Processing and Characterization of Cr-Cu Alloys through Liquid Phase Sintering for Vacuum Circuit Breakers

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Abstract

Powder metallurgical processing of Cr-Cu has advantages over other processes. Vacuum Cirbuit Breakers are well known as vacuum interrupters (VI). The essential properties required for materials used in VI are high electrical conductivity, good skeleton strength and spark erosion resistance. The effect of sintering temperature, compaction pressure and composition on microstructure, sintered density, mechanical properties (tensile strength, hardness) electrical conductivity and skeleton strength of Cu-Cr contacts was investigated. The effect of microstructure on net-shape consolidation and macrostructure evolution during sintering are also detailed. Liquid phase sintering of Cr-Cu alloys resulted in better density without any significant shape distortion. Tensile strength increased with compaction pressure and chromium content. Higher compaction pressure also led to increased bulk hardness. Electrical conductivity increased with increasing compaction pressure and Cu content.

Keywords: Cr-Cu, liquid phase sintering, vacuum interrupters

1. Introduction

In power delivery engineering, cronium-copper (Cr-Cu) powder metallurgy (P/M) contact materials developed in the past have been widely accepted for medium-voltage, high-current vacuum circuit breakers (VCB) or vacuum interrupters (VI).[1-3] Based on processing, there are two main groups of Cr-Cu contact materials: one is synthesized by powder metallurgy (either by infiltration or sintering), and the other is by vacuum induction melting (VIM) and casting[2] or surface alloying.[3] In spite of other processing routes, powder metallurgical processed Cr-Cu contact materials have more than half share of the VI market. In Cr-Cu, Cu acts as an electric conductor and Cr serves the purpose of giving strength and erosion resistance to the whole material. Cr also initiates the breakdown for the circuit because of its low dielectric strength.[1] Microstructure plays an important role during breakdown.

Even though infiltration (powder metallurgical process) is a well established technique for Cr-Cu vacuum interrupters, it is not economical because the material has to be machined to the net shape. Our objective is to process these materials by a sintering technique, which is economic and saves the time in machining. For our experimental studies, we took two different compositions (wt%) 50Cu-50Cr and 75Cu-25Cr and three different temperatures 1100 °C, 1200 °C and 1400 °C.

2. Powder Characterization

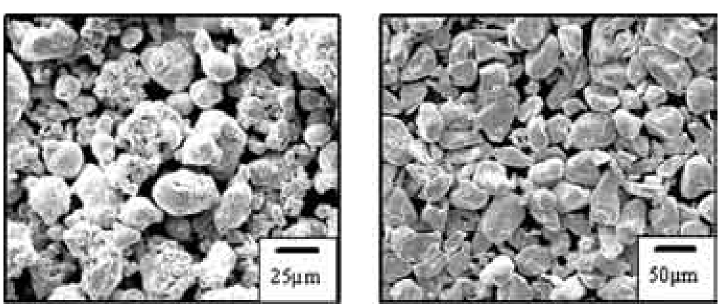
The as-received powder was characterized using scanning electron microscope (SEM) for the morphological studies, as shown in Figure 1. Figure 1a) revealed the presence of pores in the Cu powder which was well understood with the gas atomization process. Figure 1b) shows the chromium powder, which was produced by a reduction process followed by milling. Energy Dispersive X-ray Analysis (EDAX) analysis, to analyze the elemental composition of the powders, shows the presence of oxygen (2.5 wt%) in copper powder (Table 1). The powder size distribution was obtained by using MALVERN Instruments particle size analyzer which works based on the principle of laser diffraction. Apparent density and flow rate of the powders were experimentally measured by using a Hall-flow meter. In addition to the above analysis, specific surface area of powders was measured by using a BET.

