text{Co}_{60}\text{C}_{40})_X$ ($X = 1, 2, 5, 10$ and 20 vol.%) after being attritor milled for 2 hour then compacted (SPS) at 300 MPa for 10 minutes at 350°C. An investigative study of their microstructural features, mechanical and magnetic properties have been performed in order to understand their mechanical and magnetic characteristics.

6.2. Experimental procedure

Cobalt powder -400 mesh (99.5%, 57 μm) supplied by Alfa Aesar served as the matrix for the composites with a density of 8.90 g/cc. The cobalt amorphous reinforcement powder ($\text{Co}_{60}\text{C}_{40}$ milled for 40h) was measured to have a density of 6.993 g/cc using a helium Micromeritics Accupyc 1330 Pycnometer. The two powders were blended to form composites with up to 20 volume percent reinforcement as shown in Table 6.1. A Union Process Szegvari Attritor with a vertical stainless steel milling tank (Figure 3.4) was used to blend the reinforcement and matrix powders with a total mass of 25g per run and ball mass of 500g with powder ratio of 20:1. Stainless steel balls (Winsted Precision Ball Company 440C) size of 1/4" (6.35mm) were used for this study. The agitator's rotational speed was set at 300 rpm, and the duration time was 2h. The mixing can was cooled with a water jacket so as to avoid crystallization of the amorphous phase and was filled with argon flowing at 10-50 ft^3/h to minimize oxidation.

The consolidation process of the composite powders (Co/Co₆₀C₄₀) performed by spark plasma sintering (SPS) was subcontracted to California Nanotechnologies, Inc. in Cerritos, California. Approximately 3.5 grams of each composite powder were compacted (SPS) into a disk 1/2" (12.7mm) in diameter and 0.140" (3.56mm) in thickness. The pressure and temperature of the SPS was set at 300 MPa and 350°C for 10 minutes with heating rate of 50°C/min.

Table 6.1: Five composite blends with differing reinforcement volumes.

Reinforcement (vol.%)	Matrix (vol.%)	Reinforcement (wt.%)	Matrix (wt.%)	Reinforcement Weight (g)	Matrix Weight (g)
0	100	0.00	100.00	0.000	25.000
1	99	0.25	99.75	0.197	24.803
2	98	0.50	99.50	0.394	24.606
5	95	1.25	98.75	1.001	23.999
10	90	2.50	97.50	2.008	22.992
20	80	5	95	4.120	20.880

X-ray diffraction was performed on the Co/Co₆₀C₄₀ composites of 1, 2, 5, 10, and 20 vol.% amorphous reinforcement (Co₆₀C₄₀) before and after consolidation, using a PANalytical X'Pert Pro PW 3040 diffractometer. The thermal behavior of mechanically alloyed Co₆₀C₄₀ amorphous powder also was determined by differential scanning calorimetry (DSC). The DSC measurements was performed under argon atmosphere and a heating rate of 10 °C/min by a Netzsch STA 449 C Jupiter TG-DSC. The Co₆₀C₄₀ amorphous powder was then examined by transmission electron microscopy (TEM) to validate the amorphous phase formation. TEM was performed on a JEOL 2100 TEM operating at 120 kV. Optical Microscopy was performed on each SPS composite sample in order to assess the microstructure evolution as well as the amorphous particles morphology and distribution in the samples matrix. Furthermore, the bulk density of each SPS composite sample was determine by Archimedes' principle in order to assess densification. Also, microhardness testing was use to assess mechanical properties on micro scales, as a function of reinforcement volume fraction. A Phase II Micro Vickers Hardness tester was used a load of 0.98N for 15 seconds and ten tests were run per sample, with more runs on some samples for statistical

reliability. Moreover, room temperature Vibrating Sample Magnetometry (VSM) was used in this work to determine the magnetic properties of the SPS composite samples using a Princeton Measurements Corporation Vibrating Sample Magnetometry (VSM Model 3900).

6.3. Results and Data Analysis

6.3.1 Selection and Analysis of Reinforcement Particles

As the main objective of this study was to create a composite material formed from cobalt matrix and cobalt amorphous particulate reinforcements. Therefore, several different compositions in the Co-C system were mechanically alloyed and studied by X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and Transmission Electron Microscopy (TEM) to produce amorphous powders, as seen in Chapter 4. However, the XRD, DSC and TEM investigation was showed that an amorphous phase forms in all the compositions of 2 to 40 at.% of carbon after milling for 40h, but the complete amorphous phase transformation can only be obtained where the concentration of carbon is approximately more than 10 at.%. According to the results of this investigation, the composition of the amorphous reinforcement was chosen to be Co- 40 at.% C milled for 40h.

6.3.1.1 X-Ray Diffraction (XRD)

The Co- 40 at.% C milled 40h X-ray analysis is shown for comparison with unmilled blended powder of Co-C in Figure 6.1. Figure 6.1 shows prominent cobalt and carbon peaks in the unmilled sample, as expected. Therefore, after 40 hours of milling, the carbon peaks disappeared as compared with the unmilled sample, as shown in Figure 6.1. Otherwise, the cobalt peaks also disappeared, but a broad peak was formed that is centered on an angle slightly smaller than the predominant cobalt peak ($2\theta = 44.416^\circ$) in the unmilled sample analysis, which is the distinguishing feature of an amorphous material. The peak broadening and shifting to a lower angle indicates there has been significant diffusion of larger carbon atoms into the areas of the cobalt, thus indicating that a complete amorphous phase transformation has occurred, as explained in section 4.3.1. This result was independently demonstrated by the results of the differential scanning calorimetry (DSC) and transmission electron microscopy (TEM), as shown in Figures 6.2 and 6.3.

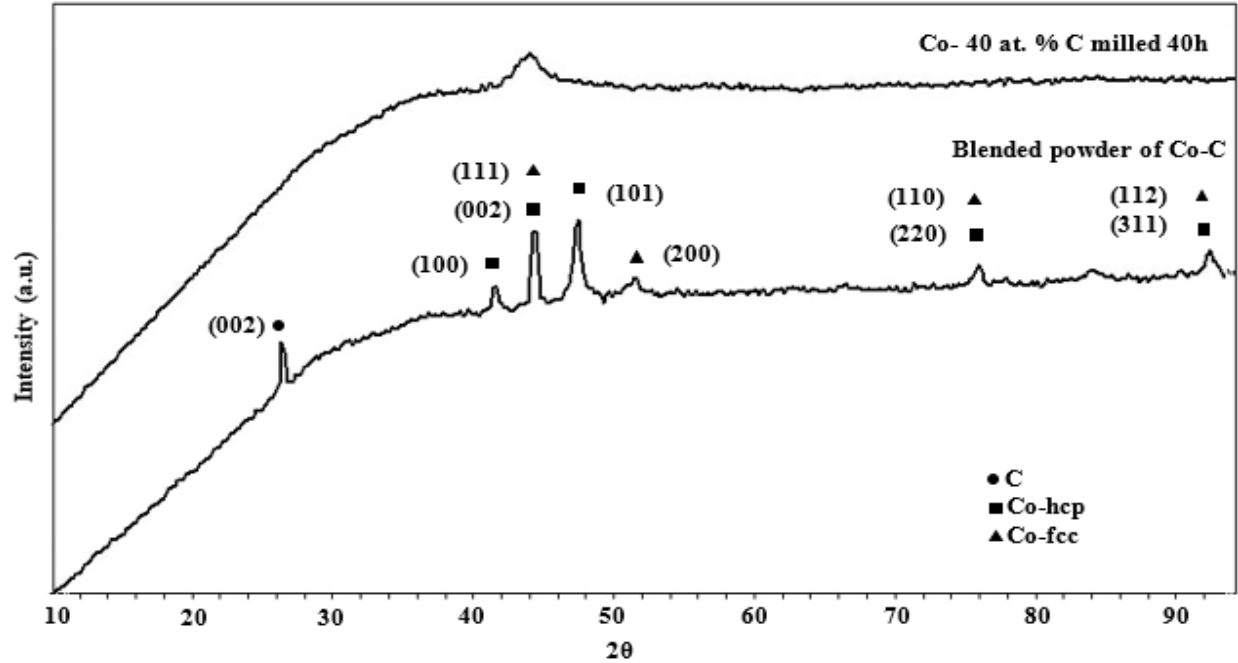


Figure 6.1: X-ray diffraction patterns for Co- 40at. % C milled for 40 hours, compared with the blended powder of unmilled Co-C.

6.3.1.2 Thermal Behavior and Differential Scanning Calorimetry (DSC) Analysis

The thermal behavior analysis and typical DSC result is shown in Figure 6.2. As shown Figure 6.2, the DSC trace of the powder mechanically alloyed for chemical composition of $\text{Co}_{60}\text{C}_{40}$ showed exothermic peak after 40h of milling compared to the unmilled Co specimen, suggesting that the amorphous phase was created during the milling. Therefore, as shown in Figure 6.2, the $\text{Co}_{60}\text{C}_{40}$ milled powder showed an exothermic peak occurred in 407°C, which is a crystallization peak of the amorphous phase. However, this exothermic peak is a precipitation of the crystalline cobalt in the amorphous carbon [29], which is predominantly a fcc phase, with a concomitant hcp phase, as discussed in Chapter 4.

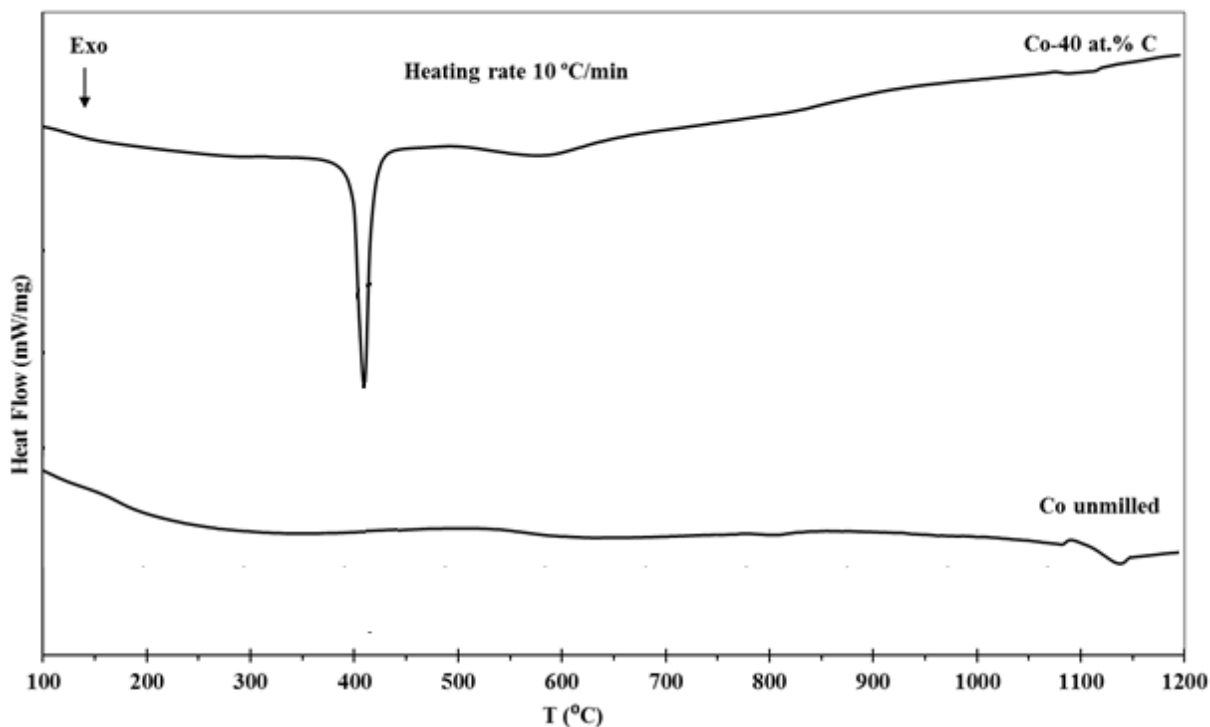


Figure 6.2: Differential scanning calorimetry curves of the unmillled Co and Co- 40 at.% C, milled for 40 hours at a heating rate of 10 °C/min.

6.3.1.3 Transmission Electron Microscopy (TEM) Analysis

The selected area electron diffraction (SAED) pattern for the TEM characterization of the Co-40 at. % C powder milled for 40h in Figure 6.3 confirmed that the milled powder contained no crystalline phase. As can be seen from Figure 6.3, no diffracted rings were found in either the cobalt or the carbon on the SAED patterns, suggesting that it was completely amorphous, as discussed in Chapter 4. However, in the case of the completely amorphous phase, the feature of concentric rings in the pattern disappeared and a halo was left around the bright center spot, which shows that the electrons were scattered randomly by the amorphous structure of the specimen, as shown in Figure 6.3. Consequently, it can be concluded that the mechanically alloyed powder of $\text{Co}_{60}\text{C}_{40}$ milled for 40h is a completely amorphous structure. Indeed, the TEM characterization seen here qualitatively verifies the data found by XRD and DSC of mechanically alloyed powder of $\text{Co}_{60}\text{C}_{40}$ milled for 40h, which is a completely amorphous phase.

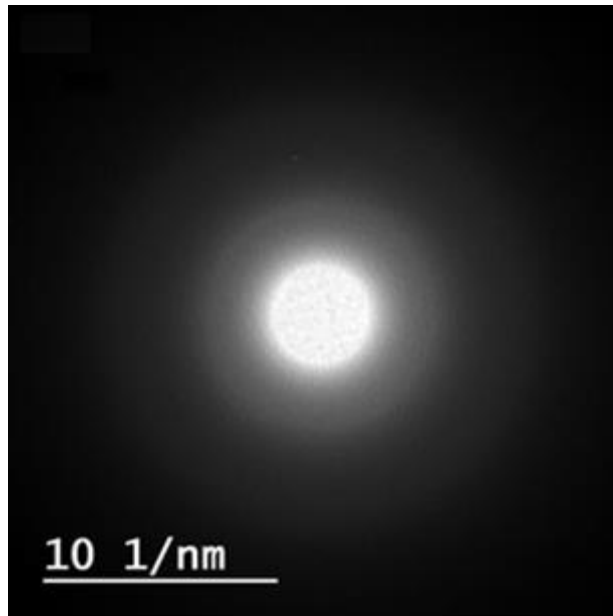


Figure 6.3: A SAED pattern of mechanically alloyed powder of Co- 40 at.% C, milled for 40h. However, in the SAED pattern, the feature of concentric rings disappears and a halo is left around the bright center spot, which confirms that the structure is a completely amorphous phase.

