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Mechanical alloying of Sm and Fe with the composition of $SmFe_3$ was studied using x-ray-diffraction (XRD), Mössbauer, and magnetization measurements. Data taken as a function of milling time for up to 20 h show significant changes occurring during ball milling. The XRD studies show that the initial crystalline Bragg reflections changed to a broad maximum, which is attributed to the formation of an amorphous phase. The initial six-line pattern in the Mössbauer spectrum, characteristic of magnetic ordering, changed to a broad singlet, characteristic of a nonmagnetic material. Magnetization measurements revealed that the coercive field was at its maximum after 5 h of milling and decreased sharply as the milling time increased. The remanent magnetization was at its maximum between 5 and 10 h of milling. The final product of the ball milling, which exhibited the characteristics of an amorphous paramagnetic material in its XRD and Mössbauer spectrum, was studied after heat treatment. The XRD and the Mössbauer spectra of the heat treated alloy show that substantial changes occurred during heat treatment in that sharp Bragg reflections, characteristic of crystalline materials, reappear and the alloy changed from a paramagnetic to a ferromagnetic state. © *1997 American Institute of Physics.* [S0021-8979(97)32008-8]

I. INTRODUCTION

Mechanical alloying has been used during the last few years to prepare a variety of application related magnetic materials.[1-5] This technique also allows one to prepare amorphous materials in compositional ranges that cannot be prepared by conventional means.[6] Interest in studying the Sm–Fe system is related to its role as a precursor of Sm–Fe based magnetic materials, which constitute a very promising alternative to traditional permanent magnetic materials.

A review of the intrinsic magnetic properties of $REFe_3$ (where RE denotes rare earth) is given by Buschow.[7] The Curie temperature of $SmFe_3$ is about 380 °C with a saturation magnetization of $4.5\mu_B$. The easy magnetization direction is along the c axis over the whole ferromagnetic temperature range, as determined by Mössbauer spectroscopy.[8] The $SmFe_3$ phase crystallizes in the hexagonal $PuNi_3$ structure (space group $R\bar{3}m$) which consists of an alternate stacking of three $RETM_5$ ($CaCu_5$ type) and three RE_2TM_4 (Laves-phase type) layers[9] (where TM denotes transition metal).

The goal of this work is to prepare, characterize and measure the magnetic properties of mechanically synthesized $SmFe_3$. X-ray diffraction (XRD) was used to measure long-range atomic ordering, while Mössbauer measurement was used to sense the immediate environment of the absorbing nucleus. The 14.4 keV gamma ray in ^{57}Fe was used as a probe to follow the mechanical alloying process. The XRD and the Mössbauer spectra indicate that the mechanically alloyed $SmFe_3$ became amorphous and paramagnetic after 20 h of milling. Heat treatment at 650 °C for 1 h changed it back to a crystalline, ferromagnetic α-Fe phase and an unidentified crystalline phase.

II. EXPERIMENT

The starting materials used for mechanical alloying were elemental powders of α-Fe having a purity of 99.9% and particle size 300 μm, and Sm having a purity of 99.9% and particle size 44 μm. The elemental powder of α-Fe and Sm was mixed in the proportions $SmFe_3$. High-energy ball milling was carried out for up to 20 h in an argon atmosphere using a SPEX 8000 mixer/mill and stainless-steel balls and a container with a ball-to-powder ratio of 4 to 1. A small amount of reaction product was removed from the vial for analysis at various intermediate stages in the milling process. A sample of the 20 h milled product was annealed at 650 °C for 1 h in an Ar atmosphere and was cooled to room temperature in an Ar atmosphere for analysis.

X-ray analysis of the samples was made on an x-ray powder diffractometer with 2θ geometry using Cu $K\alpha$ radiation. Mössbauer measurements were performed in standard transmission geometry and at constant acceleration using a 25 mCi ^{57}Fe source in a Rh matrix. The absorber, a pellet 2 mm thick and 20 mm in diameter, was a mixture of the powder sample and anhydrous dextrose mixed at room temperature. Evaluation of the sampled data was done using a least-squares-fit program assuming Lorentzian line shape with a parabolic baseline. Magnetic measurements were performed with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design model MPMS). All measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