2. Experimental Procedure

For the present investigation, copper and chromium powders were supplied by Crompton Greaves Ltd., Mumbai (India). The composition and characteristics of the as-received chromium and copper powders are presented in Table 1. The chromium and copper composites (with 50 and 25 wt% Cr) were prepared by mixing in a Turbula mixer (model: T2C, supplier: Bachoffen, Basel, Switzerland) for 2 hours. The mixed powders were uni-axially compacted at 200 MPa and 600 MPa using a semi-automatic hydraulic press (model: CTM-50, supplier: FIE, Ichalkaranji, India) with a floating die. All the powder mixes were pressed into cylindrical pellets (12 mm diameter and 6 mm height) and tensile bars, as illustrated in Figure 2, to different green densities, which are shown in Table 2. Zinc stearate was used as die wall lubricant during compaction to minimize friction. Sintering was carried out in a $MoSi_2$-heated horizontal tubular furnace (model: OKAY 70T-7, supplier: Bysakh, Kolkata, India). The samples were heated at a constant rate of 5 °C/min in pure hydrogen atmosphere (dew point: -35 °C). The compacts were liquid phase sintered at 1100 °C, 1200 °C and 1400 °C respectively. The sintered density was measured through dimensional measurements and by using Archimedes' principle. The densification response was expressed numerically in terms of densification parameter, which is shown in Equation 1.

$$\text{Densification parameter} = \frac{(\text{sintered density - green density})}{(\text{theoretical density - green density})} \quad (1)$$

The sintered compacts were prepared for metallographic study without using any etching reagent. The microstructural observations and quantitative analysis were carried out using an optical microscope (model: Q5001W, supplier: Leica Imaging System Ltd., Cambridge, UK) attached to a computer. After the metallographic studies, hardness of the composites was measured by using a Vickers hardness tester (supplier: Blue Star, Mumbai, India) at a load of 5 kg using a diamond indenter. Composites were measured for electrical conductivity using a digital electrical conductivity meter (supplier: TechnoFour, Pune, India) with the advantage of the Weidmann-Frenz Law; thermal conductivity of composites was obtained from the electrical conductivity. For measuring the chromium skeleton strength, copper was removed by dissolving the sample in 70% nitric acid (HNO_3). Finally, segregation studies were done by analyzing the change of microstructure throughout the cross section of the composite. Tensile testing of the samples was done by hydraulic assisted automatic tensile testing machine, at 10 kN load and with a head speed of 5 mm/min.



a) b)

Figure 1. Scanning electron micrographs of as-received: a) copper and b) chromium powders

Table 1. Characterization of the powders in as-received condition used in the present study

	Chromium	Copper
Particle size (µm)		
D_{10}	18.9	23
D_{50}	35	52
D_{90}	58	114
Apparent Density (g/cc)	2.91	2.89
Flow rate (s/50g)	47	29
Specific surface area (m^2/g)	0.219	0.145
Theoretical density (g/cc)	7.14	8.9
Melting point (°C)	1907	1083