6.3.1.4 Particle Size Analysis

Thus, to complete the analysis investigation for the reinforcement powder particles, Horiba laser light scattering particle size distribution analyzer was also used to measure the reinforcement particle size. Figure 6.4 shows a typical plot of both the cumulative and regular distribution of Co-40 at.% C milled 40h powder with size on the x-axis and frequency on the y-axes. However, the result showed that the corresponding mean reinforcement particle (Co- 40 at.% C milled 40h) diameter was $\approx 3.44 \mu\text{m}$. However, the two powders of the pure cobalt and Co- 40 at.% C milled 40h were blended to form composites with up to 20 volume percent reinforcement as shown in Table 6.1.

From this results it can be concluded that a composition of Co- 40 at.% C milled 40h is complete amorphous phase occurred during the mechanical alloying process. Therefore this particular composition (Co- 40 at.% C milled 40h) was selected as a reinforcement material in order to create a composite material formed from a cobalt matrix and cobalt amorphous particulate reinforcements.

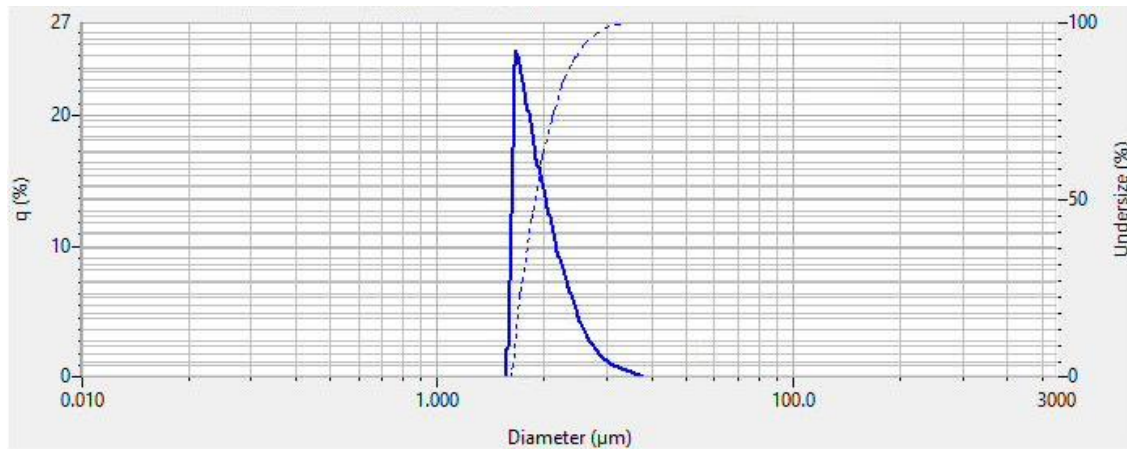


Figure 6.4: Co- 40 at.% C milled 40h particle size distribution.

6.3.2 Analysis of Composite Materials

This section presents the results and analysis for the characterization of the powders composite as well as bulks.

6.3.2.1 X-Ray Diffraction (XRD)

Typical X-ray diffraction patterns for the composites of the cobalt matrix and cobalt amorphous particulate reinforcements in Figures 6.5 and 6.6. Figure 6.5 shows scans of composite powders samples for different volume fraction of reinforcements, while Figure 6.6 shows scans of their corresponding composite bulks samples. In general, there is no significant difference between the XRD patterns of the composite powders. As can be seen in Figure 6.5, the unmilled Co powder is a mixture of hcp and fcc cobalt phases. However, the amount of fcc phase rapidly reduces after milling for 2h (composites processing), as evidenced by the decrease in intensity of the Co-fcc peaks in the XRD patterns of the composites, for example of the Co-fcc peak (200), as shown in Figure 6.5. Thus, note that this peak almost disappears after milling for 2h. It is well known that the metastable phase tends to transform to a stable one under cold working, meanwhile the ball milling process also considered to be as a cold working process. However, the ball milling process produces heavily strained crystallites on a nanometer scale with high density structure defects [30]. Therefore, the ball milling process ultimately lead to the increase of the stored energy of the ball milled materials, which is leading for phase transformation, such as seen in this work for the transformation of Co-fcc $\rightarrow$ Co-hcp [31-33]. However, the fcc phase of cobalt is a high temperature phase, and it is metastable at room temperature. So it tends to transform to the room

temperature stable phase (hcp phase) under ball milling [34-37]. In contrast, the Co-hcp phase after the 2h of milling (composite processing) also showed small humps at the position of their peaks. Moreover, XRD patterns reveal that the hcp peaks for example the (101) or (002) peaks are slightly extra broadened compared with the unmilled Co powder. This is an indication of the existence of stacking faults as well as crystallite size refinement [37-39]. However, these conditions create microstrains in the Co lattice system, ultimately leading to XRD peak broadening.

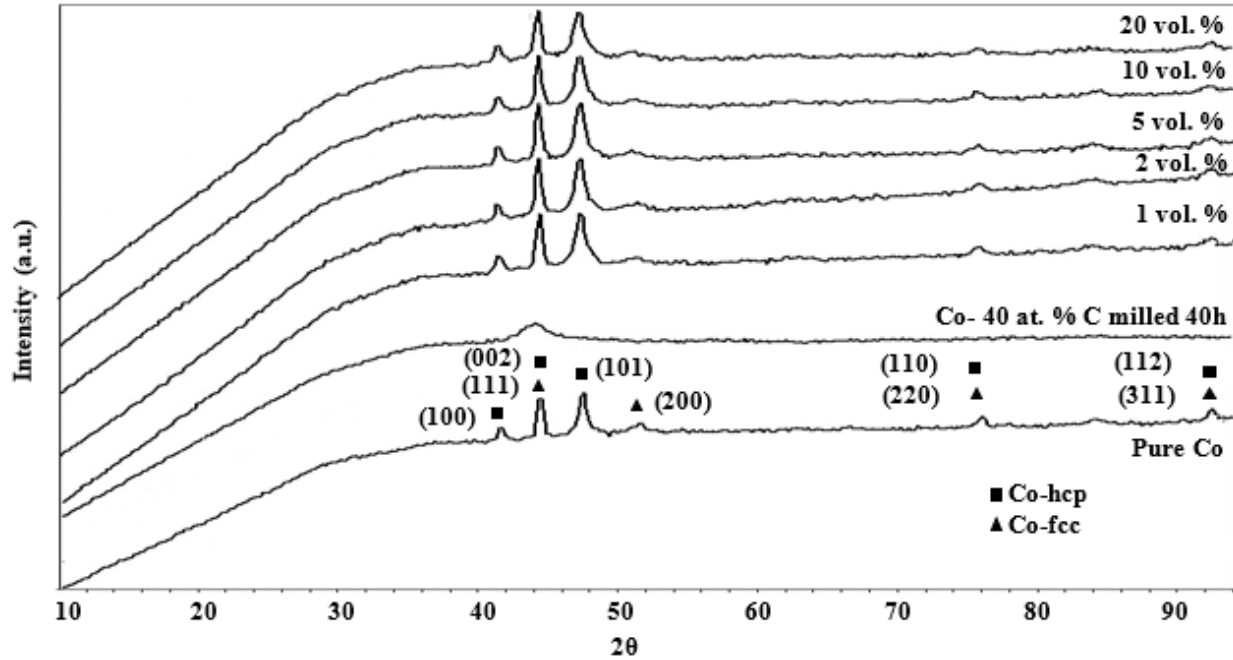


Figure 6.5: XRD patterns of 1, 2, 5, 10 and 20 vol.% reinforcement composites powders compared with unmilled Co powder as well as amorphous particles (Co- 40 at.% C milled 40h).

On the other hand, Figure 6.6 offers the typical XRD patterns for the SPS bulk composites of the cobalt matrix and cobalt amorphous particulate reinforcements compared with unmilled Co powder. As can be seen in Figure 6.6, there is no significant difference between each other of the XRD patterns of the bulk composites. However, the patterns display crystalline cobalt peaks (predominantly Co-hcp phase as discussed and illustrated earlier) from the matrix on the top of the maxima of the $\text{Co}_{60}\text{C}_{40}$ amorphous particles (002) peak). If the reinforcement ($\text{Co}_{60}\text{C}_{40}$ amorphous) contained fully crystalline cobalt, then the cobalt peaks shown would be very narrow and defined. The patterns however exhibit slightly broader cobalt peaks; the higher the volume fraction of reinforcement the broader the peaks.

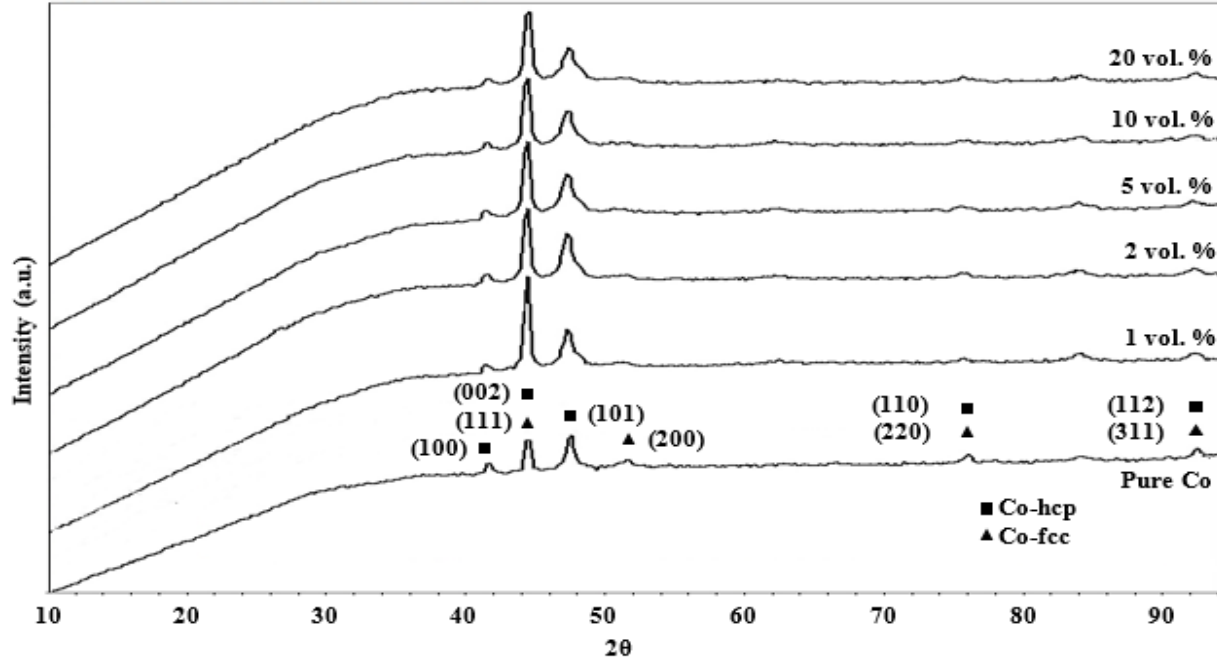


Figure 6.6: XRD patterns of 1, 2, 5, 10 and 20 vol.% $\text{Co}_{60}\text{C}_{40}$ milled 40h reinforcement composites bulks compared with unmilled Co powder.

6.3.2.2 Crystallite Size Analysis

To determine the crystallite size of the SPS bulk composite materials, Scherrer formula (Eq. 6.1) was used to calculate the crystallite domain sizes from the XRD line broadening of the Co-hcp (101) peaks, which has the relation:

$$L = \frac{0.9\lambda}{B \cos\theta_B} \quad \text{Eq. 6.1 [2]}$$

Where L is the crystallite size, λ is the X-ray wavelength, B is the full width at half the maximum intensity of a diffraction peak (FWHM) and θ_B is the peak diffraction angle in radians. The average Scherrer's crystallite size for the different compositions of the SPS bulk composite samples was found to be 11.46 nm.

6.3.2.3 Optical Microscopy

Optical micrographs of the SPS bulk composite materials with 1, 2, 5, 10 and 20% volume fractions of reinforcements are shown in Figures 6.7 through 6.27. Figure 6.7 and Figure 6.8 show the optical micrographs of the Co matrix reinforced with 1 vol.% $\text{Co}_{60}\text{C}_{40}$ amorphous particles. As can be seen in Figures 6.7 and 6.8, the bulk composite with 1% volume fraction of the

reinforcement show homogeneous microstructure with a presence of substantial porosity. Therefore, the gray regions are Co matrix and the dark gray spots are the amorphous particles of the $\text{Co}_{60}\text{C}_{40}$ while black areas are pores. However, this porosity resulted from the low temperature that was used during the sintering process, so as to avoid crystallization of the reinforcement particles ($\text{Co}_{60}\text{C}_{40}$ amorphous particles).



Figure 6.7: Optical micrograph of a composite of Co with 1 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 50X.

