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Exchange interactions through amorphous paramagnetic layers in ferromagnetic nanocrystals

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Exchange interactions between ferromagnetic layers through paramagnetic spacers have been widely observed and studied in thin multilayers. In this paper we report an experimental analysis of the exchange correlation length in soft ferromagnetic nanocrystals. It has been observed that for an average distance between crystallites below 5 nm they are coupled by exchange interactions even above the Curie temperature of the amorphous matrix. The experiment indicates that exchange can propagate through noncrystalline paramagnetic layers. An estimation of the exchange strength has been made.

Exchange interactions between ferromagnetic layers separated by paramagnetic spacers is an exciting topic on which notable interest has been recently focused.[1-3] Other types of interesting magnetic materials also consist in a mixture of different magnetic phases. This is the case for hard $4f$-$3d$ metallic alloys[4] and soft two-phase Fe-based nanocrystalline alloys.[5-7] The coexistence of different magnetic phases enhances the importance of exchange interactions through different media.

An important group of soft nanocrystals is that consisting of nanocrystallites randomly nucleated in a soft amorphous matrix. The magnetic softness of nanocrystalline materials is related to the ratio, δ, of the exchange correlation length (or domain wall thickness), L, to the orientation fluctuation length, l, of the local easy axes. For $\delta > 1$ the macroscopic anisotropy averages out and the walls can move without undergoing pinning forces. For this case the sample shows ideal soft behavior for either domain wall motion or magnetization rotation.[5,8]

By assuming that the atomic cluster with noncorrelated orientation of the easy axes, and local anisotropy constant D, are coupled directly to each other by exchange interactions with strength A (which is proportional to JS^2/a, where J is the exchange integral, S the spin value and a the interatomic distance), Alben, Becker, and Chi[9] found for amorphous ferromagnets the following relation for δ

$$\delta = 16A^2/9D^2l^4 . \tag{1}$$

Even though the Alben-Becker-Chi model has been successfully applied to account for the overall magnetic behavior of soft nanocrystals,[10] it must be taken into account that it was developed for single-phase materials. Since in multiphase systems, as nanocrystals, the exchange coupling between grains depends on the magnetic nature and average thickness of the intergranular region[11,12] we will substitute the direct exchange strength A by γA, where A is the intragrain exchange strength and γ is a phenomenological parameter which accounts for the capability of the matrix and interfaces to transmit exchange. By taking this substitution into account, it is found that for nanocrystals or multiphase systems $\delta(\gamma)$ can be written as

$$\delta(\gamma) = L/l = \gamma^{3/2}\delta . \tag{2}$$

Since the local anisotropy decreases with temperature faster than the exchange in magnetic single-phase samples ($\gamma = 1$), it generally follows from (1) that δ increases as the temperature does. In general, the increases of δ is faster than the decrease of the magnetization, M_s; therefore, the coercive field H_c, which roughly varies as the inverse of δM_s, should decrease as the temperature increases. However, in a multiphase sample $\delta(\gamma)$ is a product of two functions; one of them, δ, increases with temperature whereas the other one, $\gamma^{3/2}$, should exhibit a different thermal dependence.

For the case of α-Fe(Si) single domain crystallites embedded in a soft amorphous matrix, whose Curie temperature, $T_{C[Am]}$, is well below the Curie temperature of the crystallites, the thermal dependence of γ is expected to be closely related to that of the spontaneous magnetization of the amorphous matrix. It is worthwhile to point out that as the magnetization of the matrix decreases, γ should decrease so that H_c increases. For $\gamma = 0$, the exchange interaction between crystallites disappears, the sample becomes an assembly of uncoupled single domains and the magnetization process can only be achieved by magnetization rotation. As the anisotropy decreases with temperature, H_c should decrease with further increase of temperature. Hence, H_c will exhibit a maximum at the temperature for which $\gamma = 0$.

The aim of this paper is to show that, when the distance between crystallites is sufficiently small, $\gamma = 0$ does not occur at $T_{C[Am]}$ but at higher temperatures. From this result it turns out that exchange interactions propagate through a few paramagnetic layers of the amorphous matrix even at elevated temperatures.