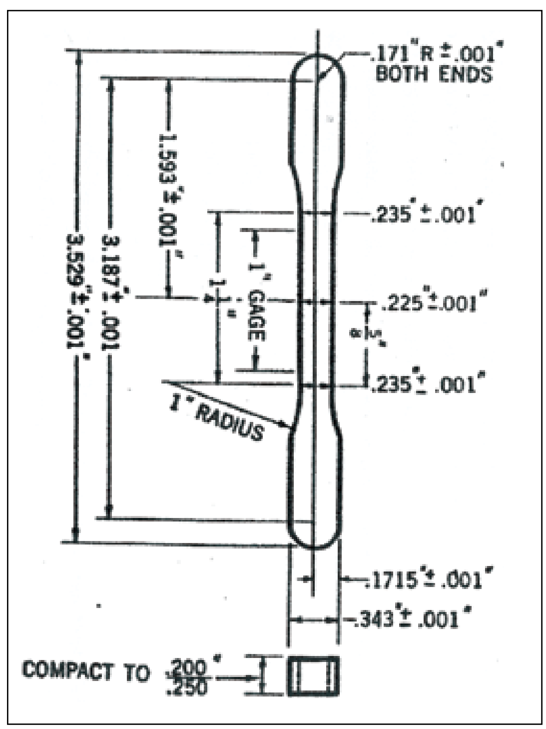


Figure 2. Dimensions of the tensile bar used for present study

3. Results and Discussions

Figure 4 shows the effect of sintering density variation with the compaction pressure and the temperature. Except for the 75Cu-25Cr composite compacted at 600 MPa and sintered at 1400 °C, all other composites show improvement in sintered density with higher compaction pressure and higher sintering temperature. When the composites were compacted at 600 MPa, the number of contacts it makes with the nearby particles is increased. This improves contacting surface area, which makes the diffusion better. There are two mechanisms by which densification occurs: one is capillary induced pore filling by the liquid melt, and the other is dissolution-reprecipitation. In liquid phase sintering, a liquid melt is formed and fills the pores present by capillary action. The grains also dissolve in the liquid melt and reprecipitate as bigger grains, leading to Ostwald ripening. The final sintering response depends on the dominant mechanism by which densification takes place at particular conditions. It is clear from the Cr-Cu phase diagram (Figure 3), that with the increase of temperature from 1100 °C to 1400 °C, the chromium solubility in copper increases. At all temperatures (1100 °C to 1400 °C), the chromium solubility in copper is more than the copper solubility in chromium. If this is not the case, liquid phase sintering does not yield densification. Instead, it results in swelling because more liquid copper goes inside the chromium

Table 2. Green density of various composites compacted at different compaction pressures

Composition	Pressure (MPa)	Green density (g/cc)	Green density (%th.)
50Cu-50Cr	200	5.62	70.64 ± 0.2
	600	7	87.7 ± 0.9
75Cu-25Cr	200	6.09	72.49 ± 0.1
	600	7.58	90.27 ± 0.2

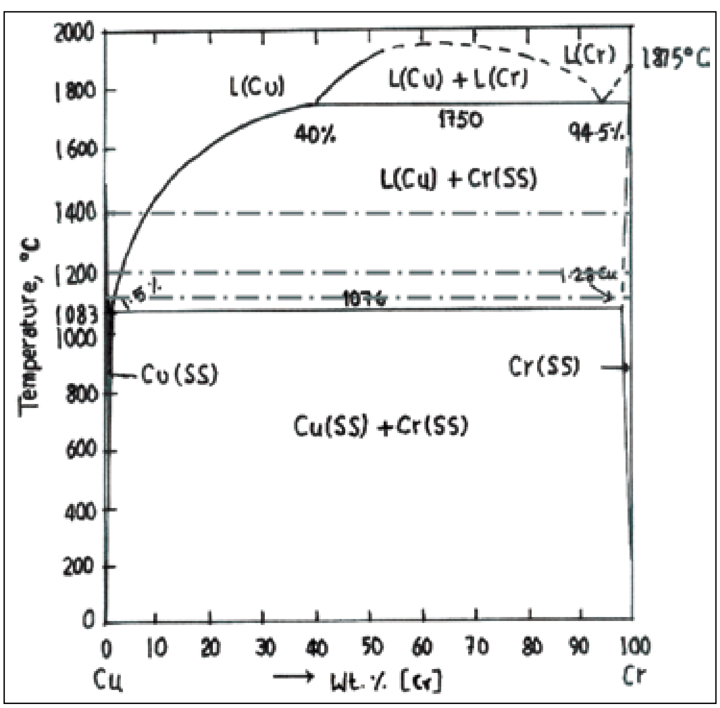


Figure 3. Cr-Cu phase diagram [wt. %]