A. Sample characterization

The XRD patterns obtained after 1, 3, 5, and 10 h of milling are shown in Fig. 1. The line intensity of α-Fe at
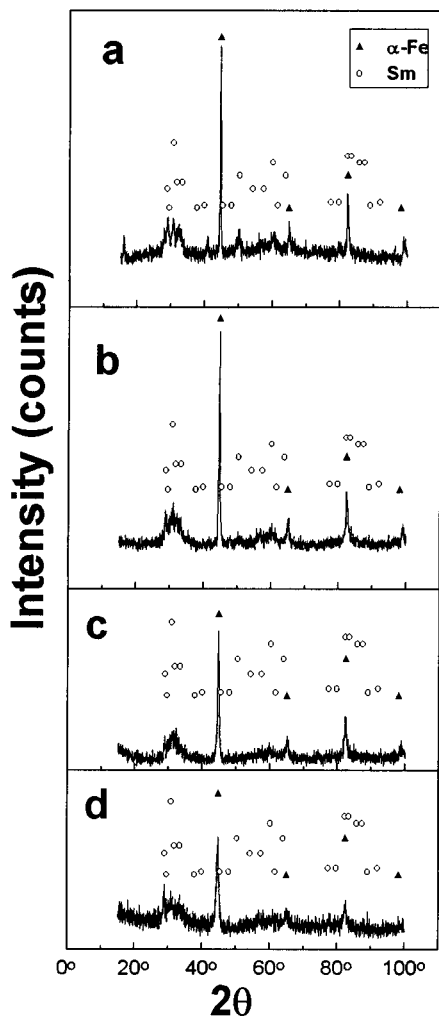
FIG. 1. X-ray-diffraction patterns of mechanically alloyed Sm and Fe (a) milled for 1 h, (b) milled for 3 h, (c) milled for 5 h, and (d) milled for 10 h.

44.7° decreased with milling time indicating a reduction in the amount of pure α-Fe present. A small increase in the line broadening with milling time is also observed, which is due to smaller particle size. Figure 2(a) shows the XRD pattern of the 20 h mechanically alloyed SmFe$_3$. The diffractogram of the 20 h milled sample shows a broad line indicating the absence of a crystalline phase. Figure 2(b) shows the XRD of the 20 h milled sample after heat treatment at 650 °C for 1 h;
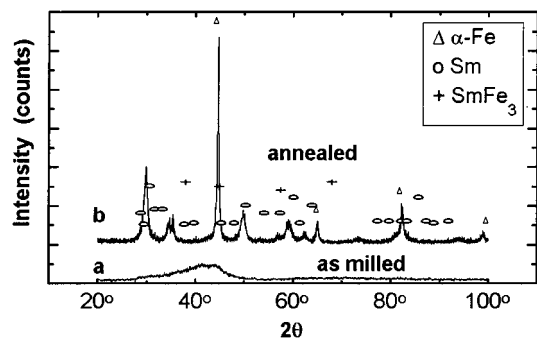

FIG. 2. X-ray-diffraction patterns of mechanically alloyed Sm and Fe milled for 20 h (a) as milled, (b) annealed for 1 h at 650 °C.
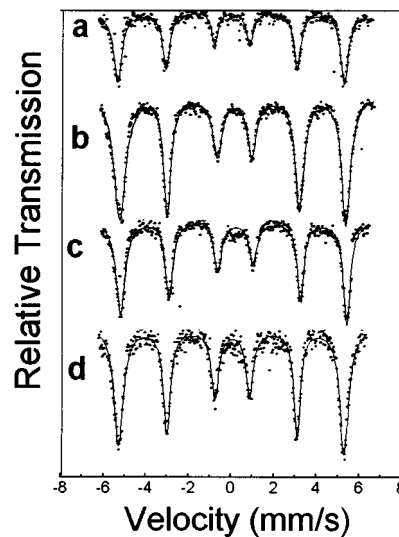

FIG. 3. Mössbauer spectra of mechanicaly alloyed Sm and Fe (a) milled for 1 h, (b) milled for 3 h, (c) milled for 5 h, and (d) milled for 10 h. The solid lines are Lorentzian fits.

sharp diffraction lines are observed, corresponding to well-crystallized alloys. From the XRD spectra it can be concluded that the material formed by mechanical milling is an amorphous alloy which crystallizes during annealing at 650 °C. Since amorphous alloys are stable only below the glass transition temperature T_g, a requirement for the formation of amorphous alloy by mechanical milling is that the milling take place below T_g. For pure iron, T_g is far below room temperature; therefore, one or more other elements must be present in order to stabilize the amorphous structure at room temperature. As shown by Shaaf et al.[10] prolonged milling transforms pure α-Fe to nanocrystalline state, but never to an amorphous phase. In this work the Sm atoms served as a stabilizing element in the formation of the amorphous phase. The stability of the amorphous phase is also influenced by the concentration of the elements in the alloy. It has been shown by Murillo et al.[11] that for Sm$_{30}$Fe$_{70}$ milled for up to 60 h there is still a pure α-Fe peak in the x-ray diffraction; but, as shown in this work, for SmFe$_3$ milled for up to 20 h, no crystalline α-Fe phase is observed in the XRD.
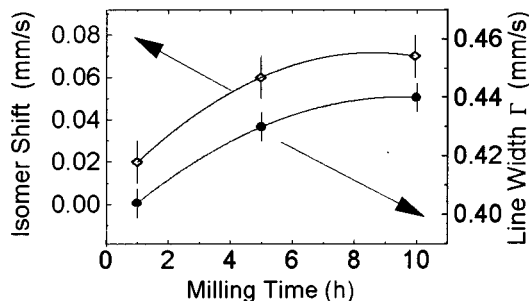

