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Fe-Al₂O₃ nanocomposites prepared by high-energy ball milling

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Nanocomposites of α -Fe and α -Al₂O₃, prepared by high-energy ball milling, exhibit coercivities which are enhanced by about two orders of magnitude with respect to the bulk value. The degree of enhancement depends on the volume fraction (x_v) of Fe, with a maximum for $x_v \approx 0.25$. The effect is ascribed to the production of single-domain magnetic grains. Mössbauer spectroscopy reveals the presence of iron oxide phases which could not be seen by x-ray and electron diffraction measurements.

I. INTRODUCTION

Magnetic particles in the size range below about 15 nm are single-domain particles. Such particles are of significant technological importance because single-domain particles exhibit superior magnetic properties compared to multidomain materials, e.g., single-domain particles can yield coercivities 100–1000 times higher than that of the bulk material.¹ Agglomeration of single-domain sized particles typically diminishes the otherwise enhanced magnetic properties. Separation of the magnetic particles by a nonmagnetic material may retain, or even improve, the superior magnetic properties, e.g., films of ultrafine magnetic particles embedded in a metal or ceramic matrix have resulted in large-coercivity materials.² Usually such films are prepared by cosputtering of two immiscible elements, e.g., Fe-Cu or Fe-Al₂O₃.^{2,3} Here we report on the preparation of Fe-Al₂O₃ nanocomposite powders by high-energy ball milling.

II. EXPERIMENTAL

Ball milling of fine powders of α -Al₂O₃ and α -Fe (1–10 μm) was performed in a Fritsch (Pulverisette 5) planetary mill. Powder to ball weight ratio was 1:20 with a total of 9.6 g powder per vial. The ball and vial materials were tungsten carbide. The vial was sealed in an argon-filled glove box before milling the powder for 70 h. Samples with Fe volume fractions (x_v) in the range 0.1–0.5 were prepared and investigated.

The prepared samples were studied by a number of techniques: x-ray and electron diffraction, transmission and scanning electron microscopy, Mössbauer spectroscopy, and magnetization measurements.

X-ray diffraction measurements were obtained by using Cu K α radiation from a Philips powder diffractometer equipped with a single-crystal monochromator in the diffracted beam.

Transmission electron microscopy and electron diffraction studies were performed by using a JEOL 2000 \times microscope operating at 200 kV.

Mössbauer spectroscopy spectra were obtained by using a constant acceleration spectrometer with a source of ⁵⁷Co in rhodium. The linewidth obtained for an α -Fe foil reference

sample was smaller than 0.25 mm s⁻¹ (FWHM), both at room temperature and at 80 K. The spectra were fitted with Lorentzian lines using a least-squares method.

Magnetization measurements were performed at room temperature employing a vibrating-sample magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction spectrum of the Fe_{0.3}(Al₂O₃)_{0.7} sample. The peaks are significantly broadened with respect to the peaks in spectra obtained of μm -sized particles. Besides α -Fe and α -Al₂O₃ also WC is observed in the x-ray diffraction spectrum. From the excess broadening of the lines the crystallite size of the α -Fe is estimated to be about 9 nm. The x-ray diffraction spectra of the samples with different volume fraction of Fe indicated similar mean sizes. Dark-field transmission electron micrographs of the sample with $x_v=0.1$ confirmed the presence of nanometer-sized crystallites, but indicated a wide distribution of crystallite sizes.

Neither the x-ray nor the electron diffraction patterns indicated any presence of iron oxides in the samples. However, Mössbauer spectra of the samples clearly showed the presence of iron oxide. Figure 2 shows Mössbauer spectra obtained at 80 K. The six-line pattern of α -Fe is easily recognized. The remaining spectrum is well described by a doublet ($\delta=1.1$ mm s⁻¹ and a quadrupole splitting of about 1.9 mm s⁻¹) due to Fe²⁺. The linewidth of absorption lines due to α -Fe are broadened with respect to the intrinsic linewidth. This broadening is most probably due to a large fraction of the iron atoms being situated in interface regions, with modified hyperfine parameters due to lattice distortions in this region. Plastic strain may also be affecting the Mössbauer spectrum. Mössbauer spectra of assemblies of 5 nm nanoparticles of α -iron have previously been shown to exhibit broad absorption lines due to the presence of an interfacial component.⁴

The relative area of the component ascribed to iron oxide was, from the Mössbauer spectra, observed to increase with decreasing x_v . In Table I the relative number of oxidized iron atoms, obtained from fittings of the spectra in Fig. 2, are given as a function of x_v . Surely, this is the main reason for the observed decrease of the saturation magneti-