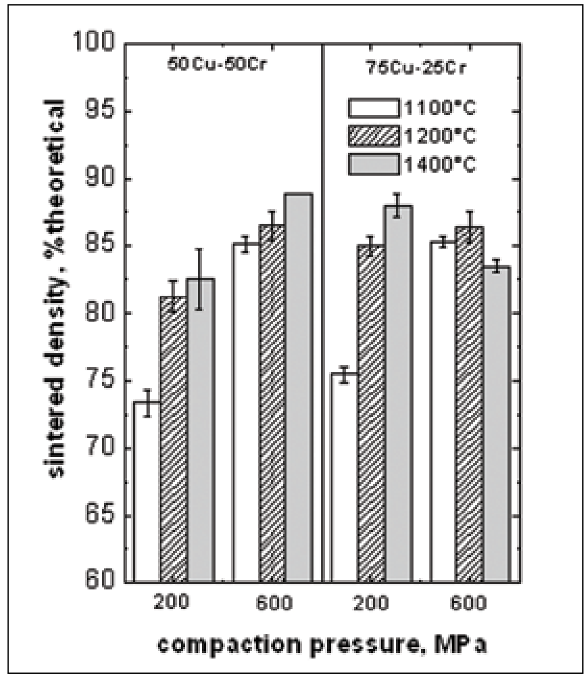


Figure 4. Sintered density at different tempera-

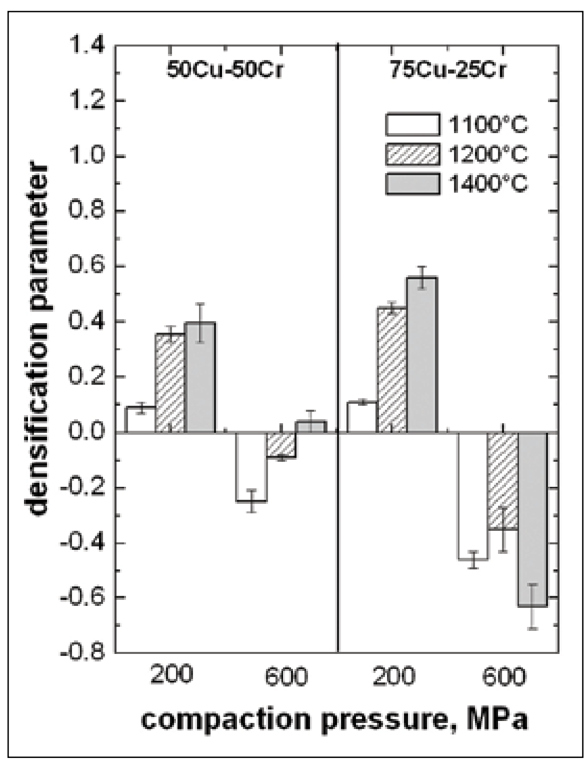


Figure 5. Densification parameter at different temperatures for different Cu-Cr composites

solid solution. When the temperature is lowered, the solubility decreases, and the copper comes out leaving pores in chromium solid solution, hence leading to swelling. The solubility limit of chromium and copper in each other, at different temperatures, is tabulated in Table 3.

At higher temperatures, as the solubility also favors the dissolution-reprecipitation mechanism, it can also contribute to the enhancement of densification. As the copper powder is processed by the gas atomization technique, it inherits some oxygen, which causes the swelling of the compact, mainly when sintering is carried out in a hydrogen atmosphere. Compacts pressed at 200 MPa can easily accommodate the swelling of the powders compared to those pressed at 600 MPa because of a higher volume fraction of pores. This swelling is predominant for the compacts pressed at higher pressures (600 MPa). From Figure 5, it is clearly visible that the compacts pressed at 600 MPa show a negative response to densification. In spite of a negative densification parameter, final sintered density is better at higher sintering temperatures and higher compaction pressures.