FIG. 4. Isomer shift and linewidth of mechanically alloyed Sm and Fe as a function of milling time.
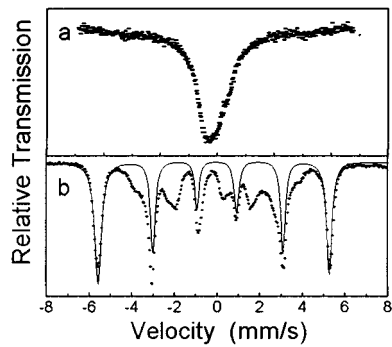
FIG. 5. Mössbauer spectra of mechanically alloyed Sm and Fe (a) milled for 20 h, and (b) milled for 20 h and annealed at 650 °C for 1 h. The solid lines correspond to the subspectrum of the α-Fe phase.
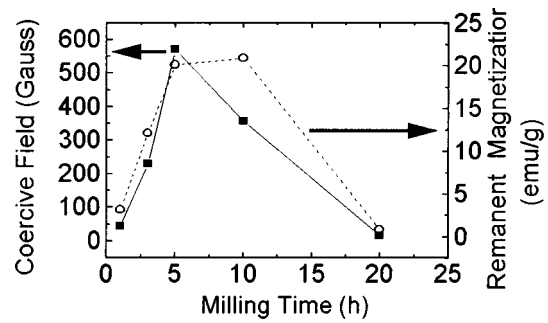

FIG. 6. Coercive field and remnant magnetization of mechanically alloyed Sm and Fe as a function of milling time. The lines are drawn connecting the points as a guide.

B. Mössbauer measurements

Mössbauer spectra of milled Sm and Fe at different milling times are shown in Fig. 3. Between 1 and 10 h of milling no significant change was observed in the spectra. As shown in Fig. 4, however, the isomer shift and the linewidth increased with milling time. The increase in linewidth is well correlated with the decrease in particle size, and the increase in the isomer shift is due to a simultaneous increase in both microstrain and lattice constant. Since the ^{57}Fe Mössbauer isomer shift can be taken as a measure of the s-electron charge density at the Fe nucleus, its increase also indicates reduction in the electron density.

The Mössbauer spectrum of Sm and Fe milled for 20 h is shown in Fig. 5(a). Although as for most Fe-rich amorphous compounds the two peaks are poorly resolved, the spectrum can be well described by fitting the data to two independent Lorentzians. The two peak positions then define the effective isomer shift and the effective quadrupole splitting. The isomer shift with respect to that of α-Fe is $-0.18\pm.01$ mm/s. The isomer shift is negative, as is typical of most amorphous RE–Fe and amorphous TM–Fe compounds. The small asymmetry observed in the spectra of amorphous SmFe$_3$ is empirically explained to be a correlation between the isomer shift and the electric-field gradient. The quadrupole splitting is $0.48\pm.01$ mm/s.

Figure 5(b) shows the Mössbauer spectrum of Sm and Fe milled for 20 h and then annealed for 1 h at 650 °C in an argon atmosphere. The spectrum shows lines consistent with crystalline α-Fe (solid lines) plus other weaker lines.

C. Magnetic properties

Figure 6 shows the coercive field and the remanent magnetization, determined from measured hysteresis loops, of mechanically alloyed Sm and Fe as a function of milling time. The coercive field increased from 44 G after 1 h of milling to 569 G after 5 h and then decreased to 16 G after 20 h of milling. This sharp decrease in the coercive field after 5 h of milling is due to the reduction of particle size, and other factors such as increase of mechanical stresses, formation of new grain boundaries, and amorphization of the material. The remanent magnetization showed a peak that was similar, but displaced to a milling time an hour or two

longer. It began at 3.21 emu/g, increased to 20.9 emu/g at 10 h, and dropped to 0.89 emu/g at 20 h of milling.

The coercive field and the remanent magnetization of the 20 h milled alloy increased after heat treatment. The coercive field increased to 25.0 G and the remanent magnetization increased to 2.52 emu/g.

The saturation magnetization, also determined from measured hysteresis loops, decreased with milling time. After 1 h of milling the saturation magnetization was 80 emu/g, and 20 h of milling reduced it to 32 emu/g. Heat treatment increased the saturation magnetization of the 20 h milled sample to 88 emu/g.

IV. CONCLUSIONS

This study has revealed that Sm and Fe mechanically milled for up to 20 h became an amorphous alloy which crystallized when annealed. The coercive field and the remanent magnetization of mechanically alloyed sample were at their maximum after about 5 h of milling. The saturation magnetization after 20 h of milling decreased to less than half of its value after 1 h of milling. Heat treatment increased the saturation magnetization of the 20 h milled alloy above that of the 1 h milled alloy.

As shown in this study, formation of the SmFe$_3$ phase occurred between 10 and 20 h of the mechanical synthesis. Therefore, it is important to sample the product at short intervals during this process in order to observe the alloy in transition from a ferromagnetic crystalline state to a paramagnetic amorphous state.

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