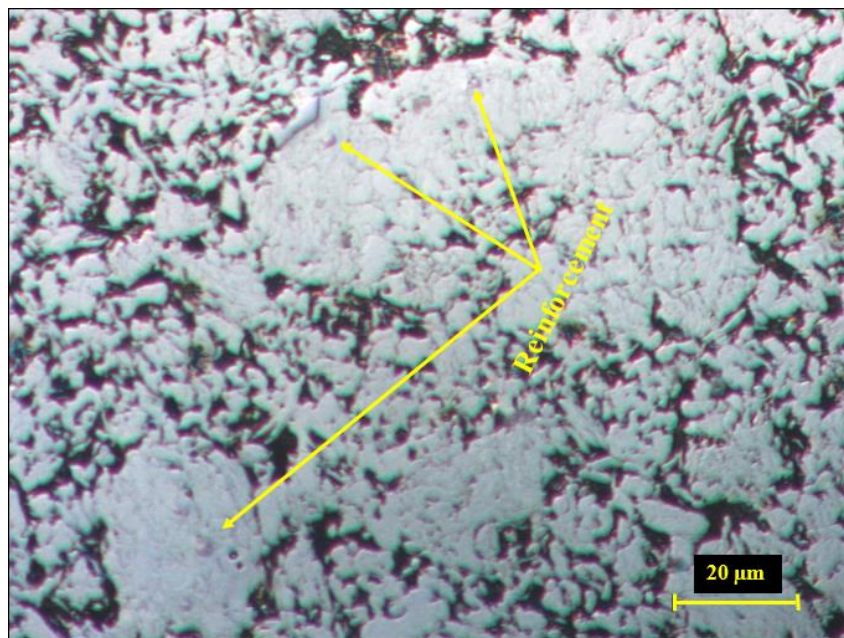


Figure 6.8: Optical micrograph of a composite of Co with 1vol. % $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

The optical micrographs of SPS bulk composite containing 2 vol.% $\text{Co}_{60}\text{C}_{40}$ amorphous particles are shown in Figures 6.9, 6.10 and 6.11. These figures show typical microstructure for this sample, which show a homogeneous distribution of fine reinforced particles in the alloy matrix with presence of porosities. However, optical micrographs of 2 vol.% depict homogeneous distribution of particles which are arranged in random fashion due to limited amount of amorphous particle reinforcement. Therefore, the grey areas with the dark gray spots are composite Co/ $\text{Co}_{60}\text{C}_{40}$ while black areas are pores. As can be seen from Figures, a fraction of the matrix grains are elongated, while most of the reinforced particles remain equiaxed. This observation on the composite morphology is of course attributable to the attritor milling process, in which the repeated welding, deformation and fracture of the reinforcement and matrix particles occurs. Moreover, the reinforcement particles are protruding in the matrix depicting a good bonding between the particle and alloy matrix as observed in these Figures. However, this observation suggests that the compatibility in the chemical and physical properties of the reinforcements and matrices helped establish a strong interface bonding between the reinforcement particles of the

$\text{Co}_{60}\text{C}_{40}$ and the alloy matrix of the cobalt. Thus, these factors are of course attributable good bonding between the particles and alloy matrix.

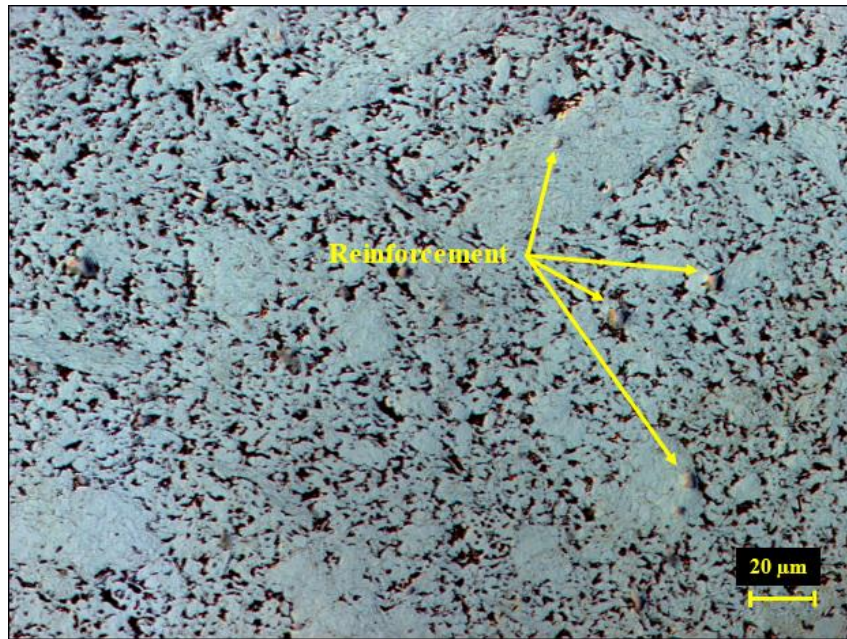


Figure 6.9: Optical micrograph of a composite of Co with 2 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 50X.

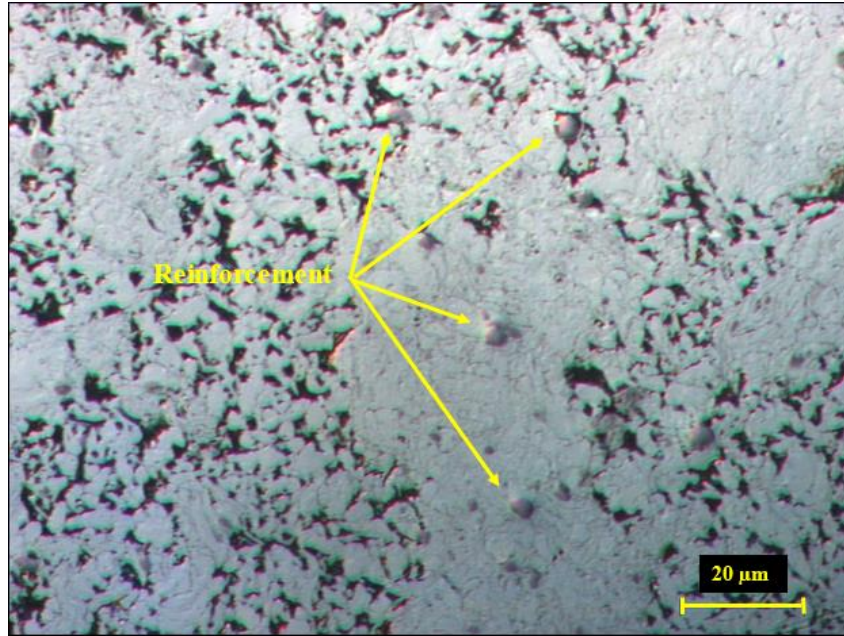


Figure 6.10: Optical micrograph of a composite of Co with 2 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSeD by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

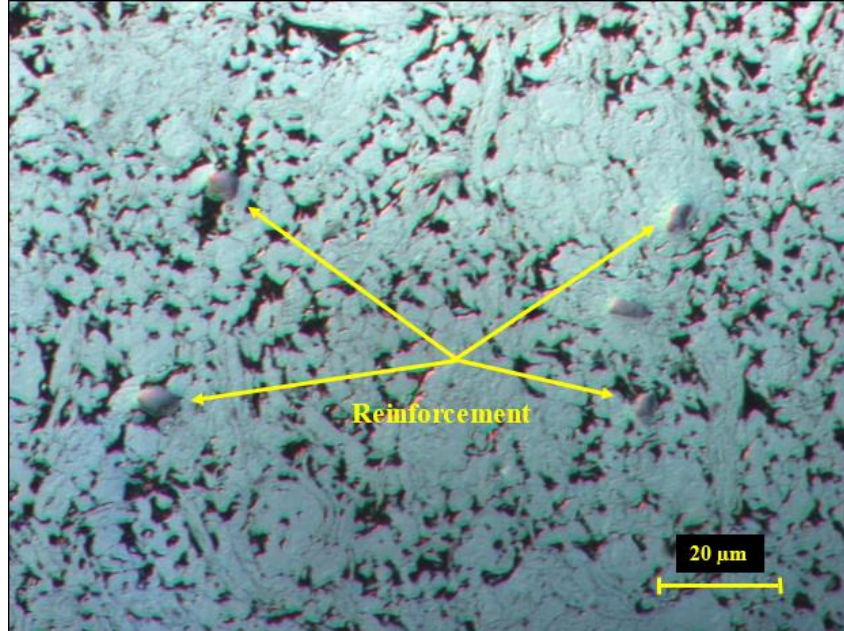


Figure 6.11: Optical micrograph of a composite of Co with 2 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSeD by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

Figures 6.12, 6.13, 6.14, 6.15, and 6.16 illustrate the optical micrographs for the SPS bulk composite containing 5 vol.% $\text{Co}_{60}\text{C}_{40}$ amorphous particles. However, Figure 6.12 shows the optical micrograph for the microstructure of the composite reinforced with 5 vol.% of $\text{Co}_{60}\text{C}_{40}$ amorphous particles by low magnification for a good overview of the sample at magnification of 5X.

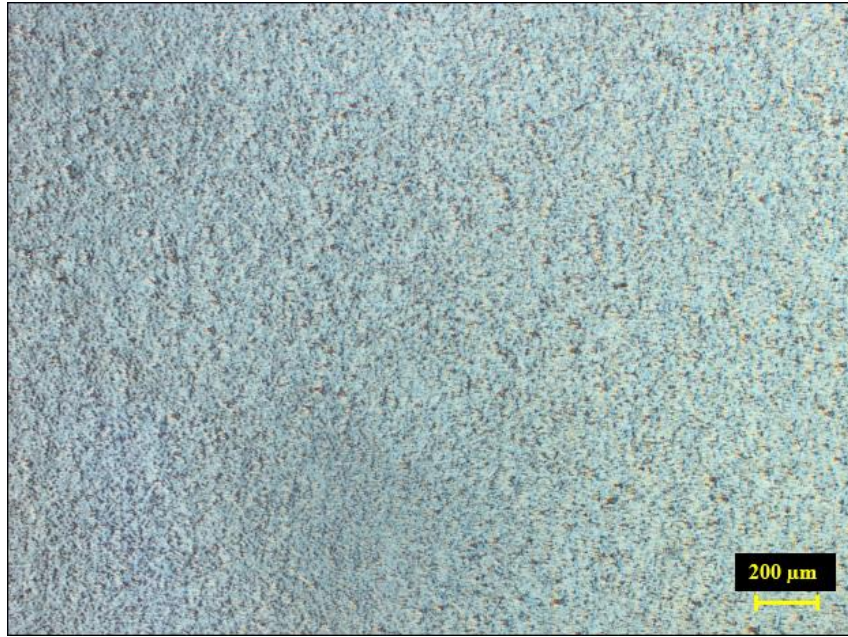


Figure 6.12: Optical micrograph of a composite of Co with 5 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Photomicrograph is shown at 5X, which provides a scan with low magnification for a good overview of the sample, essentially a “scan” of the sample.

While, Figure 6.13 shows the optical micrograph for the microstructure of the composite at magnification of 50X. As can be seen from Figure 6.13, the microstructure clearly demonstrates that the grains of the matrix are elongated, while most of the reinforced particles remain equiaxed. Furthermore, it is clear the microstructure of 5% volume fraction of reinforcements has also a homogeneous distribution for the reinforced particles in the alloy matrix with some of porosities, as seen in the optical micrographs of the SPS bulk composite materials with 1, 2% volume fractions of reinforcements. However, the grey areas with the dark gray spots are composite Co/ $\text{Co}_{60}\text{C}_{40}$ while black areas are pores.

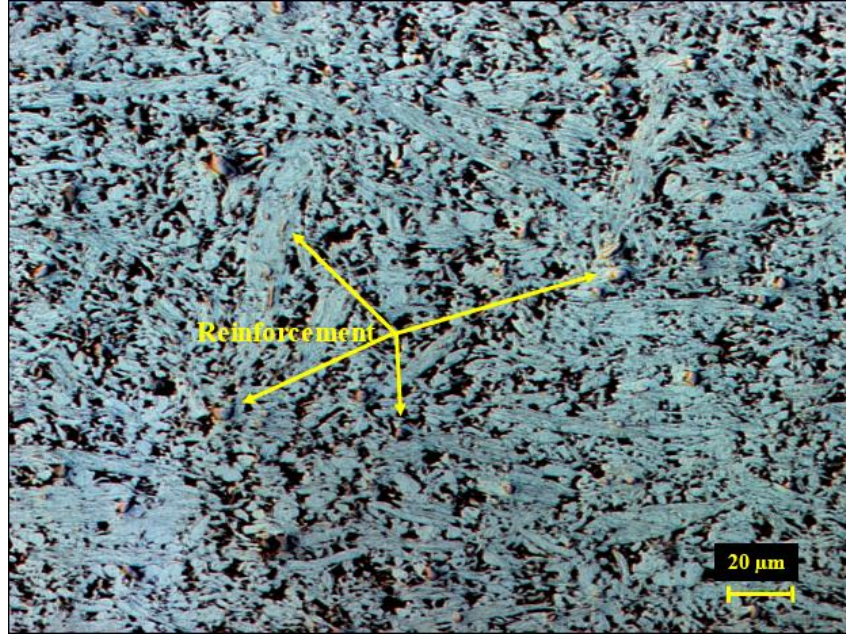


Figure 6.13: Optical micrograph of a composite of Co with 5 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 50X.

On the other hand, Figures 6.14, 6.15, and 6.16 show the optical micrographs for the microstructure of the composite at magnification of 100X. However, these Figures show higher magnification to the microstructure of Co matrix reinforced with 5 vol.% of $\text{Co}_{60}\text{C}_{40}$ amorphous particles. As can be seen from Figures 6.14, 6.15, and 6.16, the optical micrographs for the microstructure confirm that the nearly uniform distribution of the reinforced particles in the alloy matrix as seen in the SPS bulk composite materials with 1, 2% volume fractions of reinforcements, which is clearly observed with the increase in the volume fraction of reinforcements to 5 vol.%. However, similarly to the microstructure in the composite reinforced with 1 and 2 vol.% of $\text{Co}_{60}\text{C}_{40}$ amorphous particles (Figures 6.7 through 6.11), it can be observed that the composite matrix (Co) was showed as gray region and the reinforced particles ($\text{Co}_{60}\text{C}_{40}$) as dark gray, whereas the pores region was appeared as black. Thus, the presence this porosity as mentioned earlier is due to the lower temperature that was used during the sintering process, so as to avoid crystallization of the reinforcement particles ($\text{Co}_{60}\text{C}_{40}$ amorphous particles).