Figure 6 shows the optical microstructures of 50Cu-50Cr pressed at 200 MPa, 600 MPa and sintered at different temperatures. It is evident from the figure that increasing the compaction pressure increases the contiguity and connectivity, shown in Figure 6b. This is because of increased number of contacts at higher compaction pressure, which leads to better diffusion through them. Higher sintering temperature leads to the improvement in shape factor (roundness) of chromium grains due to enhanced solubility at higher temperature. When the solubility is high, the sharp edges of the chromium dissolve in copper and reprecipitate at other areas. Because of this high solubility, grain coarsening is observed at higher temperature. This phenomenon is also called Oswald ripening. With the combined effects of higher pressure and higher temperature, the quantity of open porosity decreases and the solid phase becomes more rounded. Figure 7 shows the optical microstructures of 75Cu-25Cr composites. In this case, temperature and pressure have a similar effect as with 50Cu-50Cr. As the copper content is higher in this case, roundness of the chromium grains is improved.

Variation of hardness for different composites sintered at different temperature is shown in Figure 8. Higher compaction pressure results in higher hardness, which could be because of a more contiguous microstructure of chromium phase.

Figure 9 shows the stress-strain curves for the Cu-Cr composites sintered at 1100 °C. A slight deformation in shape was observed at higher sintering temperatures due to the liquid phase sintering. This deformation makes the samples unsuitable for tensile testing. The measurements obtained from the curves are shown in Table 3. Composites which were pressed at 200 MPa showed less strength and elongation as compared to 600 MPa, due to the lower sintered density and relatively lower contiguous microstructure in the former one. Composites containing higher copper content resulted in high ductility, because the copper phase is softer. Because the chromium content is high in 50Cu-50Cr alloy, it resulted in a higher young's modulus.

Figure 10 shows the electrical conductivity variation of the all the composites. It is clear that, except for the 75Cu-25Cr pressed at higher pressure and sintered at 1400 °C, all the composites follow the same trend as density (Figure 3). When the copper fraction of composite increases, there is an enhancement in

