Magnetic Properties of Fe-Cu-Nb-Si-B Nanocrystalline Magnetic alloys

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Abstract-Several ribbons of composition $Fe_{73.5}Cu_1Nb_3Si_{16.5}B_6$ and $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ were prepared by annealing the as-quenched samples between 525°C and 700°C, which induced nucleation of nanocrystallites of Fe bcc-type composition. Mean grain sizes were obtained from X-ray diffraction. Static magnetic properties were measured with both a Magnet Physik Hysteresis-Graph (up to 200 Oe) and a SHE S.Q.U.I.D. Magnetometer (up to 50 kOe). Soft magnetic parameters (coercive field and initial permeability) were very sensitive to grain size. The ZFC magnetization at low field showed a broad peak at a temperature T_M, thus signalling a certain distribution of nanocrystalline sizes, and T_M strongly decreased when the mean grain size decreased. Isothermal magnetization curves at low temperature showed the expected asymptotic behavior of a random magnet material at low and high fields.

I. INTRODUCTION

Recently, Yoshizawa et al. [1] reported on new ferromagnetic Fe-base alloys with ultrafine grain structure, exhibiting excellent soft magnetic properties. The material is as-cast as an amorphous ribbon. A subsequent heat treatment above the crystallization temperature produces the appearance of an ultrafine grain structure of α-FeSi embedded in a disordered matrix. Typical grain size diameter of the Fe-Si phase is D≈10nm. The formation of this nanocrystalline structure is ascribed to the addition of Cu and Nb, due to the enhancement of the inhomogeneity and instability of the amorphous structure.

We present in this paper a study of the dependence on grain size of some physical properties of these new Fe-Cu-Nb-Si-B. We have chosen two different compositions, with a fixed doping rate of Cu and Nb (the optimum one concerning the soft magnetic properties) and we have varied the Si and B contents, which strongly affects the crystallization behavior.

Finally, we study the law of approach to saturation. The asymptotic behavior of the isothermal magnetization curves M(H) at low and high fields are explained in the framework of the random anisotropy model [2].

II. EXPERIMENTAL

Amorphous ribbons of the composition $Fe_{73.5}Cu_1Nb_3Si_{16.5}B_6$ (sample A) and $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ (sample B) were supplied by VAC. They were produced by rapid quenching from melt. The as-quenched samples were annealed at different temperatures between 525°C and 700°C, in order to obtain different crystallization stages. The heat treatments were performed in a conventional furnace under Ar atmosphere, and the annealing time was one hour in all the cases. X-ray diffraction patterns were recorded at room temperature using the Cu Kα radiation with a graphite monocromator. Magnetic flux density measurements were carried out with a Magnet Physik Hysteresis-Graph (maximum applied field of 200 Oe). Magnetization measurements were recorded with a SHE S.Q.U.I.D. magnetometer in the temperature range 6 -300 K and magnetic fields up to 50 kOe. The zero-field-cooled (ZFC) and field-cooled (FC) processes were measured at low fields (at about 25 Oe).

III. RESULTS AND DISCUSSION

A. *X-ray Diffraction*

X-ray diffraction patterns of the annealed samples show a bcc peak. The average grain size was calculated from the grain size distribution (see Fig.1), and the line profile analysis reached the proofed sensitivity at a minimum grain size of about 25 nm, which corresponds to the grain size of the gold reference sample.Therefore, the smallest values indicate only that the grain size is much smaller than 25 nm.

It is observed that the size of the α-Fe(Si) solid solution increases with the annealing temperature (see Table I), and the recrystallization behavior depends on the Si and B contents, as previously noted by Polak et al.[3].

B. *Soft Magnetic Properties*

The coercive field H_c and the initial permeability μ_i (see Table I) have been obtained at room temperature from the dependence of the magnetic flux density on the applied field (H_{max}=200 Oe). It is shown that above a critical annealing temperature (and consequently, above a critical grain size) H_c sharply increases and μ_i decreases. This critical temperature is about 600-625°C and the critical grain size is about 30 nm for both series of samples. The observed behavior is in agreement with the theoretical results obtained by Herzer [4], assuming the random anisotropy model developed by Alben et al. [2].

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TABLE I

GS: average grain size.