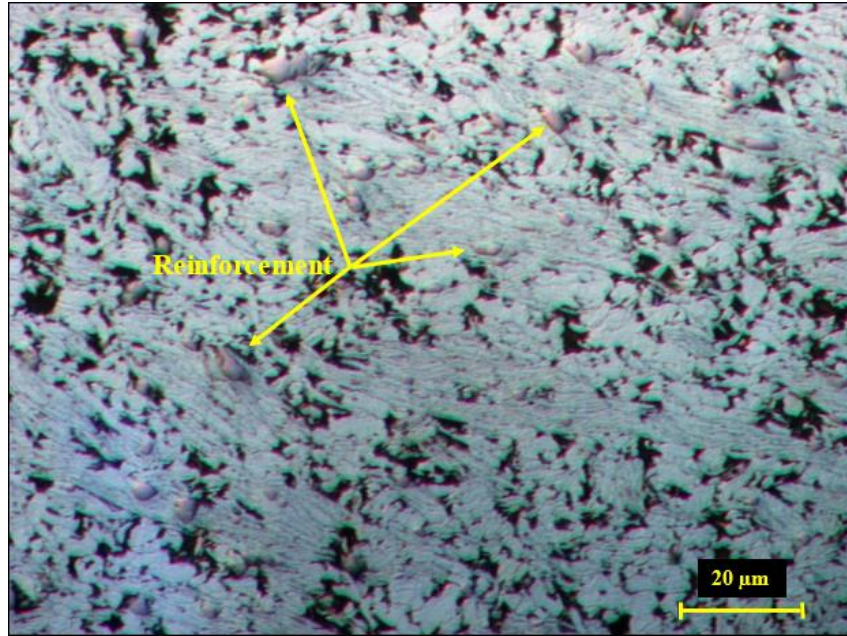


Figure 6.14: Optical micrograph of a composite of Co with 5 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

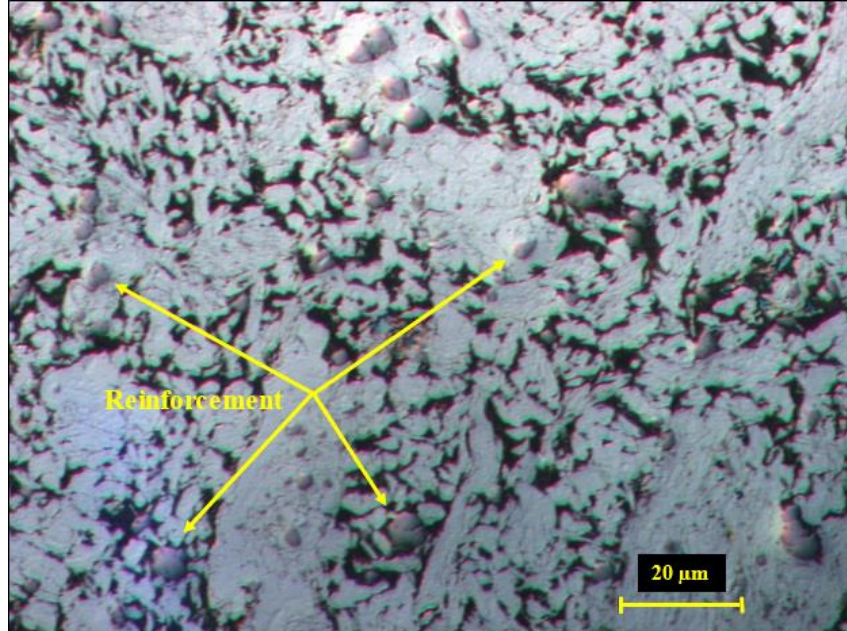


Figure 6.15: Optical micrograph of a composite of Co with 5 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

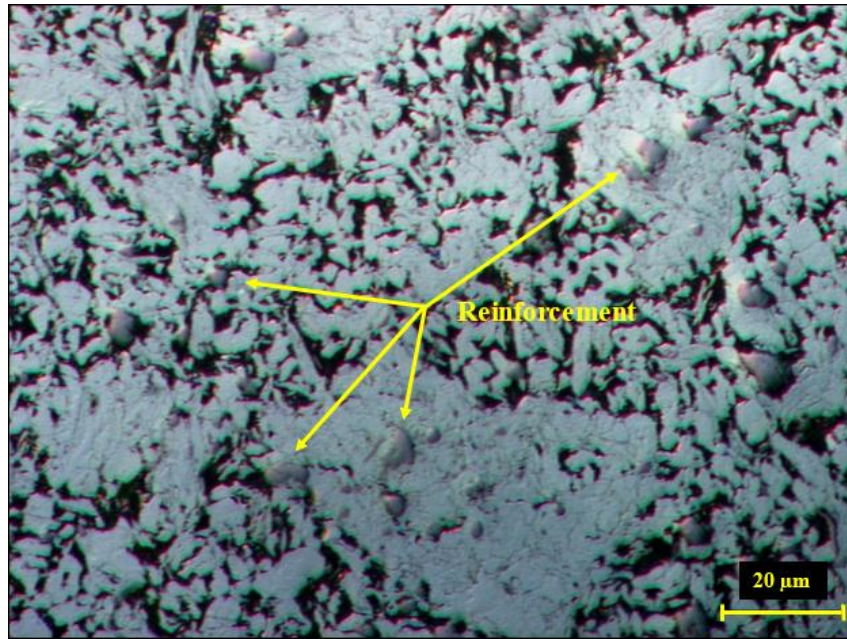


Figure 6.16: Optical micrograph of a composite of Co with 5 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

Figures 6.17 through 6.27 show typical optical micrographs of the Co matrix reinforced with 10 and 20 vol.% $\text{Co}_{60}\text{C}_{40}$ amorphous particles. However, the optical micrographs of the composite containing 10 vol.% $\text{Co}_{60}\text{C}_{40}$ amorphous particles are shown in Figures 6.17 through 6.22, while the optical micrographs of the composite containing 20 vol.% $\text{Co}_{60}\text{C}_{40}$ amorphous particles are shown in Figures 6.17 through 6.27. These Figures of the high reinforced particles composition show more clearly details about the microstructure of the Co matrix reinforced with $\text{Co}_{60}\text{C}_{40}$ amorphous particles. However, with further increase of the vol.% of the reinforcement to 10 and 20%, the number of reinforced particles increase and become more convergent, but the overall distribution of the reinforcements in the matrix remain fairly uniform. As can also be seen from Figures 6.17 through 6.26, the microstructures of these compositions also show a few microns size pores as black spots. Therefore, the presence of this porosity as mentioned earlier is due to the lower temperature that was used during the sintering process, so as to avoid crystallization of the reinforcement particles ($\text{Co}_{60}\text{C}_{40}$ amorphous particles). However, this porosity located in the matrix and not at the particle/matrix interface regions that usually are most preferred site for the porosity. This observation may be attributed to the wetting behavior of the matrix and

reinforcement particles [40-43]. However, the good interface bonding between the particles and matrix is largely due to the effectiveness of the compatibility in the chemical and physical properties of the reinforcements and matrix. Therefore, the protruding of the particles in the matrix is depicting good bonding between particle and alloy matrix as observed in the optical micrographs Figures, however the smooth interface between the particles and matrix provides better mechanical and tribological properties as transfer of load occurs through the interface [44 and 45].

Thus, it can be concluded that the microstructures of the composites of the cobalt matrix and cobalt amorphous particulate reinforcements revealed a fairly uniform and homogeneous distribution of reinforcing particles of the $\text{Co}_{60}\text{C}_{40}$ amorphous. Moreover, these composites exhibited a consistent and better bonding between the cobalt amorphous particles and the alloy matrix of cobalt. However, the good bonding between the reinforcement particles and the alloy matrix reflects the good interface bonding between the particles and matrix in the composite, which is largely due to the effectiveness of the compatibility in the chemical and physical properties of the reinforcements and matrix. This result is promising since this strong and good interface bonding between the matrix and the reinforcement occurred through towards maximum compatibility in the chemical and physical properties in the reinforcements and matrix, using cobalt matrix and cobalt amorphous particles reinforcement in order to create a successful applicable composite.



Figure 6.17: Optical micrograph of a composite of Co with 10 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 20X.

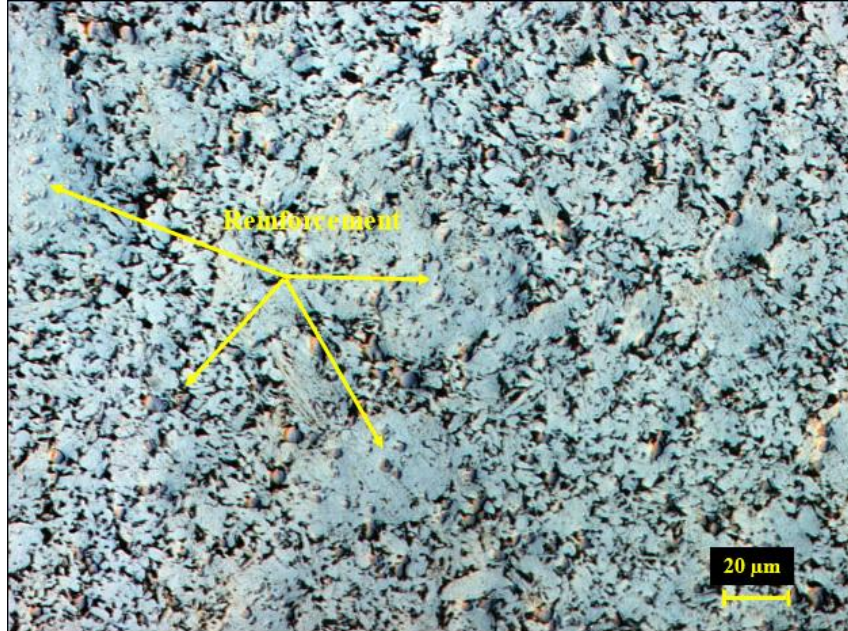


Figure 6.18: Optical micrograph of a composite of Co with 10 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 50X.

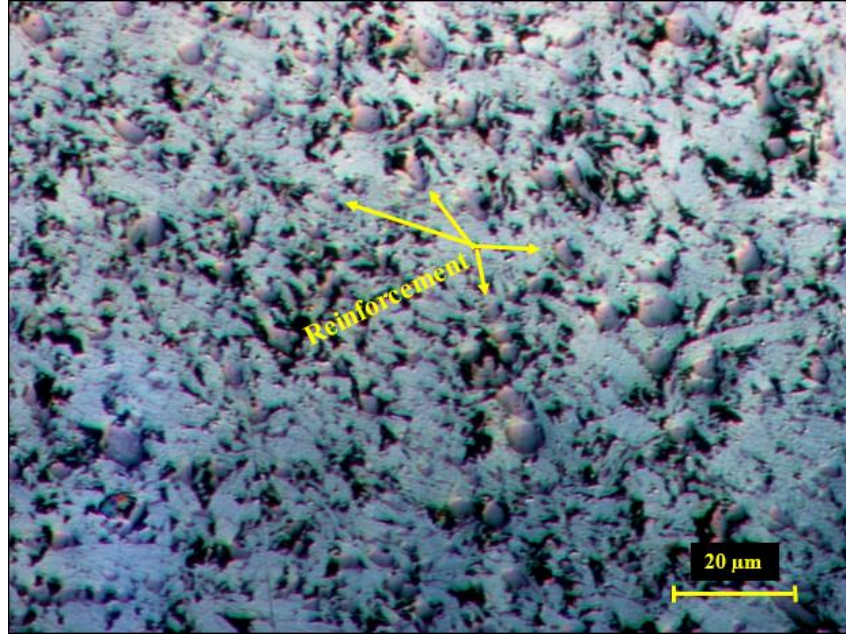


Figure 6.19: Optical micrograph of a composite of Co with 10 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

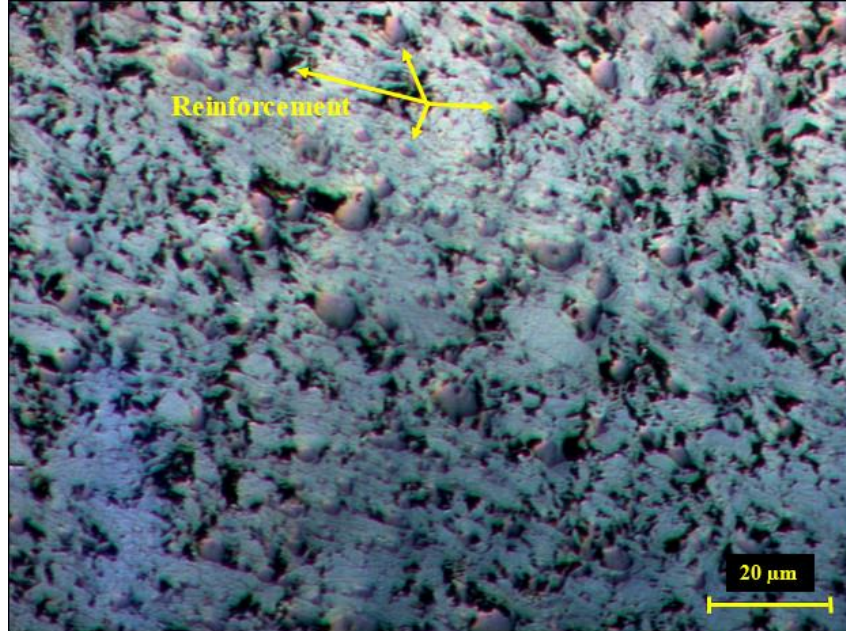


Figure 6.20: Optical micrograph of a composite of Co with 10 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

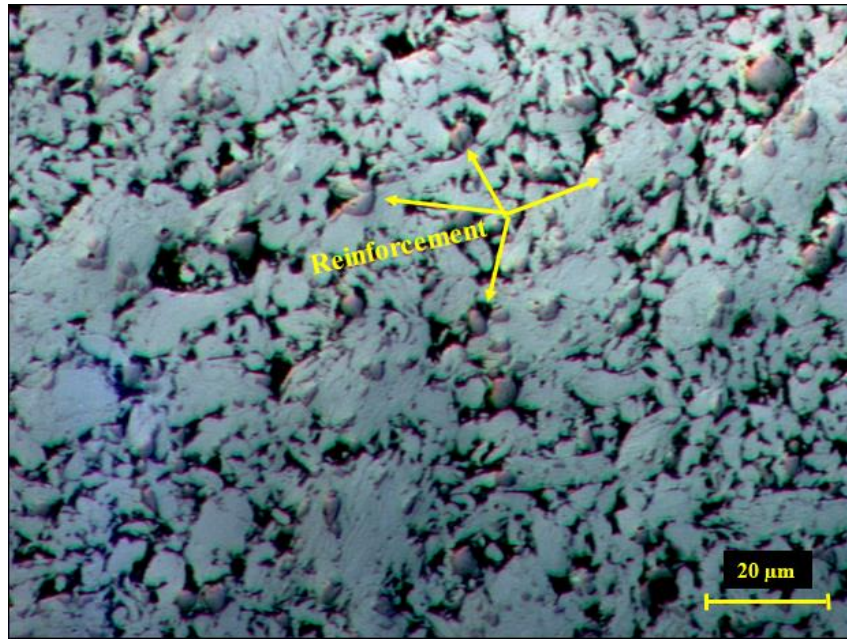


Figure 6.21: Optical micrograph of a composite of Co with 10 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

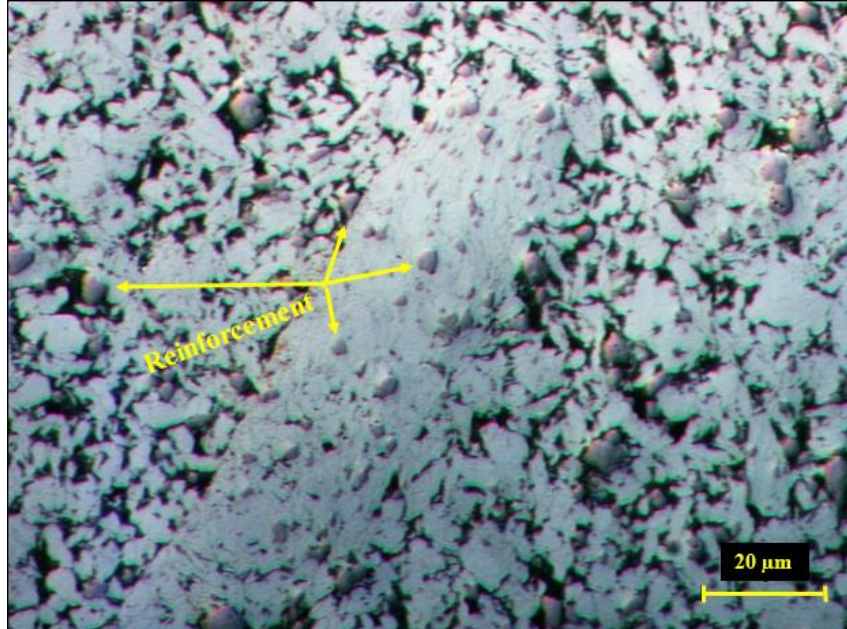


Figure 6.22: Optical micrograph of a composite of Co with 10 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.