Table 3. Solubility limits of Cu in Cr and Cr in Cu at different temperatures

Temperature (°C)	Cr(Wt.%) in Cu	Cu(Wt.%) in Cr
1100	1	1.2
1200	3.3	1
1400	8	0.68

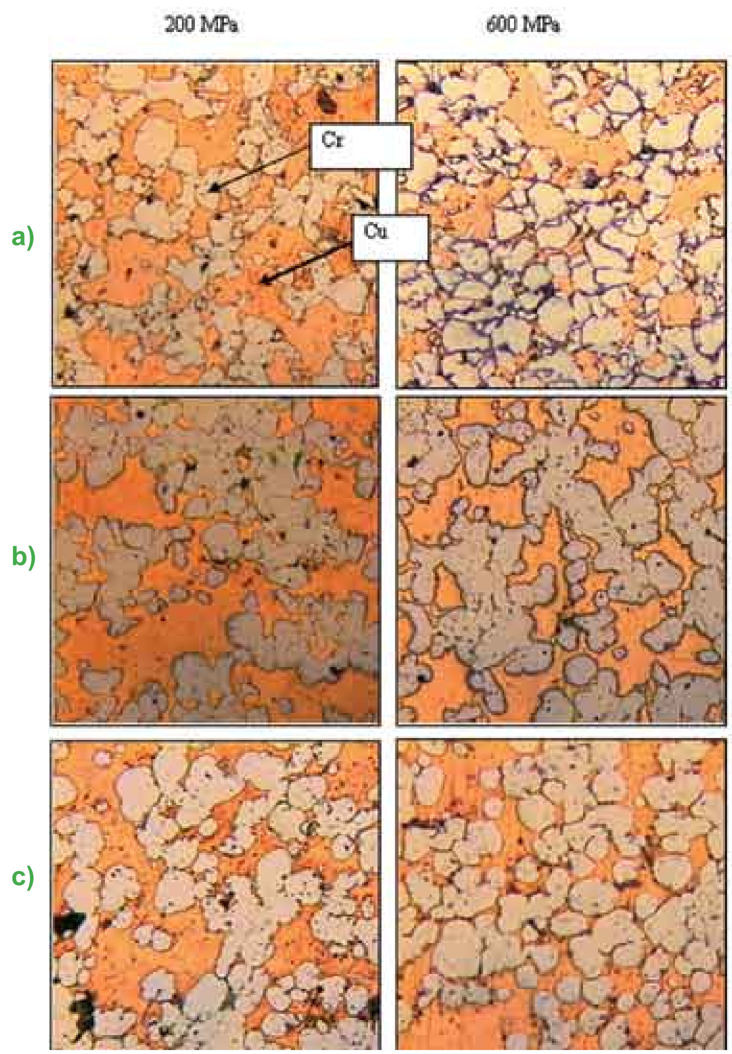


Figure 6. Optical microstructures of 50Cu-50Cr composites sintered at a) 1100 °C, b) 1200 °C and c) 1400 °C which were compacted at 200 MPa (left) 600 MPa (right)

electrical conductivity, because copper is the main constituent contributing to electrical conductivity. As thermal and electrical conductivity are related to the motion of electrons, thermal conductivity can be obtained from the electrical conductivity by using the Wiedemann-FranzLaw.

$$\frac{k}{\sigma} = LT \tag{1}$$

$$L = \frac{\Pi^2 k^2}{3e^2} \tag{2}$$

k = Boltzman's constant ($1.38 \times 10^{-23} JK^{-1}$)
e = electron charge (1.6×10^{-19} C)
T = temperature (K)
σ = electrical conductivity ($ohm^{-1}m^{-1}$)
100% IACS = $58*10^6\ \Omega^{-1}m^{-1}$
K = thermal conductivity ($Wm^{-1}k^{-1}$)
L = Lorentz Number (unitless)

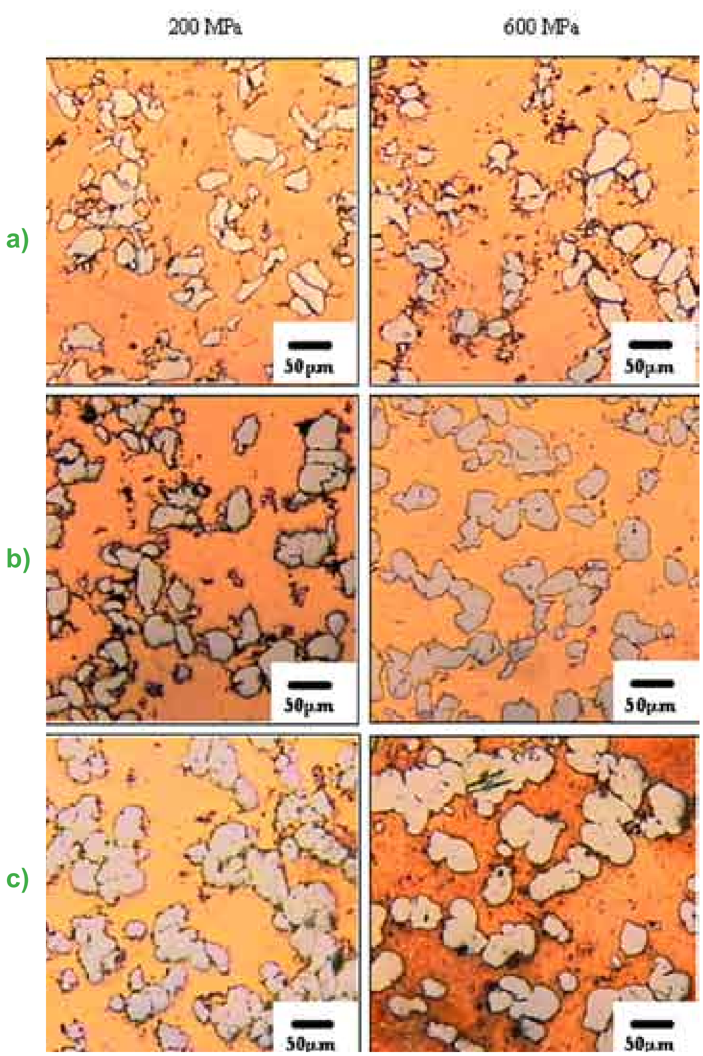


Figure 7. Optical microstructures of 75Cu-25Cr composites sintered at a) 1100 °C, b) 1200 °C and c) 1400 °C which were compacted at 200 MPa (left) 600 MPa (right).

