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Magnetic properties of amorphous $Fe_{80-x}Cr_xB_{20}$ particles

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Abstract

The magnetic properties of amorphous fine particles of $Fe_{80-x}Cr_xB_{20}$ ($0 < x \leq 70$) were investigated by Mössbauer and magnetization experiments. With increasing x the particles show a progressive change from a ferromagnetic to a disordered character. The results reveal the existence of size ($10 < \phi < 150$ nm) and composition distribution and the presence of different iron species.

1. Introduction

Amorphous metallic powders have been receiving growing attention in the last years for their engineering applications, made possible by their compactability. The reduction of dissolved metal ions using aqueous borohydride has proved to be a successful method for preparing amorphous $Fe_{80-x}M_xB_{20}$ (M is a transition metal) particles in a large composition range [1–3], not obtainable by rapid quenching techniques. In this paper we report the results of a magnetic investigation on the amorphous particles system $Fe_{80-x}Cr_xB_{20}$ ($0 < x \leq 70$), prepared by the reduction method. Amorphous $Fe_{80}B_{20}$ alloy is ferromagnetic ($T_c \cong 650$ K). The substitution of iron with chromium introduces competing antiferromagnetic correlations leading in the bulk material to a rapid decrease of T_c and to a spin glass phase for the composition range $28 \leq x \leq 32$ [4].

2. Results and discussion

The alloys $Fe_{80-x}Cr_xB_{20}$ ($0 < x \leq 70$) were prepared by the reduction of aqueous solutions of $FeSO_4$ and $CrCl_3$ using aqueous solutions of $NaBH_4$. The molecular ratio between the metal salts and the reductant was 8 : 100. The reactions were carried out in an atmosphere of high purity nitrogen; the samples were washed thoroughly with water to remove residual ions from the reaction mixture, and this was followed by washing with acetone to remove the water. Finally, the samples were dried overnight under vacuum. Passivation, needed because the particles are pyrophoric, was performed by controlled introduction of air in the reaction vessel.

The amorphous structure of the particles is shown by X-ray, electron diffraction, TGA measurements and is confirmed by broad Mössbauer spectra, indicating a large distribution of hyperfine fields. TEM measurements show that the particles are spherical, with diameters ranging within the series between 10 and 150 nm. The average diameter changes with the composition x, decreasing with increasing x (e.g. for $x = 40$, $\langle\phi\rangle = 120$ nm; for $x = 60$, $\langle\phi\rangle = 50$ nm). The particles size distribution is accompanied by a chemical composition distribution, as confirmed by Mössbauer data, the chromium content increasing with decreasing particle size.

The magnetic properties were investigated by Mössbauer and magnetization measurements in the temperature range 4.2–300 K.

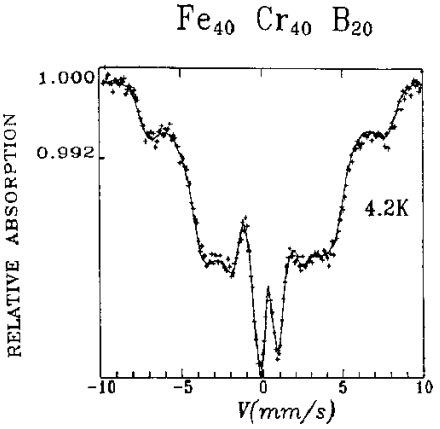

Fig. 1. Mössbauer spectrum for $x = 40$ at 4.2 K.

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The Mössbauer spectra of all samples consist, for all the samples at any temperature, of a broad sextuplet, due to the magnetically ordered particles, and a central paramagnetic doublet (Fig. 1). The intensity ratio between the two components varies with the composition x and evolves with temperature. The analysis of the spectra reveals the existence of different Fe species and three types of particles:

(a) Ferromagnetic, metallic Fe–Cr–B particles, surrounded by oxidized layers. They represent for each composition x the dominant component of the spectra, more and more important with decreasing x. The transition temperature is largely distributed, according to the chemical composition distribution among the particles. The T_c values indicate that such ferromagnetic particles are richer in iron than the nominal composition. This is more and more evident with increasing x. The average hyperfine field values, in the range 200–250 kOe, are in agreement with those reported for ribbon materials, although a quantitative comparison is difficult because of the composition distribution, not well known for each x value.

(b) Antiferromagnetically ordered particles, containing oxidized iron with low transition temperature, which does not depend, in first approximation, on the composition x. These particles contain both Fe^{2+} (in this case $20 < T_N < 40$ K) and Fe^{3+} ($40 < T_N < 77$ K) ions, whose populations change slightly with the composition x (e.g. at 4.2 K: for $x = 5$, the percentage of Fe^{2+} and Fe^{3+} in A.F. particles is 3 and 7% respectively; for $x = 40$ the percentages are 6 and 9% respectively). The volume of these particles should be small, because the oxidation also concerns the core of the particles.

(c) Paramagnetic particles containing Fe^{3+} ions. The paramagnetic fraction of the spectrum does not tend to zero with decreasing temperature and then these particles are paramagnetic at any temperature. These particles should be those very rich in chromium, the very small ones. This is confirmed by the increase of the paramagnetic population with increasing x (e.g. at 4.2 K: for $x = 5$, the percentage is 1.5%, while for $x = 40$ it is 11%).

Magnetization measurements were performed by a SQUID and a vibrating sample magnetometer as a function of both temperature and magnetic field. The zero field cooled (ZFC) and the field cooled (FC) magnetizations, measured applying a field of 50 Oe, show a very broad maximum. An irreversible behaviour is observed in all the examined temperature range, the merging of the two curves occurring above 300 K.

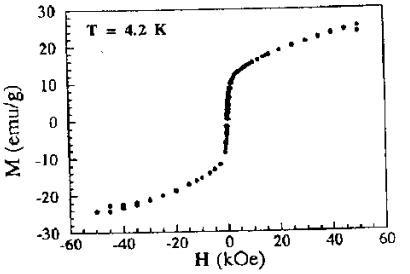

Fig. 2. M vs. H for $x = 60$ at 4.2 K.

Magnetization vs field measurements ($H_{max} = 5$ T) at 5 K show an hysteresis cycle with saturation for $x < 25$ (e.g. for $x = 5$: $M_s = 108$ emu/g), indicating the dominant ferromagnetic character of the particles in this composition range. For $x > 25$ the M vs. H curves do not show saturation (Fig. 2), revealing the coexistence of antiferromagnetic and ferromagnetic particles. This is in agreement with the growing fraction of antiferromagnetic particles detected by Mössbauer spectroscopy. The coercive field is found to increase with x (e.g. for $x = 40$, $H_c = 70$ Oe and for $x = 60$, $H_c = 300$ Oe), indicating that the chromium introduction increases the anisotropy.

The temperature variation of the coercive field, which strongly increases at low temperature, should be responsible of the splitting between the ZFC and FC magnetization curves. In conclusion, the results indicate that the variation of the magnetic properties within the amorphous particles $Fe_{80-x}Cr_xB_{20}$ system is also influenced by the size and composition distribution.

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