Figure 6.23: Optical micrograph of a composite of Co with 20 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 20X.



Figure 6.24: Optical micrograph of a composite of Co with 20 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C. Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 50X.

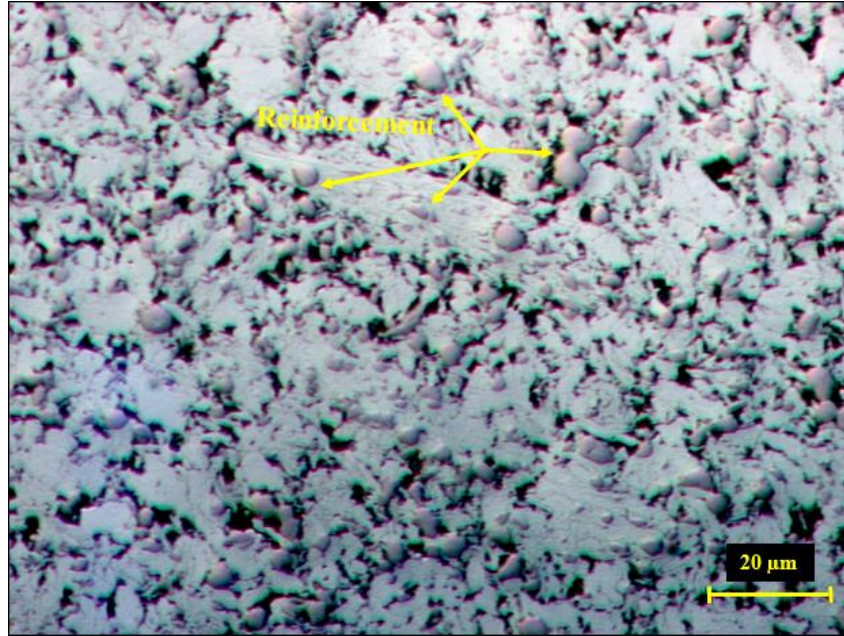


Figure 6.25: Optical micrograph of a composite of Co with 20 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

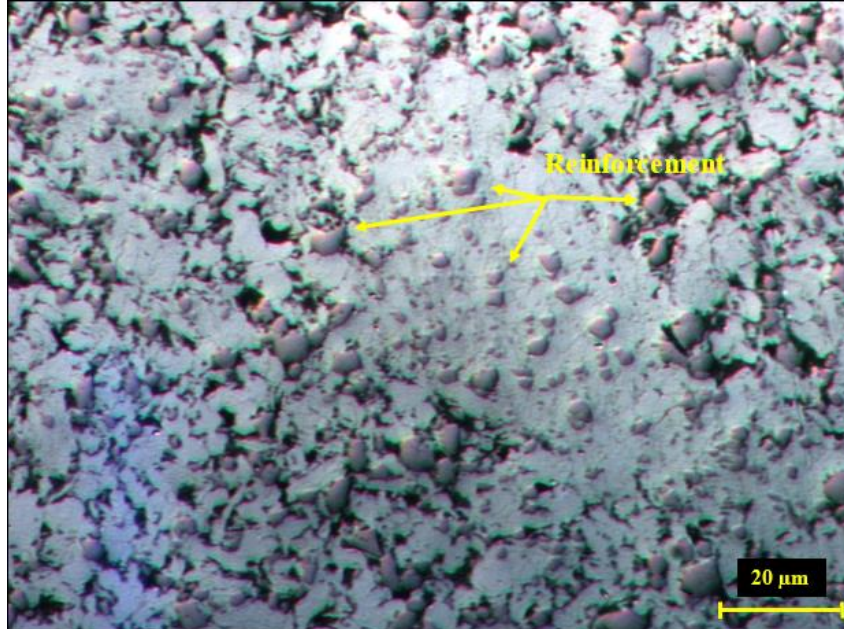


Figure 6.26: Optical micrograph of a composite of Co with 20 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

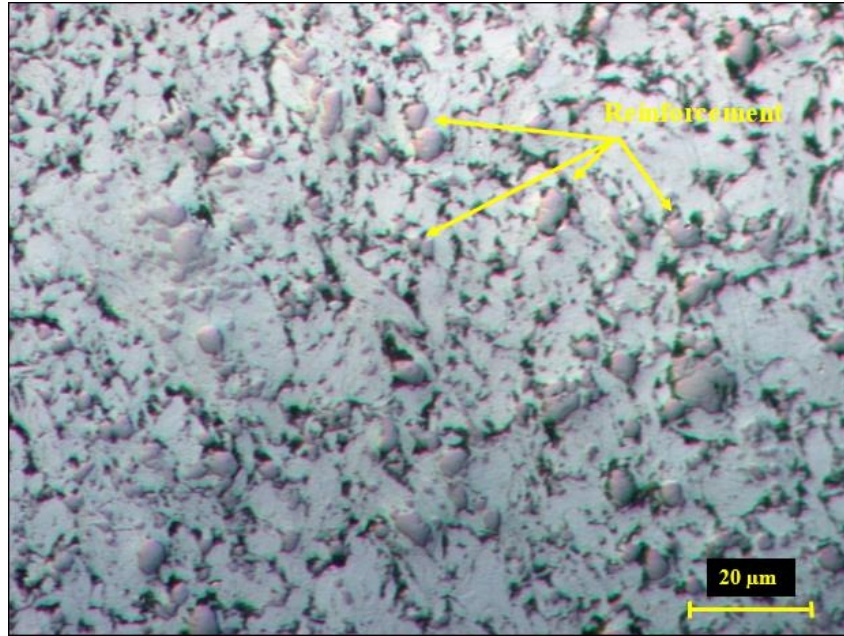


Figure 6.27: Optical micrograph of a composite of Co with 20 vol.% $\text{Co}_{60}\text{C}_{40}$ after being attritor milled for 2 hour then SPSed by 300 MPa for 10 minutes at 350°C . Grey areas are composite of Co matrix and $\text{Co}_{60}\text{C}_{40}$ particles while black areas are pores. Photomicrograph is shown at 100X.

6.3.2.4 Density Measurement

Density of SPS bulk composite materials with 1, 2, 5, 10 and 20% volume fractions of reinforcements was measured using Archimedes' principle. However, the measurement results are plotted in Figure 6.28 as a percentage of the theoretical and experimental values. Additionally, the experimental values are shown in Table 6.3. It can be observed from Figure 6.28 and Table 6.3 that the density of the composites show densities between 81 and 85% of the theoretical density value, thus indicating that the composites weren't fully dense. However, a substantial porosity is evident in the microstructures of all samples, as confirmed by the optical micrographs of the microstructures; this is the result of insufficient sintering temperature (350°C) during the sintering process, so as to avoid crystallization of the reinforcement particles ($\text{Co}_{60}\text{C}_{40}$ amorphous particles).

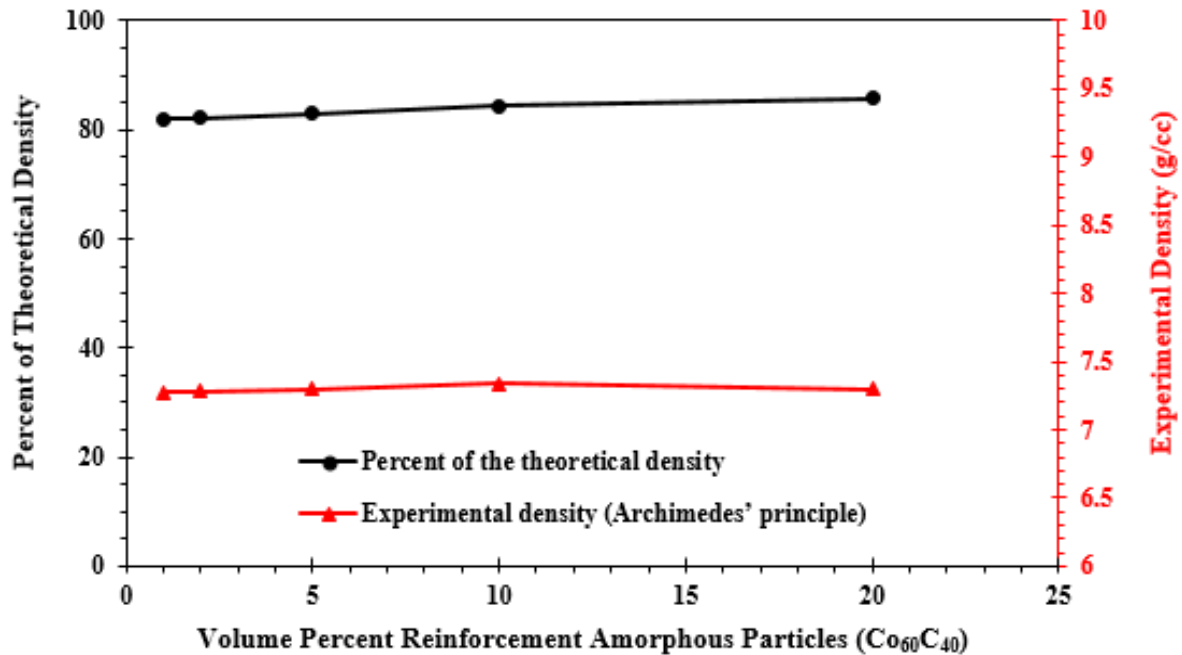


Figure 6.28: Density measurements as a percentage of the theoretical and experimental values plotted with respect to volume percent reinforcement amorphous particles (Co₆₀C₄₀).

Overall, density shows a steady trend even though with the increase of the reinforced particles (amorphous Co₆₀C₄₀) content, and the lack of increase in density at this sintering temperature (350°C) provides evidence that there is no further densification to be achieved with this sintering temperature (350°C). Thus, this data also seems to confirm at least the approximate accuracy of the calculated theoretical density, with most of the values falling in the same range of 81 and 85%, indicating fairly acceptable densification.

Table 6.3: Density measurement values for all composites.

Sample (volume % reinforcement)	Archimedean Density (g/cc)	Theoretical Density (g/cc)	Archimedean percentage of Theoretical
1 vol.% Co ₆₀ C ₄₀	7.276	8.881	81.932
2 vol.% Co ₆₀ C ₄₀	7.281	8.862	82.161
5 vol.% Co ₆₀ C ₄₀	7.299	8.805	82.904
10 vol.% Co ₆₀ C ₄₀	7.342	8.709	84.298
20 vol.% Co ₆₀ C ₄₀	7.302	8.517	85.722

6.3.2.5 Hardness Testing and Mechanical Properties

The microhardness measurement of the composites has been carried out to know the effect of reinforced particulates on the mechanical behavior of the composites. Generally, several factors would affect the microhardness of the composites such as particle size, amount of reinforcement and method of preparation. Therefore, Vickers microhardness tests were performed on the SPS bulk composite samples using a 0.98N for 15 seconds and ten tests were run per sample, with more runs on some samples for statistical reliability. However, the averages of the measurement results are recorded in Table 6.4 and plotted in Figure 6.29.

Table 6.4: Averages of Vickers microhardness measurements on composite sample.

Vickers microhardness testing (0.98N for 15 seconds dwell)					
Sample (volume % reinforcement particles of Co ₆₀ C ₄₀)	1 vol.%	2 vol.%	5 vol.%	10 vol.%	20 vol.%
HV	220	251	283	438	517

The results presented in this study suggest that reinforcing cobalt matrix with Co₆₀C₄₀ particulates result in improvement in the hardness of cobalt matrix as evident in Figure 6.29. Indeed, the Co/Co₆₀C₄₀ composite samples exhibited reasonable and high hardness values, when compared to those reported in the literature for pure cobalt, which is 253 HV [46 and 47]. However, it can be clearly seen that the microhardness of the Co/Co₆₀C₄₀ composites gradually increased with the increase in volume fraction of the reinforcement particles (amorphous Co₆₀C₄₀) content, as seen in Figure 6.29. Therefore, the increase in hardness of the composite samples is obviously due to high hardness value of the reinforcing materials, amorphous Co₆₀C₄₀ and the good interfacial bonding achieved between particulates and the matrix alloy and also the dispersion hardening effect [48 and 49].

