ELSEVIER

Journal of Magnetism and Magnetic Materials 196–197 (1999) 201–203

Journal of magnetism and magnetic materials

Superparamagnetic behaviour of a nanocrystalline Fe(CrMo)SiBCuNb alloy

L. del Riego[a], M. El Ghannami[a], M. Domínguez[a,*], C.F. Conde[b], A. Conde[b,1]

[a]*Departamento Física de la Materia Condensada, Universidad de Cádiz, 11510 Puerto Real, Spain*
[b]*Departamento Física de la Materia Condensada, Universidad de Sevilla, 41080 Sevilla, Spain*

Abstract

Samples of a-$Fe_{68.5}Cr_4Mo_1Cu_1Nb_3Si_{13.5}B_9$ have shown superparamagnetic (SPM) behaviour, after annealing at 773 K for 1 h, as a consequence of the crystallization of α-Fe, Si particles inside the ferromagnetic amorphous matrix. The SPM response has been studied in detail in the wide temperature range between the Curie temperature of the remaining amorphous phase, and the nanocrystallization onset.

Keywords: Superparamagnetism; Nanocrystallization; Fe amorphous alloys

Amorphous ferromagnetic alloys are among the softest magnetic materials, but normally they lose their softness after crystallization. However, a few well-known Fe-rich amorphous alloys [1] become softer after nanocrystallization [2]. This feature was explained by means of the reduction of magneto-crystalline anisotropy due to the exchange ferromagnetic interactions between crystallites. Substitution of Fe by Cr or Mo enhances the thermal stability against nanocrystallization, lowering the Curie temperature of the amorphous phase, while the nanophase magnetic transition remains almost unchanged [3].

Generally, a-FeSiBCuNb alloys turn into a two-phase system after annealing at ~ 800 K: a nanocrystalline phase, made of ultrafine α-FeSi grains (size ≈ 5–15 nm), coexists with the intergranular amorphous residual phase [2]. Their magnetic behaviour depends on the nanophase characteristics (crystalline volume fraction, grain size, inter-grain distances, etc.) and the remaining amorphous matrix composition.

In this work, we have carried out, using a Faraday Balance technique, the study of the thermomagnetic properties of alloys with a nominal composition $Fe_{68.5}Cr_4Mo_1Cu_1Nb_3Si_{13.5}B_9$ prepared by 'melt-spinning', after annealing. These results qualitatively agree with previously reported values [4], obtained with a thermomagnetic balance, but here absolute values of magnetization are obtained. Structural transformation on heating was previously studied by differential scanning calorimetry and X-ray diffraction [3].

Fig. 1 shows the typical thermomagnetic behaviour for the sample under study. The as-cast amorphous sample (curve *a*) has a magnetic transition at $T_{c,am} \approx 520$ K, followed by an increase in magnetization at $T \approx 780$ K, due to the onset of crystallisation of the α-FeSi nanophase. Curie temperature for this phase is $T_{c,crys} \approx 855$ K, which means a Si-content around 22 at% [5]. If the material is heated up to 1000 K, full crystallization of the amorphous phase occurs, and the sample exhibits the $M(T)$ curve *b* on cooling. This two-stage drop to zero-magnetization has been explained [4] by considering the T_c's for the crystalline ferromagnetic phases (FeSi and $Fe_{1-x}B_x$).

Depending on the amount and size of the nanocrystalline phase (which can be changed by varying annealing time and temperature in the first crystallization range), the magnetic behaviour may be rather different. As part of a systematic study of this material, we have characterized a sample previously anneled at 773 K for 1 h. The

* Corresponding author. Tel.: + 34-956-830966; fax: + 34-956-834924; e-mail: manolo.dominguez@uca.es.

[1] Project No. MAT95-961-CO2-01.