		T_a(°C)	GS(nm)	H_c(A/cm)	$\mu(10^4)$
SAMPLE	A1	575	6	0.08	1.78
	A2	600	6	0.10	1.75
	A3	625	31	0.20	0.97
	A4	650	31	17.0	0.61
	A5	675	70	22.5	0.21
SAMPLE	B1	525	24	<0.01	1.91
	B2	600	31	0.30	1.51
	B3	675	56	55.0	0.46
	B4	700	76	53.0	0.53

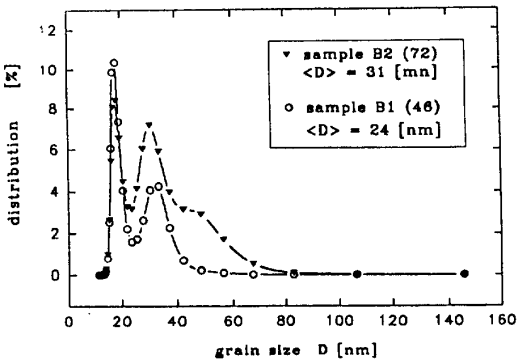

Fig.1. Distribution in % of the grain size of the sample B1 and B2:the average grain size was calculated using this distribution. The first peak corresponds to the reference sample (gold).

C. *ZFC-FC Magnetization*

We show in Fig. 2a, 2b, 2c the ZFC and FC magnetization data for three samples of the A-type compound: A1 (T_a=575°C, grain size=6nm), A4 (T_a=650°C, grain size=31nm) and A5 (T_a=675°C, grain size=70nm). The different behavior of the ZFC and FC curves is a typical feature of a magnetic system in which energy levels do not only depend, at a given temperature, on the Boltzman distribution but it is also strongly afected by the thermomagnetic story. This magnetic behavior is also observed, for example, in spin glasses, small particle systems, ultrafine grains embedded in an amorphous matrix and clusters of atoms.

In our present case, the ZFC curves show a very wide maximum, indicating that we have a certain distribution of blocking temperatures (because of grain sizes) for each sample. The strong decrease of this average blocking temperature in the samples follows the strong reduction of the mean grain size. Moreover, the ZFC magnetization decreases below the peak (where the magnetic moment of each grain is blocked), showing the randomness of the easy magnetization direction of each grain.There also appears a clear irreversibility between the ZFC and FC measurements. The FC magnetization is always above the ZFC values since, in the former process, the magnetic moments of the grains tend to block along the magnetic field axis below a certain temperature (maximum of the FC magnetization).

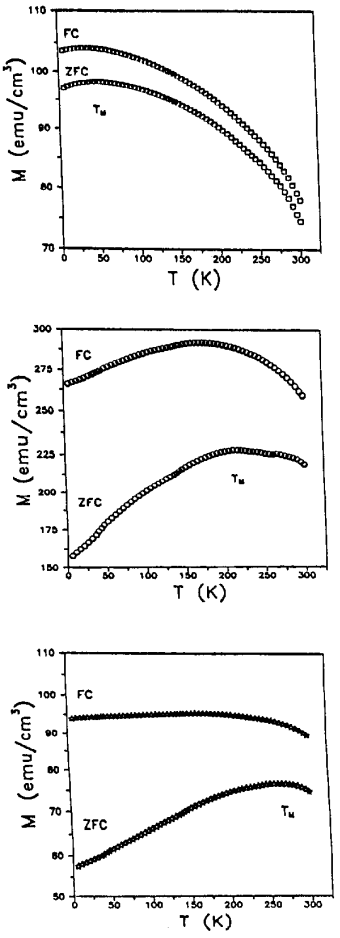

Fig.2 ZFC and FC magnetization of three selected samples of the A-type compound. The maximum of the ZFC is observed at $T_M \approx 50$ K for sample A1(a), $T_M \approx 210$ K for sample A4(b) and $T_M \approx 262$ K for A5(c).

D. *Isothermal Magnetization Curves*

The isothermal magnetization curves M(H) were measured at 6 K for samples A1, A4 and A5, with a maximum applied field of 50 kOe.

We may explain the behavior of the magnetization as we approach saturation in the framework of the random anisotropy model, applied to amorphous ferromagnets [5].

This model assumes that the local anisotropy axes are correlated along a certain distance R_a and their spatial distribution is characterized by a certain distribution function C(x) which reflects short range crystallographic order. Further, the magnetic behavior of a disordered system depends on the ratio between the random anisotropy field $H_r = 2K_r/M_o$ (where K_r is the anisotropy constant) and the exchange field $H_{ex} = 2A/(R_a^2 M_o)$ (where A is the exchange strength). If we define the crossover parameter [5] λ_r, as