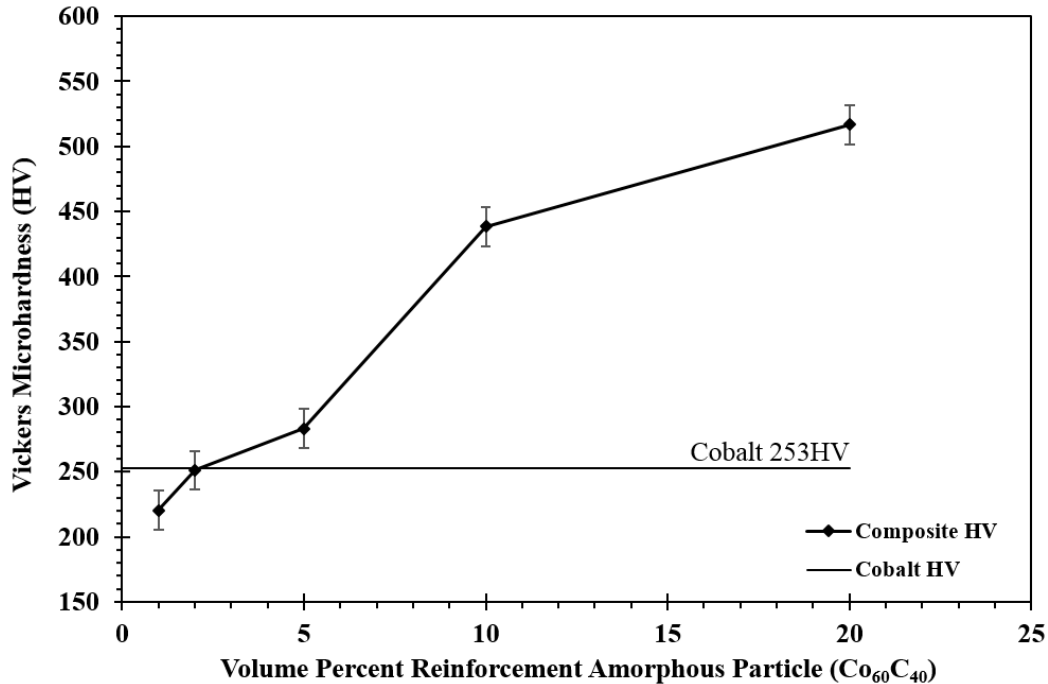


Figure 6.29: Vickers microhardness of Co/ $\text{Co}_{60}\text{C}_{40}$ composites versus volume fraction of the reinforcement amorphous particles ($\text{Co}_{60}\text{C}_{40}$) content as well as compared with the pure cobalt Vickers microhardness. The plot showing average composite Vickers microhardness increase with higher volume fraction of reinforcement.

It is evident from Figure 6.29 that the composites have significantly improved in the hardness values as the volume fraction of the reinforcement was increased, so it is expected that the high hardness values of the reinforcement would contribute and play a role in the mechanical properties of the composites. Thus, the high hardness in the composites is due to the uniform distribution of $\text{Co}_{60}\text{C}_{40}$ particles in the Co matrix, which confirmed by optical micrographs. These results of the hardness test indicate that the composite system of Co/ $\text{Co}_{60}\text{C}_{40}$ had significantly high strength characteristics based on the relation that strength increase with hardness [50]. However, as the amount of $\text{Co}_{60}\text{C}_{40}$ reinforced particles increases in the alloy matrix, the dislocation blocking builds up and amplifies as the amount of these reinforced particles increases, which leads to a rapid increase in the hardness. Thus, the Vickers microhardness assay can be used to evaluate the mechanical properties of the Co/ $\text{Co}_{60}\text{C}_{40}$ composite system by predicting the particulates strengthening contribution. However, Kampe et. al. [51] established a method for predicting the strengthening produced by particulate reinforcements based on the assumption that the

strengthening was resulted from the increasing dislocation densities at the matrix/reinforcement interface. Thus, the strengthening can then be related to the particle spacing of the reinforcement and particle modulus, assuming that the particles do not fracture by the equation as below Eq. 6.2:

$$\Delta\sigma_p = \sqrt{G_m \cdot E_p \cdot \vec{b} / \lambda_{e-e}} \quad \text{Eq. 6.2 [51]}$$

Where $\Delta\sigma_p$ is the strengthening directly attributed to the particles, G_m is the elastic shear modulus of the matrix, E_p is the elastic modulus of the particles, b is the magnitude of the matrix Burger's vector, and λ_{e-e} is the edge-to-edge interparticle spacing.

When considering the strength of a metal or metal matrix composite system, the Orowan effect on the system with the presence of small incoherent phases or particles can increase the overall strength of the material. However, as dislocations move to exceed these particles, they form loops that surround these particles and interfere with subsequent dislocation motion, thus raising the strength of the material [52 and 53]. Thus, this phenomenon implies that a small particle spacing will provide the best composite strengthening. It is also known that if the spacing between these particles is too small, then the dislocations will not pass between the particles; in contrast, widely spaced particles affected by these loops do not typically impact the strengthening significantly. An intermediate distance between the particles must therefore be determined to obtain the optimum strengthening. Thus, the degree of strengthening is a function of size, shape, spacing, hardness, and distribution of the second phase particles within the matrix. Since the hardness is a measure of a material's ability to resist the plastic deformation, it is related to the stress needed to activate the dislocations motion in the material. Therefore, the elevation in hardness that was showed the composites is due to the bowing of dislocations between neighbouring undeformable particles and bypassing particles leaving a dislocation loop around them with presence of the small particle spacing. Therefore, the dependence of hardness on particle spacing might directly follow the relation (Eq. 6.2) and, thus, the hardness–particle spacing relation can be described by Eq. 6.3:

$$\Delta H_p = \sqrt{G_m \cdot E_p \cdot \vec{b} / \lambda_{e-e}} = k \sqrt{1 / \lambda_{e-e}} \quad \text{Eq. 6.3 [51]}$$

Where ΔH_p is the strengthening directly attributed to the particles, G_m is the elastic shear modulus of the matrix, E_p is the elastic modulus of the particles, b is the magnitude of the matrix Burger's

vector, and λ_{e-e} is the edge-to-edge interparticle spacing. However, the edge-to-edge interparticle spacing λ_{e-e} can be calculated by using the equation below Eq. 6.4:

$$\lambda_{e-e} = 1.25 \cdot r \sqrt{2\pi/3f} - 2r \sqrt{2/3} \quad \text{Eq. 6.4 [54]}$$

Where r is the radius of the particle, and f is the volume fraction of the reinforcement. Thus, the edge-to-edge interparticle spacing λ_{e-e} was calculated for the composite samples of Co/Co₆₀C₄₀ based on the equation (Eq. 6.4) above, in order to plot the prediction strengthening contributions. However, the volume fractions of the reinforcement particles are 1%, 2%, 5%, 10% and 20% Co₆₀C₄₀ and the radius (r) of the reinforcement particles Co₆₀C₄₀ is $\approx 1.72 \mu\text{m}$. Therefore, the edge-to-edge spacing λ_{e-e} values for these conditions according to equation (Eq. 6.4) are reported in Table 6.5. Thus, the strengthening contributions due to the particulate (H_p) by following equation (Eq. 6.3) and using Vickers microhardness measurement was plotted versus the inverse square root of the edge-to-edge interparticle spacing, as shown in Figure 6.30. However, Figure 6.30 shows that the strengthening (H_p) of the particulate composites of Co/Co₆₀C₄₀ depends fundamentally on reinforcement interparticle spacing, which is representing by a sturdy proportional relationship to the inverse square root of the edge-to-edge interparticle spacing λ_{e-e} . Therefore, the strengthening (H_p) of the particulate composites of Co/Co₆₀C₄₀ follows dependence mechanism on increasing the dislocation densities and leaving them as loops and segments at the matrix/reinforcement interface as primary mechanism for strengthening and not from Orowan stress by itself [51].

Table 6.5: Calculated reinforcement particle spacing values in μm .

Reinforcement Vol.%	Reinforcement radius (μm)	Edge-to-edge interparticle spacing λ_{e-e} (μm)
1	1.72	28.31
2	1.72	19.19
5	1.72	11.11
10	1.72	7.03
20	1.72	4.15

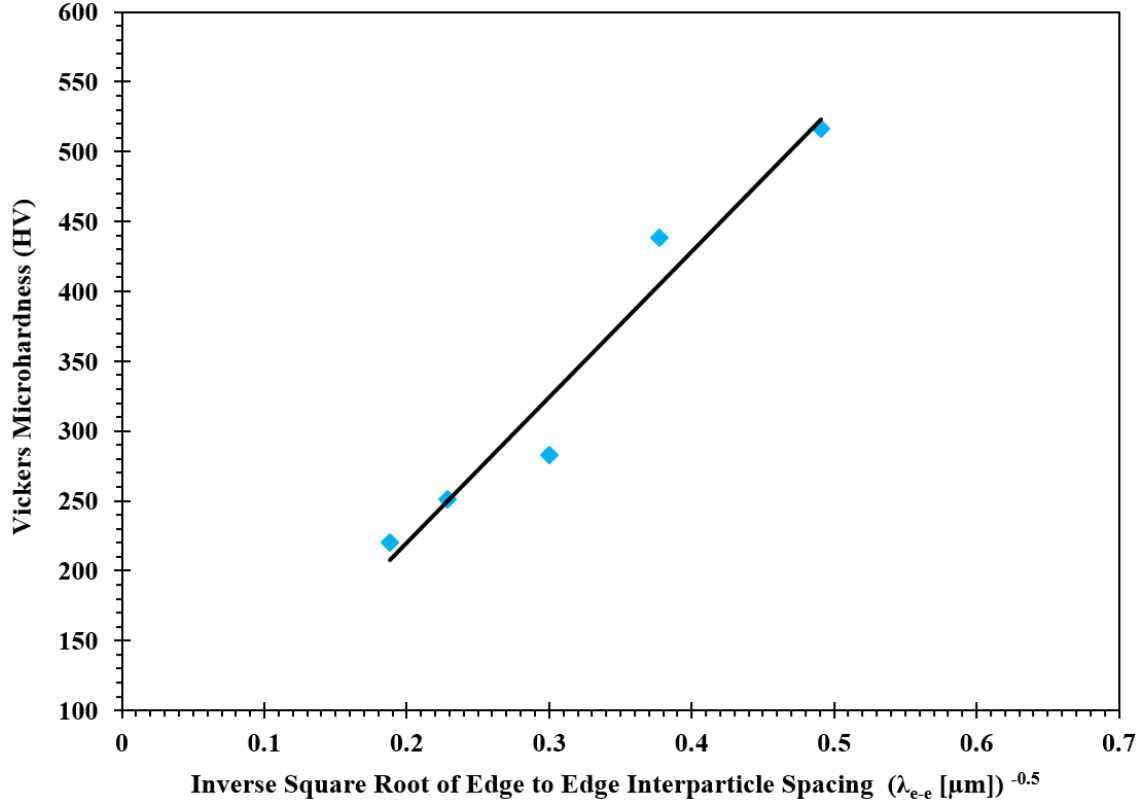


Figure 6.30: Plot of Vickers microhardness as a function of the inverse square root the edge-to-edge interparticle spacing λ_{e-e} .

However, with increasing volume fractions of the reinforcement particles in the alloy, the density of the matrix/reinforcement interfaces area increase where associated with a decreasing in the reinforcement antiparticle spacing, leading to increase the resistance to motion of dislocations and thereby contributes to strength. Thus, for the particulate composites with coarse or widely spaced particles, the Orowan equation will not predict observed values of strengthening, as strengthening will be a function of edge-to-edge interparticle spacing which will vary with the inverse square root of the edge-to-edge particle spacing.

6.3.2.6 Magnetic Properties

Magnetic hysteresis loops of the SPS bulk Co/Co₆₀C₄₀ composite materials with 1, 2, 5, 10 and 20% volume fractions of reinforcements of the amorphous particles (Co₆₀C₄₀) compared with pure cobalt are shown in Figure 6.31. These hysteresis loops were measured at 300K, using a Princeton Measurements Corporation vibrating sample magnetometer (VSM). The relation between the Magnetization (M) and the applied field (H) is given by Hysteresis loops. However, the magnetic

parameters of all the samples of Co/Co₆₀C₄₀ such as Saturation Magnetization, M_s , Coercivity, H_c , Remanent Magnetization, M_r , and Remanent-to-Saturation ratio or Squareness ratio (M_r/M_s) were extracted from the hysteresis loops and tabulated in Table 6.6.

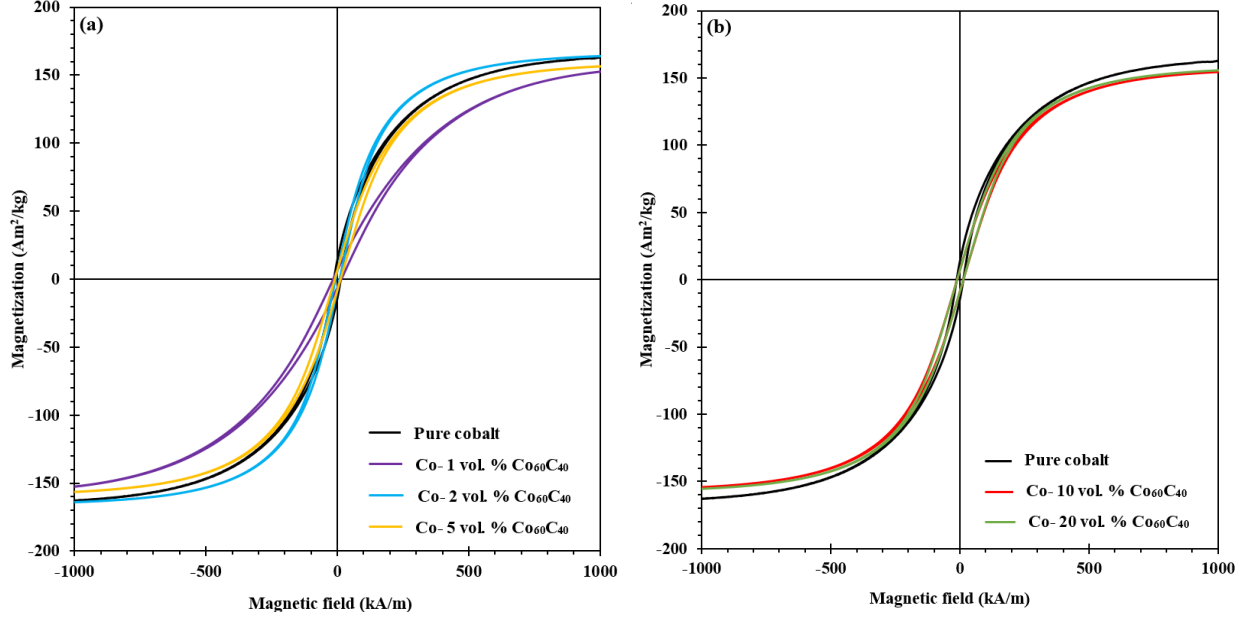


Figure 6.31: The hysteresis loops of the SPS bulk Co/Co₆₀C₄₀ composites (a) pure Co compared with 1, 2 and 5 vol.% Co₆₀C₄₀, (b) pure Co compared with 10 and 20 vol.% Co₆₀C₄₀.

