



SYNTHESIS, STRUCTURAL AND MAGNETIC PROPERTIES OF AMORPHOUS $Fe_{80-x}Cr_xB_{20}$ PARTICLES

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Abstract - The preparation, by a chemical reduction method, the morphological and structural characterization and the study of the magnetic properties of amorphous $Fe_{80-x}Cr_xB_{20}$ particles is reported. The results indicate correlation between size and composition distribution and the presence of different iron species. With increasing x the macroscopic magnetic properties evolve from a perturbed ferromagnetic state to a state characterized by coexisting ferro and antiferromagnetic interactions.

INTRODUCTION

Among amorphous materials, which exhibit unique magnetic, electric and mechanical properties, making them attractive from both a fundamental and technological point of view (1), fine particle materials present many advantages. The form of ribbons and films, prepared by conventional melt spinning and sputtering techniques respectively, implies some restrictions to technological applications. On the other hand, ultrafine amorphous powders can be compacted to produce samples with various shapes (2), extending the range of possible engineering applications (e.g. catalysis, recording media...). Another advantage of amorphous alloys in the form of particles (e.g. TM-B alloys), prepared by chemical methods, is that they can be prepared in a larger composition range with respect to the conventional techniques (3-5).

In particular the reduction of dissolved metal ions using aqueous borohydride has proved to be a successful method for preparing ternary $Fe_{80-x}Cr_xB_{20}$ alloy particles.

EXPERIMENTAL

Preparation

The powder samples with the general composition $Fe_{80-x}Cr_xB_{20}$ ($5 < x < 70$), were

prepared by chemical reduction of aqueous solutions of FeSO_4 and CrCl_3 with aqueous solutions of NaBH_4 . The reactions were carried out in an atmosphere of high purity nitrogen. In a typical preparation the molecular ratio between the metal salts and the reductant was 8:100. During the addition of the reductant to the solution of the metal salts, the reaction vessel was maintained in an alcohol bath at -10°C . The black fine powder was then washed thoroughly with water to remove residual ions from the reaction mixture, and with acetone to remove water. Finally the sample was dried overnight under vacuum. Passivation, needed because the particles are pyrophoric, was performed by controlled introduction of air in the vessel.

Characterization

The morphology and the chemical composition of the powder specimens were examined by Transmission Electron Microscopy with a Jeol 4000 FX TEM equipped with an Ultra Thin Window (UTW) X-Ray detector and operated at 400 kV. To this purpose the powders were dispersed with an ultrasonic bath and a drop of the resulting suspension was allowed to dry on a microscope grid coated with a thin carbon film.

The magnetic properties were investigated by Mossbauer and magnetization measurements in the temperature range 4.2 - 300K. Magnetization measurements were performed by a commercial SQUID magnetometer. Mossbauer spectra were recorded using a conventional spectrometer operating in the constant acceleration mode with a source of ^{57}Co in Rh.

RESULTS AND DISCUSSION

The amorphous structure of the particles is confirmed by X-ray and electron diffraction, Thermal Gravimetric Analysis measurements and Mossbauer spectra. Transmission Electron Microscopy microanalysis showed no detectable elements other than Fe, Cr and B in a revealable amount.

The samples consist of spherical particles which appear to penetrate each other during the growth. The resulting morphology is often made of agglomerates or long chains of particles of different size, as reported in fig 1, so that it is not easy to determine their size distribution; only the average diameter was then estimated.

The average particle size appears to depend on x at least for values of the parameter high enough. In fact the average diameter changes from 50 nm for $x=60$ to about 120 nm for $x=40$, without any further evident change for lower Cr concentrations.

The chemical composition of the single particles inside the same batch depends on their size, with the smaller particles showing a higher Cr content than the larger ones. This is reported in fig 2, where the relationship between the particle size and their Cr content is reported for the sample with average composition $x=10$.

Both the correlation between average particle size and the value of x and the dependence of the composition of the single particle on its size, point towards an important role played by the chemistry on the nucleation behaviour in this system. In fact a relatively high Cr content appears to promote an easy nucleation of the solid phase resulting in a smaller average diameter.

Moreover, the dependence of the particle composition on its size can be interpreted considering that the nucleation phase is richer in Cr than what expected from the relative concentrations of metallic ions, while the subsequent growth occurs in a solution which results enriched in Fe.

Mossbauer spectra show, for all samples at any temperature, a broad sextuplet, due to the amorphous ferromagnetic particles, and a central paramagnetic doublet. The intensity ratio between the two components varies with composition x and evolves with temperature (i.e. the relative intensity of the paramagnetic doublet increases with increasing x and temperature).