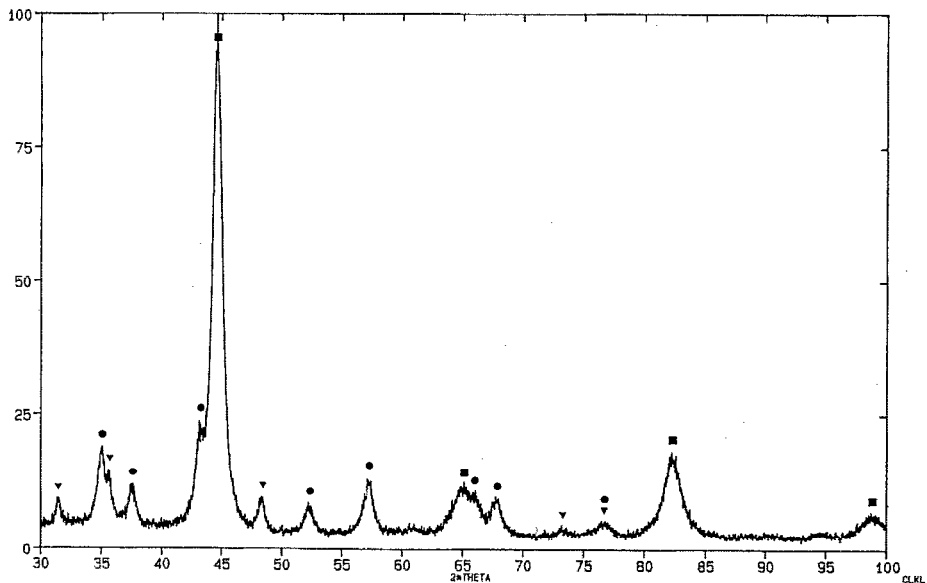


FIG. 1. X-ray diffraction curve of ball-milled $\text{Fe}_{0.3}(\text{Al}_2\text{O}_3)_{0.7}$. Squares, balls, and triangles indicate the positions of the diffraction lines of α -Fe, α - Al_2O_3 , and WC, respectively.

zation (M_s) per iron atom for decreasing x_v . Table I shows M_s , as well as M_s^{korr} , where the latter is the saturation magnetization per iron atom corrected for the number of iron atoms in the oxide when these are assumed not to contribute to the magnetization of the samples. The presence of iron

oxide may also affect other magnetic properties, e.g., the coercivity of iron particles have been found to be much influenced by surface oxide components.⁵

Figure 3 shows the coercivity, at room temperature, as a function of x_v . Maximum coercivity ($\approx 3 \times 10^4 \text{ A m}^{-1}$) is found for $x_v \approx 0.25$. For comparison, the coercivity of bulk α -iron is about $2 \times 10^2 \text{ A m}^{-1}$, i.e., about two orders of magnitude smaller. We ascribe this enhancement of the coercivity to be due to a reduction of the crystallite size to the size region of single-domain particles. If the crystallite size would be much less than the about 10 nm deduced for the crystallites of the presently investigated samples, superparamagnetic behavior would begin to cause very low coercivities.

When approaching the percolation limit ($x_p \approx 0.5$) the coercivity decreases. This is probably due to magnetic exchange interactions between the crystallites. Above the percolation threshold the particles may no longer be regarded as truly single domain. In Fig. 3 coercivities found by Ambrose

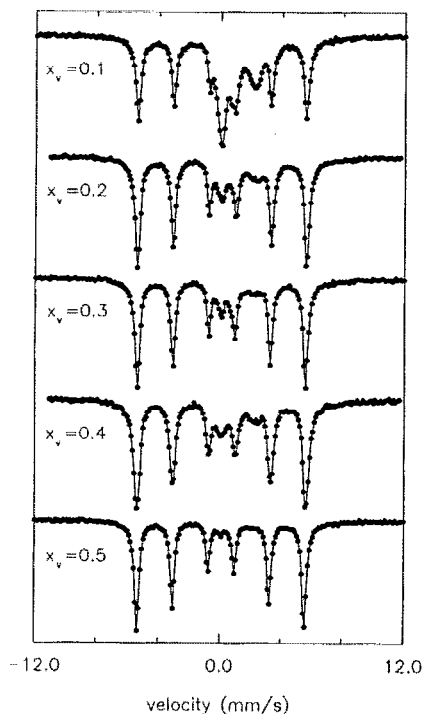


FIG. 2. Mössbauer spectra of ball-milled $\text{Fe}_x(\text{Al}_2\text{O}_3)_{1-x}$ samples, with x_v being the volume fraction of iron. The spectra were obtained at 80 K.