The saturation magnetization, M_s , however slightly decreases with increase of the reinforcement content, as seen in Figure 6.30. It can be seen in Figure 6.32 that the M_s values decrease slightly in the Co/Co₆₀C₄₀ composites with increasing the volume fractions of the reinforced particles, which is slightly lower than the M_s value of the pure cobalt and higher than the M_s value of the amorphous particles (Co₆₀C₄₀).

Table 6.6: Magnetic parameters of the composite samples at at 300K: saturation magnetization (M_s), coercivity (H_c), remanent magnetization (M_r) and Remanent-to-Saturation ratio.

Sample (volume % reinforcement)	Saturation magnetization M_s (Am ² /kg)	Coercivity H_c (kA/m)	Remanent Magnetization M_r (Am ² /kg)	Remanent-to-Saturation ratio M_r/M_s
1 vol.% Co ₆₀ C ₄₀	206.93	14.82	6.36	0.030
2 vol.% Co ₆₀ C ₄₀	185.14	7.69	6.94	0.037
5 vol.% Co ₆₀ C ₄₀	183.60	10.92	7.39	0.040
10 vol.% Co ₆₀ C ₄₀	182.14	11.99	7.97	0.043
20 vol. % Co ₆₀ C ₄₀	181.02	11.85	7.92	0.043

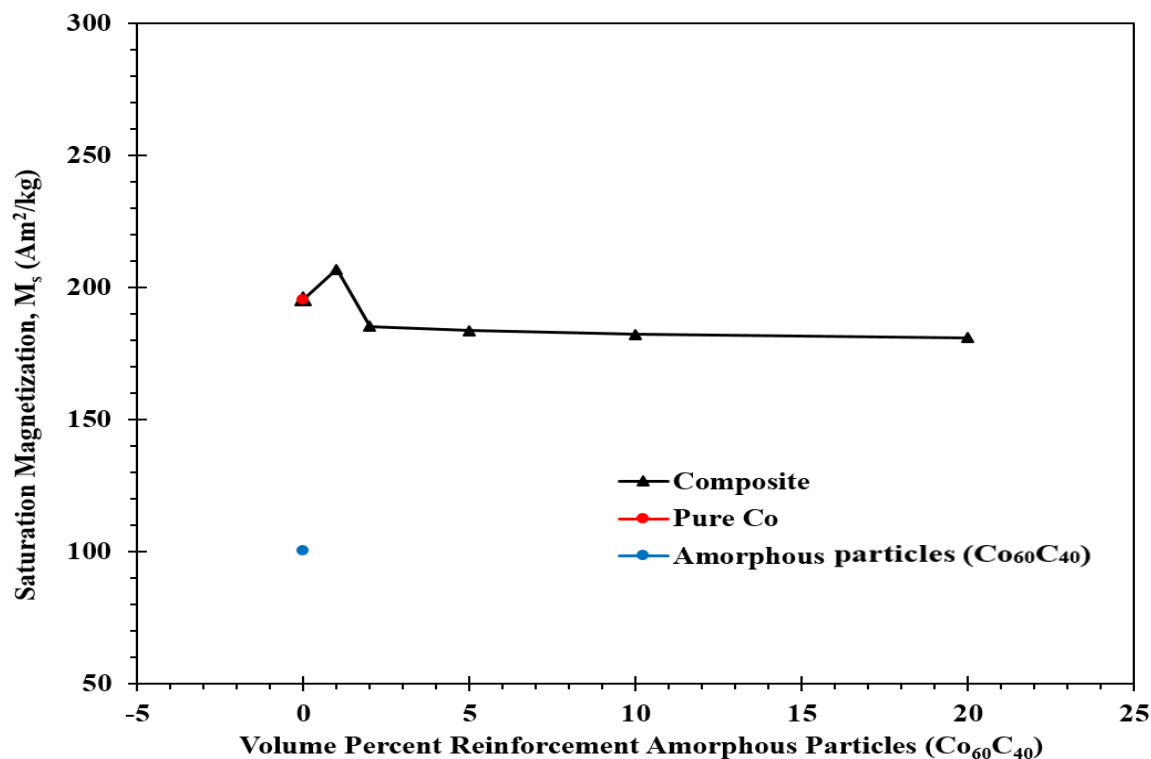


Figure 6.32: Variation of the room temperature saturation magnetization, M_s , with the volume fraction of the reinforcement amorphous particles ($\text{Co}_{60}\text{C}_{40}$) content for the pure cobalt, amorphous particles ($\text{Co}_{60}\text{C}_{40}$) and the SPS bulk $\text{Co}/\text{Co}_{60}\text{C}_{40}$ composite material.

Overall the saturation magnetization shows a steady trend even though with increase of the reinforcement content, as seen in Figure 6.32. The lower values of M_s are due to the presence of the non-magnetic carbon atoms in the chemical composition of the reinforcement particles ($\text{Co}_{60}\text{C}_{40}$). It is well known that chemical composition and particle distribution can influence the saturation magnetization value as well as coercivity because they are very sensitive to non-magnetic phase, grain size, stress, and defects if any in the microstructure of the alloy. However, the presence of nonferromagnetic elements such as carbon in the chemical composition of the alloy reduces the ratio of cobalt atoms, and thus reduces the density of the magnetic atom interactions. As a result, the interchange interaction between the magnetic atoms is reduced and in the meanwhile the saturation magnetization decreases [55-57]. In other words, the increase of non-magnetic (carbon) will result in higher inner demagnetizing field, which causes lower magnetic induction and higher coercivity.

On the other hand, the variation in coercivity, H_c , with the volume fractions of the reinforcement amorphous particles ($\text{Co}_{60}\text{C}_{40}$) content is shown in Figure 6.33. The coercivity H_c , however initially increases from 12.75 kA/m to 14.82 kA/m on increasing the reinforced particles content from 0 to 1 vol.%, and then rapidly decreases from 14.82 kA/m to 7.69 kA/m with increasing the reinforced particles content to 2 vol.%, then after that continuously increases on further addition of the reinforced particles content to reach a steady trend even though with increase of the reinforcement content, as seen in Figure 6.33. The reasons behind this initial increase of H_c is not clear enough, but it could be the consequence of the formation of nanocomposite structure and it is most probably caused by the small grain size of the matrix (cobalt) after SPSed. Thus, reducing the grain size to the region of the domain wall width in the system increases the H_c towards the maximum controlled by the existing anisotropies in the system [58]. The coercivity is usually inversely proportional to the grain size; however, the results indicate a decrease in coercivity with decreasing grain size, as seen in Figure 6.33 when the reinforced particles content reaches 2 vol.%. Indeed, the rapid drop in the coercivity that observed with increasing the reinforced particles content to 2 vol.% is attributed to the decline of the local anisotropies and demagnetization effect of the individual grains, as shown in Figure 6.33, caused by the grain size decreasing to less than the exchange length L_{ex} [59-62]. In this case, definitely the magnetization does not follow the randomly oriented easy axis of the individual grains, but increasingly is forced to align parallel by exchange interaction [60 and 63]. However, with increasing the volume fraction of the reinforced particles, the size of the matrix grains decreases below L_{ex} and this is followed by aggregation of a large number of small ferromagnetically coupled grains, which largely eliminates the local anisotropy, so in this case the effective anisotropy energy is average over a number of grains [60, 62, and 64]. As a consequence of this decay of the local anisotropy, the coercivity values decrease considerably and compulsory [60, 62, and 64], which is shown in Figure 6.33.

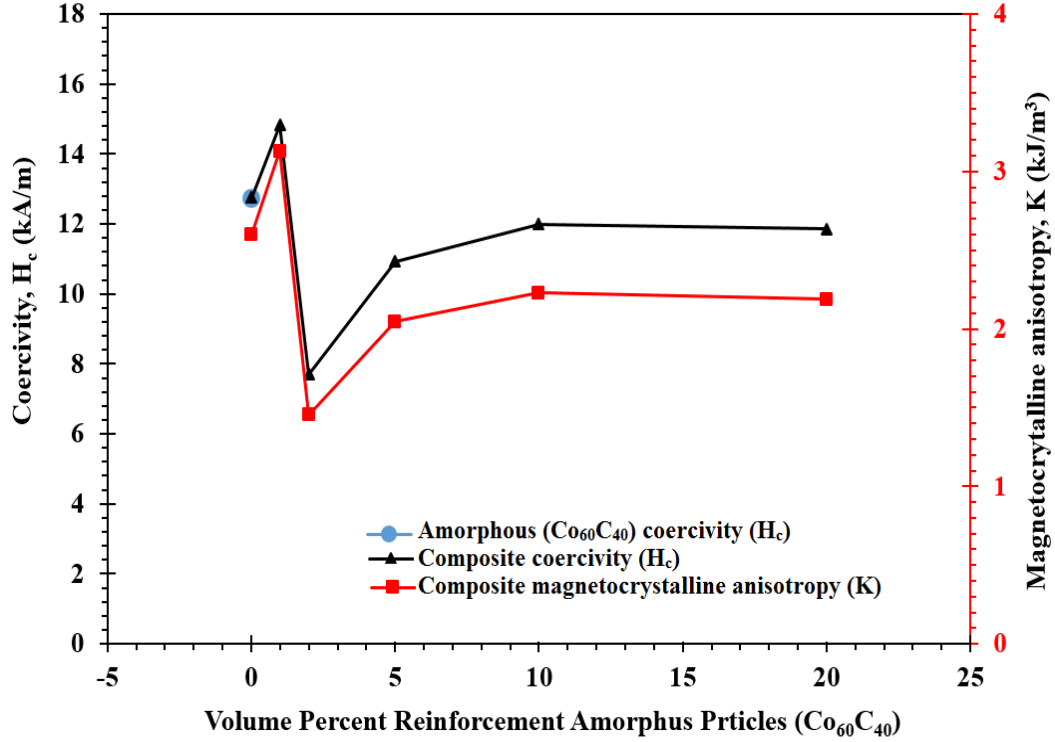


Figure 6.33: Variation of the room temperature coercivity, H_c , and magnetocrystalline anisotropy constant, K_1 , values plotted with respect to volume percent reinforcement amorphous particles (Co₆₀C₄₀).

Several previous theoretical models [59 and 60] were established to explain this behavior, where described in terms of anisotropy energy. For example, the random anisotropy model by Herzer [60] has been successfully explain the effective anisotropy even in the nanocrystalline systems. However, for the ferromagnetically coupled grain system, when the average size of magnetic grains D is a very small ($D < 100$ nm), the ferromagnetic exchange length L_{ex} will often be larger than the grain size D . Thus, the ferromagnetic exchange length L_{ex} can be given by Eq. 6.5:

$$L_{ex} = \sqrt{A/K_1} \quad \text{Eq. 6.5 [60]}$$

Where A is the exchange stiffness coefficient and K_1 is the magnetocrystalline anisotropy constant of an individual magnetic grain. According to the Stoner-Wohlfarth's theory, the coercivity H_c is linked with anisotropy constant K_1 and saturation magnetization M_s by the following relation Eq. 6.6:

$$H_c = 0.98K_1/M_s \quad \text{Eq. 6.6 [65, 66]}$$

However, the values of anisotropy constant K_1 of the SPS bulk Co/Co₆₀C₄₀ composite samples were determined by using the above relation (Eq. 6.6) and were plotted in Figure 6.32. Therefore, the ferromagnetic exchange length L_{ex} of the SPS bulk Co/Co₆₀C₄₀ composite samples could be directly calculated by following the relation (Eq. 6.5) and using exchange stiffness coefficient constant $A = 1.03 \times 10^{-11}$ J/m [67] and magnetic anisotropic constant K_1 from the relation (Eq. 6.5). Thus, the results illustrated that the exchange length L_{ex} value comprises between 53 nm and 78 nm for Co/Co₆₀C₄₀ bulk composite samples, which is in value higher than the measured ordered crystallite size, meanwhile the change in coercivity with crystallite size follows Néel's model. As a consequence, the effective anisotropy energy is averaged over a number of grains and is thus reduced in magnitude, as discussed and illustrated earlier. Therefore, with this anomalous behaviour of nanocrystalline magnetic materials, it was found that the coercivity appears to exhibit a D^6 dependence, which contrasts with the usual rule for polycrystalline magnetic materials, which are fundamentally based and follow a $1/D$ dependence. As has been discussed earlier, the Co/Co₆₀C₄₀ bulk composite samples have a crystallite size below 100 nm as shown in Scherrer's crystallite size calculations. So this may be the reason for some of the observed trends in coercivity; however, as can be seen in Fig.6.33, as the reinforced particles content increased, the coercivity values also increased. However, as Néel [68] pointed out in his work on the coercive field, the coercivity is directly proportional to the volume fraction of non-magnetic inclusions, therefore the agreement between Néel's results and this work results is systematically good, confirming that the increasing of the coercivity is a result of the increasing the reinforced particles content. According to Kersten [69] and Néel's [70] inclusion model, the presence of non-magnetic inclusions or voids become potential barriers and may lead to domain wall pinning by inhibition of nucleation and movement of the domain wall, during the magnetizing process, which may increase the coercivity. As a result, the internal stresses due to the presence of amorphous reinforcing particles (Co₆₀C₄₀) in the cobalt matrix lead to the domain wall pinning, thus increasing the coercivity and creating a trade-off between the decrease of coercivity due to the grain size and the increase due to the domain wall pinning as the volume fraction of reinforcement is increased, as seen in Figure 6.33.

The variation of Remanent Magnetization, M_r , and Remanent-to-Saturation ratio or Squareness ratio (M_r/M_s) with the volume fraction of the reinforcement amorphous particles (Co₆₀C₄₀) content

in SPS bulk Co/Co₆₀C₄₀ composite materials are shown in Figure 6.34. The remanent magnetization, M_r , however rapidly drops from 13.97 Am²/kg to 6.36 Am²/kg on increasing the reinforced particles content from 0 to 1 vol.%, and then continuously increases with further addition of the reinforced particles content to reach a steady trend even though on increase of the reinforcement content with values comprise between 7.39 and 7.97 Am²/kg, as seen in Figure 6.34.