Fig 1: Electron micrographs of $\text{Fe}_{55}\text{Cr}_{25}\text{B}_{20}$ particles

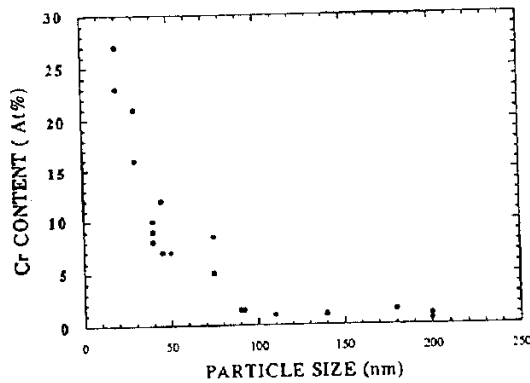


Fig.2: Relationship between Cr-content and particle size for $x=10$

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, representing the dominant component of the spectra, more and more important with decreasing x . The average hyperfine field values at 4.2K are in the range 200 - 250 kOe ; b) antiferromagnetically ordered particles, containing oxidized iron (both Fe^{2+} and Fe^{3+} ions), with low transition temperatures: $20 < T_N < 40$ K for particles containing Fe^{2+} ; $40 < T_N < 70$ K for particles containing Fe^{3+} . 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, which should be the smallest ones, very rich in chromium. Their fraction increases with increasing x (e.g. at 4.2K: for $x=5$ the percentage is 1.5%, while for $x=40$ is 11%). The trend with composition x observed in Mossbauer spectra is in full agreement with microanalysis and TEM results, confirming the existence of chemical composition and size distribution (the transition temperatures are distributed) and of chromium enrichment with decreasing the particle size.

Magnetization measurements as a function of temperature, performed after a zero field cooling (ZFC) and field cooling (FC) process, show a very broad maximum, with an irreversible behaviour in all the investigated temperature range (Fig.3) which could be due to smaller value of cooling field with respect to the coercive field value.

Magnetization measurements as a function of the magnetic field ($H_{\max} = 5T$), performed at 5K, show a progressive change with increasing x from a ferromagnetic state to a state characterized by coexisting ferro (hysteresis cycles with saturation; e.g. for $x = 5$, $M_S = 108$ emu/g) and antiferromagnetic interactions (hysteresis cycles without saturation) (Fig 4). This behaviour is determined for low x , by a perturbation of the ferromagnetic order, due to the antiferromagnetic interactions introduced by Cr substitution.

For higher x values the behaviour is determined by the progressive increase of the fraction of both antiferromagnetic and paramagnetic particles, detected by Mossbauer spectroscopy. The coercive field increases with x (e.g. for $x = 40$, $H_C = 70$ Oe; for $x = 60$, $H_C = 300$ Oe), indicating that the chromium introduction rises the anisotropy.

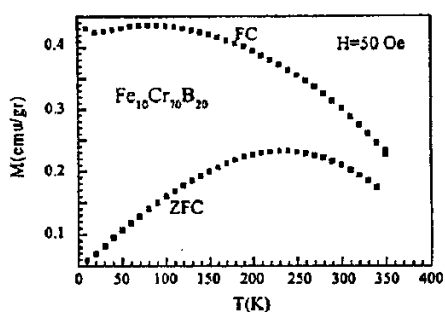


Fig. 3. Magnetization as a function of temperature

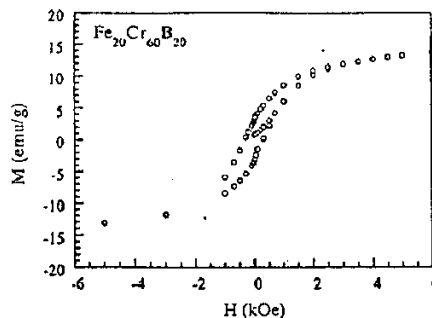


Fig 4. Magnetization as a function of magnetic field at $T = 5K$

CONCLUSIONS

TEM and microanalysis measurements on $Fe_{80-x}Cr_xB_{20}$ amorphous ultrafine powders indicate the existence of a close relationship between the mean particle size and the chemical composition (the average diameter decreases with increasing chromium content) and the presence of chemical composition distribution among particles for each sample. This fact is reflected in the observed changes of magnetic properties within the series of samples, moving from a dominant ferromagnetic character for low chromium content to a state characterized by coexisting ferromagnetic and antiferromagnetic interactions for higher chromium content.

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