0304-8853/99/$ - see front matter
PII: S0304-8853(98)00731-8

$M(T)$ curve for the annealed sample is plotted in Fig. 1 (curve *c*). Curie temperature for the amorphous matrix is slightly higher than that for the as-cast sample, as a consequence of the lower Fe-content remaining in this phase after crystallization. Interestingly, there are almost 300 K between $T_{c,am}$ and the onset of the first crystallization, and the magnetic properties of this nanophase can be studied. As an example, the inset in Fig. 1 shows the inverse susceptibility of the sample in this temperature range. $1/\chi$ clearly deviates from its linear dependence near $\theta_{c,am}$ due to the magnetic contribution of the embedded grains. Such behaviour can be modelled if the total susceptibility is considered as the sum of the paramagnetic (PM) susceptibility of the amorphous phase and the nanophase superparamagnetic (SPM) contribution:

$$\chi = \chi_{am,PM} + \chi_{crys,SPM}, \tag{1}$$

where $\chi_{am,PM} = C/(T - \theta_{c,am})$ and $\chi_{crys,SPM}$ is obtained from the low-field Langevin function approximation, neglecting interparticle interactions ($\theta = 0$):

$$\chi_{crys,\,SPM} = M_s^2(T)V/3k_BT = C_{SPM}/T, \tag{2}$$

$M_s(T)$ and V being the spontaneous magnetization and the SPM particles volume, respectively.

Fig. 2 shows the $M(B)$ curves in the temperature range between the magnetic transition of the amorphous phase and the onset of crystallization, which confirms the nanophase SPM nature. However, to model this behaviour, the response of the amorphous PM matrix, responsible for the almost linear increase in magnetization at higher fields, must be taken into account. Plots of magnetization versus applied field of the initial amorphous phase (i.e., before annealing) at this temperature range, show a linear response up to 0.5 T with a slight deviation at higher fields.

Thus, we may consider an approximated linear dependence of the PM-phase magnetization on field and the Langevin function for the field dependence of the SPM-phase magnetization:

$$M(H, T) = \chi_{am,\,PM}H + M_s(T)[\coth(\alpha) - 1/\alpha] \tag{3}$$

with $\alpha = M_sV/k_BT$. As shown in Fig. 3, it is possible to scale all these data to a single plot, the typical SPM

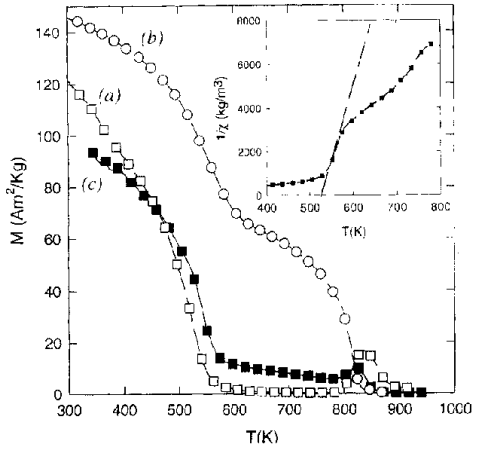

Fig. 1. Magnetization curves for (a) the as-prepared sample, (b) a sample previously heated at 1000 K for 15 min, and (c) a sample annealed at 773 K for 1 h. Heating rates were always 10 K/min and the applied magnetic field was 0.05 T. The inset shows the low-field inverse susceptibility as a function of T, around the amorphous phase magnetic transition, for sample c.

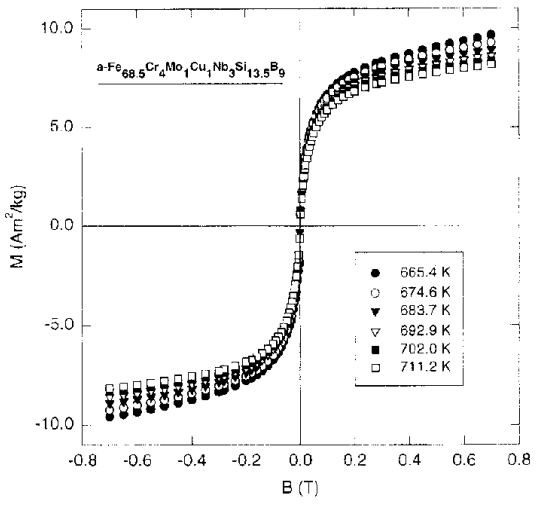

Fig. 2. Anhysteretic $M(B)$ curves at several temperatures in the interval between $T_{c,am}$ and the onset temperature for nanocrystallization, for the sample annealed at 773 K for 1 h.