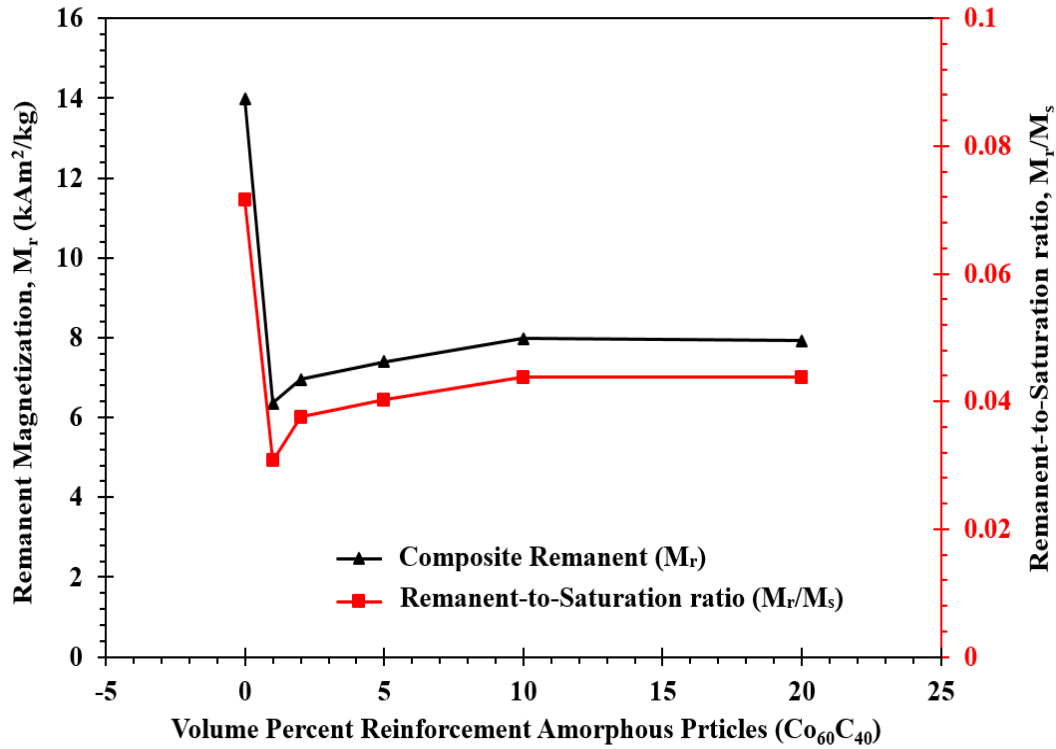


Figure 6.34: Variation of the room temperature remanent magnetization, M_r , and Remanent-to-Saturation ratio (M_r/M_s) values plotted with respect to volume percent reinforcement amorphous particles (Co₆₀C₄₀).

Since the magnet system is a nanoscale of a two-phase composite, the exchange coupling loss between the both neighboring magnetic grains phases leads to a decrease in the remanent M_r . Therefore, this rapidly dropping in the remanent (at 1 vol.% Co₆₀C₄₀) is due to the fact that the magnetization is following the randomly oriented easy axis of the individual grains controlled by the anisotropy field in the system (increasing in the anisotropy field, as shown in Figure 6.33), which results in the decrease in the remanent M_r due to which both exchange coupling and exchange interaction decreases [71 and 72]. On the other hand, as the volume fraction of the reinforced particles content increased continuously, the remanent very slightly increased in a

steady trend, which may be due to the slightly increase in the level of intergrain exchange coupling in the two phases, as show in Figure 6.34. This remanent M_r result presented an agreement with those results of coercivity, H_c , and magnetocrystalline anisotropy constant, K (see Figure 6.33). However, the exchange field from one matrix grain (Co) would land at another matrix grain (Co) located at the opposite side via the reinforcement amorphous particles grain ($\text{Co}_{60}\text{C}_{40}$) localized between them, and lead to coupling between grains of the magnetic matrix. Such a coupling will cause a rapid decrease in coercivity. It is clear that the result of Figure 6.33 supports the above argument.

In addition, the remanent-to-saturation ratio (M_r/M_s) has been calculated from magnetic parameters determined from hysteresis loop (Table 6.6). However, Figure 6.34 shows the plotting of the remanent-to-saturation ratio (M_r/M_s) for the SPS bulk Co/ $\text{Co}_{60}\text{C}_{40}$ composite materials. It can be observed from Figures 6.33 and 6.34, the variation of the remanent-to-saturation ratio (M_r/M_s) and remanent magnetization M_r with reinforcement particles ($\text{Co}_{60}\text{C}_{40}$) content exactly mimicked the coercivity H_c behaviour with reinforcement particles ($\text{Co}_{60}\text{C}_{40}$), which is an evidence for single-domain particle crossover to multi-domain particle behaviour [73]. However, the remanent-to-saturation ratio (M_r/M_s) is an indicative of domain structure and texture of magnetic materials. Therefore, the M_r/M_s value less than 0.5 is indicative of presence of multi-domain, randomly oriented assembly of spherical particles; while as lower values are usually associated with larger particles and domain-wall formation, and higher values with texture [74]. As can be seen from Table 6.6, the samples of the SPS bulk Co/ $\text{Co}_{60}\text{C}_{40}$ composites show that the M_r/M_s values are less than 0.5, indicating the formation of a multi-domain structure, therefore the prepared composites are in the multi magnetic domain.

6.4 Summary

In this study, metal matrix composites (MMCs) of the amorphous $\text{Co}_{60}\text{C}_{40}$ particles reinforced Co matrix composites were successfully synthesized using spark plasma sintering (SPS). The effect of amorphous $\text{Co}_{60}\text{C}_{40}$ particles content on the microstructural, mechanical and magnetic properties of the developed Co/ $\text{Co}_{60}\text{C}_{40}$ composites were investigated. The X-ray diffraction patterns of SPS bulk Co/ $\text{Co}_{60}\text{C}_{40}$ composite samples showed sharp Co (002) peaks with broad shoulders, which was interpreted to be representative of a presence of amorphous $\text{Co}_{60}\text{C}_{40}$ particles distribution; this was confirmed by the optical micrographs. Based on the optical microscopy

assays, microstructure of the SPS bulk Co/Co₆₀C₄₀ composite samples showed a uniform distribution of the amorphous Co₆₀C₄₀ particles in the Co matrix despite an increase in the volume fraction of the particle reinforcement. The experimental density of the composites showed a steady trend in the range of 81- 84% of the theoretical density value despite the increased content of reinforced (amorphous Co₆₀C₄₀) particles, indicating that the composites weren't fully dense. However, a substantial porosity is evident in the microstructures of all the samples, as confirmed by the optical micrographs and this due to insufficient sintering temperature (350°C) during the sintering process. Overall, this data also seems to confirm at least the approximate accuracy of the calculated theoretical density, with most of the values falling in the same range of 81 and 84%, indicating fairly acceptable densification. The magnetic properties measurements also were performed using VSM analysis which showed that the saturation magnetization and coercivity of the composites decrease slightly with an increase in the reinforcement content until a steady trend is reached despite the increase in the reinforcement content. Moreover, the mechanical properties of the composites also were studied. The composites showed significant improvement in hardness test as the volume fraction of the amorphous Co₆₀C₄₀ particles reinforcement increased. However, the Co/Co₆₀C₄₀ composites exhibited considerably higher hardness than pure cobalt, with an increase of 104% HV between the pure cobalt samples and the reinforced composites by 20 vol.%. The strengthening model contribution calculations for amorphous particulate reinforced crystalline cobalt matrix confirm that strengthening is strongly dependence on the interparticle spacing. However, the increment of the strength due to direct contributions of the reinforcement caused by the interaction of dislocations with the particles was found to increase linearly with the inverse square root of the edge-to-edge interparticle spacing. Therefore, intrinsic high hardness, strength, and elastic limit of the reinforcement contributed towards the remarkable improvement in the mechanical properties of the Co/Co₆₀C₄₀ composites. Consequently, amorphous metallic particles are promising as reinforcement materials for metal matrix composites, which can effectively replace conventional ceramic reinforced metal composites.

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7. Summary and Contributions

7.1 Summary

The primary objective of this research was to investigate and characterize the solid state interaction between the elemental powders of Co and C during high-energy ball milling in order to understand their chemical composition influence on the amorphization process of Co-C alloys. Meanwhile, as an integral part of the strategy of this project, the magnetic properties of these mechanically alloyed Co-C alloys were also studied in an attempt to better understand the soft magnetic properties of these mechanically alloyed Co-C amorphous alloys. In addition, metal matrix composites (MMCs) of a Co-matrix with mechanically alloyed amorphous of $\text{Co}_{60}\text{C}_{40}$ particles were synthesized and investigated to also better understand the behavior and properties of the composite.

In order to complete this task, elemental Co and C powders with various chemical compositions up to 40 at% C were mechanically alloyed in a SPEX mill with WC grinding media for periods ranging from 5 to 40h. The mechanically-alloyed powders were then characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). Further, compositions of 1, 2, 5, 10 and 20 vol.% C mechanically alloyed powders of $\text{Co}_{60}\text{C}_{40}$ that had prior milled for 40h were subsequently blended in an attritor mill for 2h with a pure cobalt matrix to produce amorphous Co-C-reinforced crystalline Co-matrix composites powders. The composite powders further consolidated by spark plasma sintering (SPS) to produce bulk composites of Co-C/Co and then characterized. This characterization included X-ray diffraction (XRD), differential scanning calorimetry (DSC), optical microscopy, scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), density measurements and Vickers hardness testing.

From the experimental and analytical results presented in the body of this dissertation, the following conclusions may be drawn. Amorphous Co-C alloys with compositions of up to 40 at% C were successfully synthesized from elemental Co and C using a mechanical alloying procedure. Traces of an amorphous phase were present in the Co-C alloys, where the amorphous phase was observed through XRD, DSC and TEM analysis of the alloys with low and high C content. It was

also found that the mechanically alloyed Co-C alloys with high C contents (≥ 10 at.% C), after milling for 40h, exhibited a complete amorphous phase transformation, while the low C compositions (≤ 5 at.% C) showed a composition of nanocrystals embedded in an amorphous matrix. DSC results showed that the crystallization of the amorphous mechanically alloyed Co-C powders essentially depended upon the carbon content. However, the crystallization reaction of high C compositions (≥ 20 at.% C) underwent a one-stage crystallization mechanism, with the consequences of this reaction was the precipitation of very small crystalline particles of the fcc cobalt phase with some concomitant hcp phase, and amorphous carbon. In contrast, in the low C compositions (≤ 20 at.% C), the crystallization reaction consisted of a two stage mechanism which was confirmed by the presence of two exothermic peaks in the respective DSC analysis. The first exothermic peak was the primary crystallization stage (stage I) which corresponds to the formation of the metastable phase of Co carbides and the second exothermic peak was the secondary crystallization stage (stage II), which corresponded to the decomposition of the metastable phase of the Co carbides and crystallization the remaining of the Co amorphous. Thus, the crystallization reaction ends up with the formation of fcc cobalt with a concomitant hcp phase and graphite. Finally, the formation of the metastable phases of Co carbides was shown to strongly depend on the amount of the C content. However, according to the Co carbide formation mechanism, at a very low Co content (≤ 5 at.% C), the metastable phase of Co carbide Co_3C would most likely form, whereas by increasing the Co content (> 5 to 20at.% C), the metastable phase of Co_2C became most likely to form.

The magnetic properties of the mechanically alloyed Co-C alloys were also studied using a vibrating sample magnetometer (VSM). The results of such study showed that the mechanically alloyed Co-C was also substantially dependent on the chemical composition and milling time. However, the values of the saturation magnetization, M_s , decreased gradually with increasing C content as well as milling time and so the drop in M_s was drastically from 195 Am^2/kg for un-milled pure Co to between 178 and 44 Am^2/kg after 40h of milling. While the coercivity, H_c , exhibited a reduction in the values from 12.7 kA/m for un-milled pure Co to between 7.5 and 1.3 kA/m when the C content is less than 15 at.%, and then gradually increases as the amount of C increases. Overall, the remanent-to-saturation ratio, M_r/M_s , of the Co-C mechanically alloyed powders showed very small values, especially the low C compositions, where these low values are related to the demagnetization effects as well as to the presence of fine, single-domain particles.

Lastly, mechanical alloying was used successful in producing a uniformly dispersed particles amorphous of $\text{Co}_{60}\text{C}_{40}$ reinforced the Co matrix composite. Further, evidence of such particles was seen in XRD of the SPS bulk Co/ $\text{Co}_{60}\text{C}_{40}$ composite, and by optical micrographs. However, the SPS bulk Co/ $\text{Co}_{60}\text{C}_{40}$ composites exhibited a uniform microstructure with uniform reinforcement distribution despite increased the volume fraction of the particle reinforcements (particles amorphous $\text{Co}_{60}\text{C}_{40}$). Densities of composite samples showed a steady trend in the range of 81- 85% of the theoretical value despite the increased content of the reinforcing particles, indicating that the composites were not fully dense. The magnetic measurements of the composites showed a slight decrease in the M_s and H_c values with an increase in the reinforcement content and reaching a steady trend despite the increase in the reinforcement content. In contrast, the hardness of the composite samples exhibited a significant improvement as the volume fraction of the amorphous $\text{Co}_{60}\text{C}_{40}$ particles increased. However, the hardness test measurements showed considerably higher values than the pure Co, with an increase of 104% HV between the pure Co samples and the reinforced composites by 20 vol.%. The strengthening model calculations for amorphous particulate reinforced crystalline Co matrix confirm that strengthening is strongly dependent on the interparticle spacing. The increment of the strength due to direct contributions of the reinforcement caused by the interaction of dislocations with the particles was found to increase linearly with the inverse square root of the edge-to-edge interparticle spacing. Thus, amorphous metallic particles are promising as reinforcement materials for metal matrix composites, which can effectively replace conventional ceramic reinforced metal composites.

7.2 Contributions

The major contributions of this dissertation are mentioned below:

- 1- The use of mechanical alloying completely amorphize Co-C alloys with low carbon compositions, all the way down to 10 at.% C.
- 2- Amorphous Co-C alloy particles efficiently strengthens Co matrix via the boundary strengthening mechanism. The similarity in their chemistry allows for stronger interfacial bonding, a place where there are issues with the ubiquitous ceramic-based reinforcement materials.
- 3- The production of a map that explains the thermal effects on Co-C alloys amorphized by mechanical alloying for compositions up to 40 at.% C. This will be for the thermal

processing of Co-C amorphous alloys and the designing for their potential helpful application at elevated temperature.