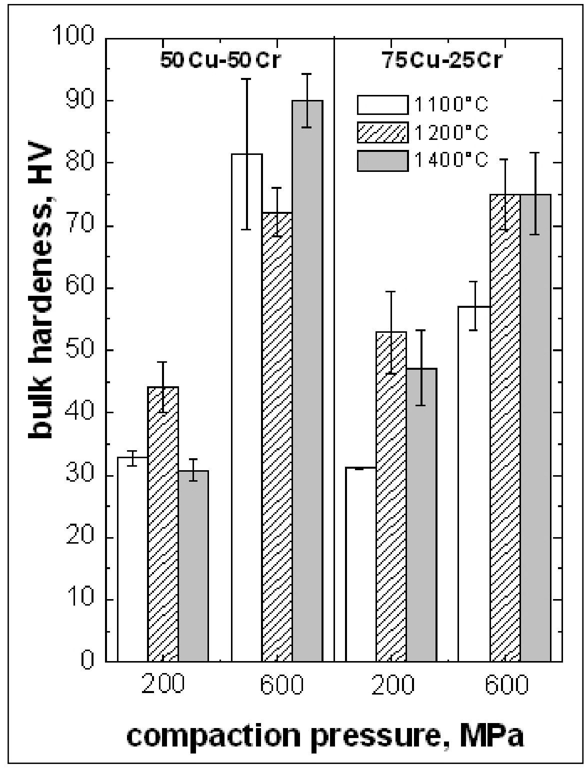


Figure 8. Optical microstructures of 75Cu-25Cr composites sintered at a) 1100 °C b) 1200 °C and c) 1400 °C which were compacted at 200 MPa (left) 600 MPa (right)

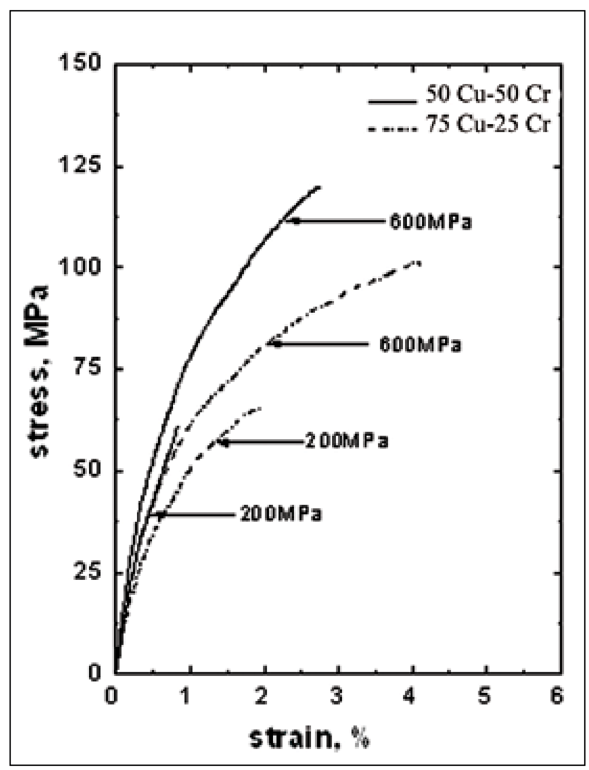


Figure 9. Stress-Strain curves for different Cu-Cr composites sintered at 1100 °C

From the above formulas (Equation 2 and 3), it is well understood that thermal conductivity is directly proportional to electrical conductivity. The obtained thermal conductivity is shown in Figure 11.