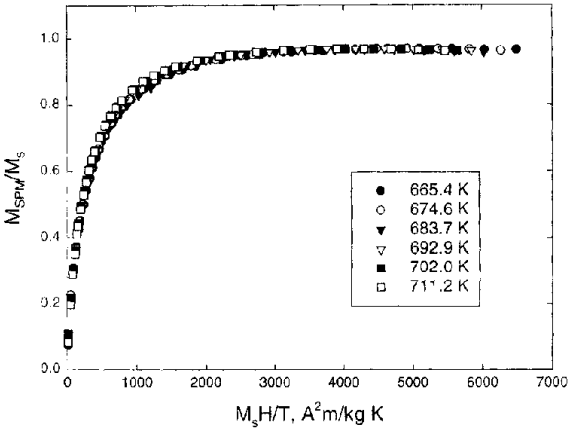

Fig. 3. Reduced magnetization M_{SPM}/M_s as a function of M_sH/T deduced from the data in Fig. 2, after subtracting the PM contribution. All the experimental results scale to a single curve.

Table 1
Parameters obtained in the non-linear fits to Eq. (3) of the experimental results, for different temperatures. The PM-phase magnetization is aproximated to a linear dependence on field.

T (K)	M_s (Am^2/kg)	V (m^3)	D (nm)	$\chi_{am.\,PM}$ (m^3/kg)
665.4	7.75	8.7×10^{-26}	5.5	3.85×10^{-6}
674.6	7.59	9.0×10^{-26}	5.6	3.48×10^{-6}
683.7	7.39	8.9×10^{-26}	5.5	3.26×10^{-6}
692.9	7.27	9.6×10^{-26}	5.7	2.85×10^{-6}
702.0	7.11	9.9×10^{-26}	5.7	2.65×10^{-6}
711.2	6.98	1.0×10^{-25}	5.8	2.55×10^{-6}

behaviour (here, M_{SPM} is obtained by subtracting the PM-phase magnetization, taken as linear on field). Parameters in Eq. (3) have been fitted by an iterative procedure with fast convergence and high correlation factors, using values deduced from different sources as starting parameters. For example, $M_s(T)$ is initially estimated from the same experimental curves, $\chi_{am,PM}$ is estimated from the fitted line shown in the inset of Fig. 1, and V is taken from previously reported TEM micrographs [3]. The fitting parameters are all summarized in Table 1, where the diameter of the particles (considered as spherical), is calculated from the volume. The estimated mean size of the SPM particles is ~ 6 nm, only slightly below the size found in direct TEM observations.

In conclusion, the magnetic behaviour of a nanocrystallized Finemet-type alloy has been well modelled by means of the SPM theory, neglecting the interactions between particles and subtracting the effect of the remnant PM amorphous matrix. The mean size of the particles, deduced from the theoretical relationship between M_{SPM} and H/T, agrees quite well with the one previously found in TEM observations.

References

[1] Y. Yoshizawa, S. Oguma, K. Yamauchi, J. Appl. Phys. 64 (1988) 6044.
[2] G. Herzer, Mater. Sci. Eng. A 133 (1991) 1.
[3] C.F. Conde, V. Franco, A. Conde, Philos. Mag. B 76 (1997) 489.
[4] C.F. Conde, A. Conde, Bol. Soc. Esp. Ceram. Vid. 36 (1997) 189.
[5] R.M. Bozorth, Ferromagnetism, Van Nostrand, New york, 1963, p. 79.