$\lambda_r = (2/15)^{1/2}(H_r/H_{ex})$, the low anisotropy regime corresponds to $\lambda_r < 1$, when the ferromagnetic correlation length, defined as $R_f = R_a/\lambda_r^2$ is larger than R_a [6], and it would lead to long range magnetic order. However, although ferromagnetic clusters of spins are formed at small distances, long range ferromagnetic order is destroyed at large distances due to random fields which cause weak fluctuations of the spin orientation, as it was noticed by Imry and Ma [7]. Assuming that there is no coherent anisotropy in our system, a correlated spin glass (CSG) state is attained [6]: magnetization smoothly and stochastically rotates over the solid. Furthermore, a partial order is induced in the solid when a magnetic field is applied. In this case, the magnetization vectors wander as one moves about the system due to random fields and the CSG state gives place to a ferromagnet with wandering axes state (FWA). For the latter, Chudnovsky et al.[5] showed that the magnetization law should follow a $H^{-1/2}$ dependence when $H << H_{ex}$ and a H^{-2} dependence when $H >> H_{ex}$ regardless the form of C(x):

$$\Delta M/M_o = (v_c/30)(H_r/H_{ex})^2(H_{ex}/H)^{1/2} \quad \text{if } H << H_{ex} \quad (1)$$

$$\Delta M/M_o = (1/30)(H_r/H)^2 \quad \text{if } H >> H_{ex} \quad (2)$$

where $v_c = \int_o^\infty dy \cdot y^2 \cdot C(y)$

Two important aspects should be taken into account before applying eq. (1) and (2) to the study of the asymptotic behavior of the magnetization curves. The first concerns the inevitable presence of some coherent anisotropy in the sample. Although a weak coherent anisotropy, satisfying $\lambda_c^{1/2} > \lambda_r^2$ (where $\lambda_c = (2/15)^{1/2}(H_c/H_{ex})$, and H_c is the coherent anisotropy field) destroys the CSG state [6], the effect of H_c becomes unimportant when $H >> H_c$. Secondly, the H_{ex} must be accessible experimentally.

We have chosen samples A5 and A1 (the largest and smallest A samples) in order to test the validity of the low anisotropy limit of the random anisotropy model when applied to these Fe-Cu-Nb-Si-B magnetic alloys.

Concerning the A5 sample, the linear dependence of ΔM with respect to $H^{-1/2}$ and H^{-2} is shown in Fig.3: in Fig. 3a we show M as a function of $H^{-1/2}$, while in Fig.3b log(ΔM) versus log(H) is displayed, whence $\Delta M = M - M_o - \chi_d H$ and χ_d is the high field differential susceptibility. Equations (1) and (2) together with the experimental magnetization curve at 6K enable us to estimate that $H_r \approx 4000$ Oe and $H_{ex} \approx 2100$ Oe, thus leading to $\lambda_r \approx 0.7\text{-}0.8 < 1$. Besides,if we assume a typical value of the coherent anisotropy for these kinds of systems ($K_c \approx 10^5$ erg/cm^3 [8]), we obtain $\lambda_c \approx 0.03$, which implies $\lambda_r^2 > \lambda_c^{1/2}$. These results verify the self consistency of the model.

Concerning the A1 sample (grain size = 6 nm), a different asymptotic behavior is observed at low fields: $\Delta M \propto H^{-1}$ (see Fig.4). This behavior, predicted theoretically by Chudnovsky [9] and Ruiz et al. [10] for a two-dimensional random

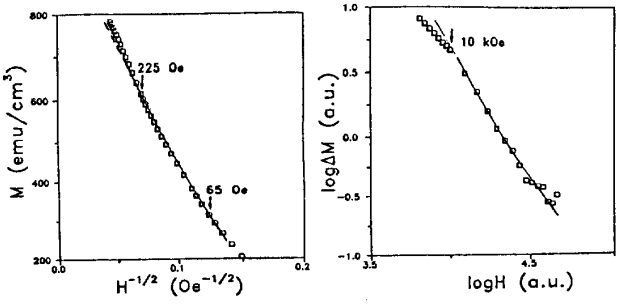

Fig.3 Two linear regimes of approach to saturation for sample A5 at 6K: M *versus* $H^{-1/2}$ and log(ΔM) *versus* log(H) (where the slope of the log-log curve is m = 2).

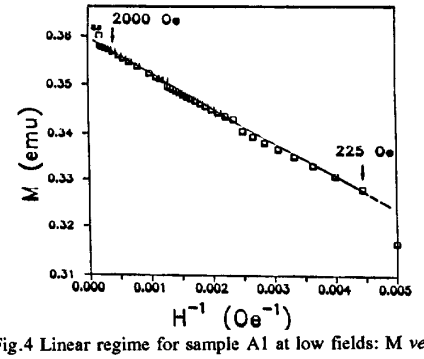

Fig.4 Linear regime for sample A1 at low fields: M *versus* H^{-1}.

anisotropy system in the low anisotropy limit, has been observed experimentally in magnetic multilayers [10]. In our case, the predicted asymptotic behavior at high fields ($\Delta M \propto H^{-2}$) is difficult to observe, since ΔM becomes so small at large fields that weak effects (magnetism of conducting electrons, paramagnetic impurities, ...) violate this dependence.

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