4. Conclusions

For optimized sintering, the compaction pressure and the sintering temperature should be high so that it leads to higher densification. However, too high sintering temperatures can lead to shape distortion, segregation, and grain growth. Also, high copper content leads to higher electrical conductivity but lower skeleton strength, so the proportion of copper and chromium should be determined in function of desirable properties. Below is a summary of how properties varied with change in processing conditions:

- Liquid phase sintering of Cr-Cu alloys resulted in better density without any significant shape distortion
- Sintered density increased as sintering temperature increased
- Tensile strength increased with compaction pressure and chromium content
- Bulk hardness increased with compaction pressure
- With increasing compaction pressure and copper content, electrical conductivity increased

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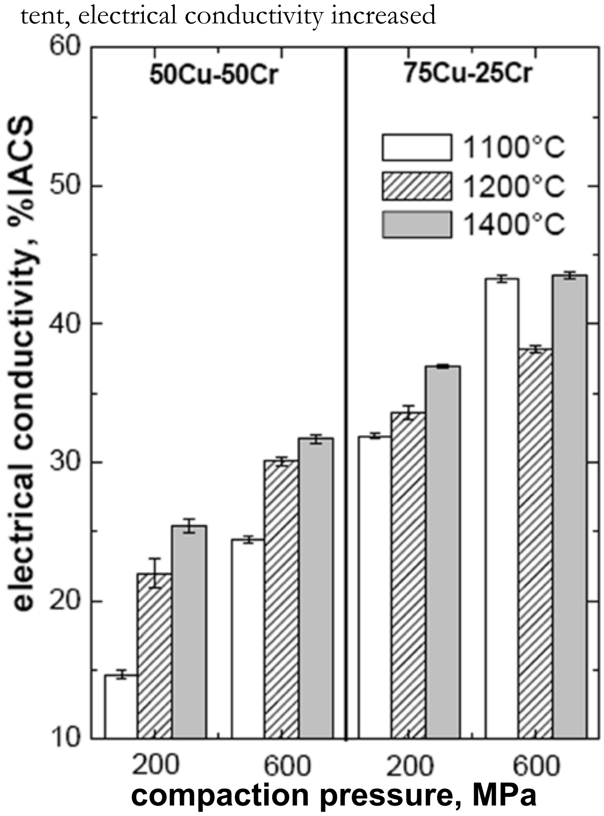

Figure 10. Electrical conductivity variation for different Cu-Cr composites at different temperatures

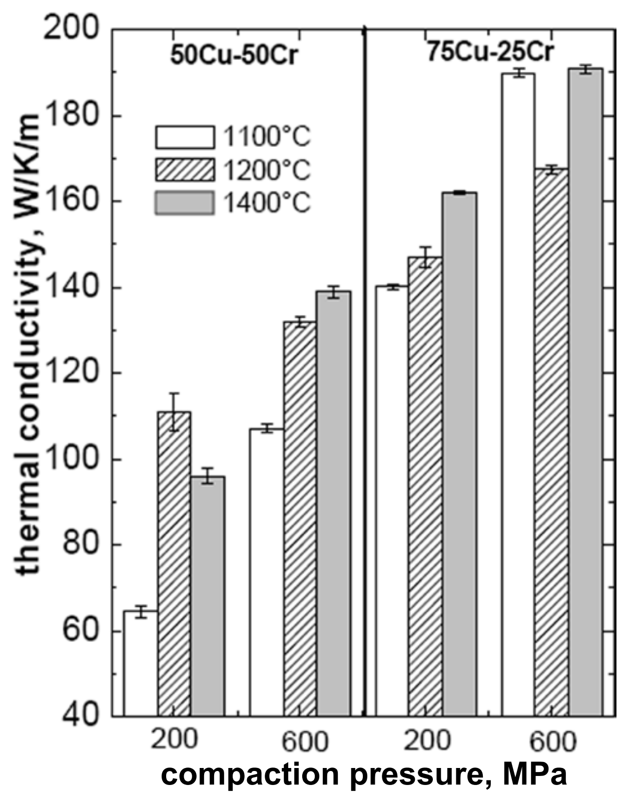

Figure 11. Thermal conductivity variation for different Cu-Cr composites at different temperatures