TABLE I. The relative number of oxidized Fe atoms are given as a function of the volume fraction (x_v) of Fe in the Fe- Al_2O_3 nanocomposites. The saturation magnetization (M_s^{Fe}) is per Fe atom in the sample. $M_s^{\text{Fe, korr}}$ is corrected for the amount of oxidized iron, assuming that oxidized iron atoms contribute insignificantly to the magnetization. The magnetization of bulk iron at 298 K is $217 \text{ J T}^{-1} \text{ kg}^{-1}$.

x_v	Oxidized Fe (%)	M_s^{Fe} ($\text{J T}^{-1} \text{ kg}^{-1}$)	$M_s^{\text{Fe, korr}}$ ($\text{J T}^{-1} \text{ kg}^{-1}$)
0.1	49.5	91.6	181
0.2	23.2	157.3	205
0.3	19.4	172.2	214
0.4	17.0	176.0	212
0.5	8.6	188.8	207

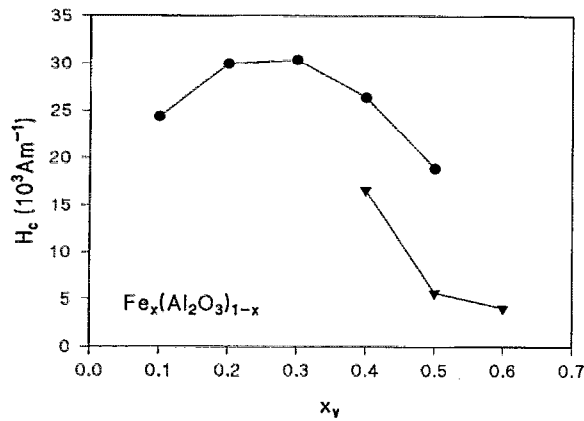


FIG. 3. Room-temperature coercivity as a function of x_v after 70 h of ball milling. Solid triangles are data from Ref. 6.

*et al.*⁶ on similarly prepared samples are also shown. The coercivities obtained in the present work are found to be significantly larger. This may be an effect of different ball milling conditions (e.g., milling velocity and weight ratios between powder and balls).

Figure 4 shows the remanent magnetization for the different samples at room temperature. The remanent magnetization is seen to peak at $x_v=0.3$, which is about the composition region where also H_c has its maximum value. The decrease of M_r for x_v below 0.3 is due to the decreasing amount of iron in the samples. When the remanent magnetization is given relative to the saturation magnetization of the samples, maximum is obtained for the sample with the lowest content of iron, decreasing monotonically for increasing x_v .

IV. CONCLUSIONS

High-energy ball milling of mixtures of μm -sized particles of α -iron and α - Al_2O_3 was found to yield nanocomposite materials with an α -Fe crystallite size of about 9 nm. The coercivity of the ball milled samples was enhanced by about two orders of magnitude with respect to bulk α -iron. Mössbauer measurements revealed the presence of iron oxide phases, which were not seen in x-ray and electron diffraction patterns of the samples.

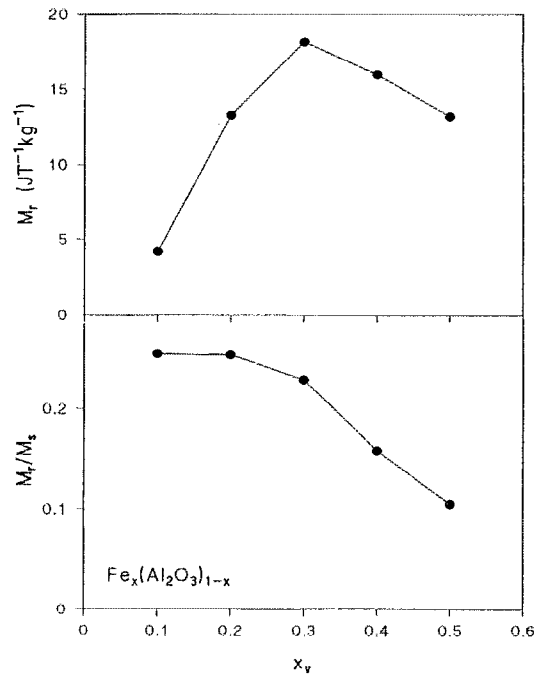


FIG. 4. The upper figure shows the remanent magnetization per mass unit of the sample. The lower figure shows the remanent magnetization, relative to the saturation magnetization, as a function of x_v . The values are obtained at room temperature.

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