The experiments were performed and their results were obtained as follows. Amorphous ribbon (4 mm wide and 20 μm thick) of $Fe_{73.5}CuTa_3Si_{13.5}B_9$ was prepared in air by the planar-flow single-roller melt spinning method. Straight samples (100 mm long) of the ribbon were annealed isothermally for 1 hour at temperatures 340–720 °C under argon atmosphere and slowly cooled down to the room temperature in a furnace. Crystalliza-

tion products were studied by x-ray diffractometry using Cu-$K\alpha$ radiation. Differential scanning calorimetry (DSC) was applied to determine the percentage of nanocrystallization obtained during furnace annealing (the first stage of crystallization). The coercive field and saturation magnetization (in magnetic field 12 kA/m) were determined from quasistatic (0.025–0.1 Hz) hysteresis loop measured at temperature range from room temperature up to 580 °C using a computerized hysteresis loop tracer.[13] Electron diffraction observations of the nanocrystallization process were reported elsewhere.[14]

The nanocrystalline structure, mainly composed of α-Fe(Si) crystals embedded in amorphous matrix, was obtained in this alloy after annealing at temperatures 450–600 °C. Annealing at temperatures exceeding 600 °C resulted in complete crystallization of the amorphous phase and the appearance of iron borides, e.g., Fe_2B, causing enormous increase of H_c.[15] The primary crystallization of α-Fe(Si) manifests itself by the first calorimetric peak. The differences in this peak measured for the alloy in as-quenched state and after annealing at different temperatures are seen in Fig. 1. The area of the peak is a measure of the enthalpy of crystallization and is expected to be proportional to the volume of amorphous phase transformed to the crystalline α-Fe(Si) during annealing in calorimeter (see Table I). As is seen in Fig. 1, the area of the first peak decreases with the increase of annealing temperature T_a, which means that more crystalline phase was created during previous annealing in a furnace. After annealing at $T_a = 580$ °C no DSC peak was detected before the second one corresponding to the crystallization of borides. This means that the first stage of crystallization is complete after annealing at this temperature.

The temperature dependence of magnetization $M_{s[12\ kA/m]}$ of the alloy studied in as-quenched state and after annealing at different temperatures is presented in Fig. 2(a). The curves $M_s(T)$ measured for the alloy after heat treatment show behavior typical for a material containing two ferromagnetic phases. An approximate value of Curie temperature $T_{C[Am]}$ of the amorphous phase, in the alloy in as-quenched and nanocrystalline state, was obtained from these curves with an estimated error below 15%.

The temperature dependence of the coercive field H_c of

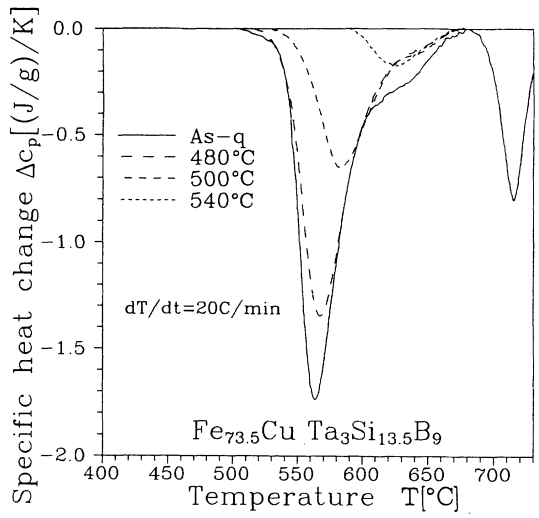

FIG. 1. DSC plots obtained during continuous heating from room temperature to 730 °C at a constant rate $dT/dt = 20\,°C/min^{-1}$ of the alloy in as-quenched state and after one hour annealing at different temperatures.

the alloy studied after the heat treatment is shown in Fig. 2(b). A peak of H_c was observed for all the nanocrystalline samples studied. However, the intensity and the width of the peak strongly depend on the annealing temperature. Arbitrarily defining the onset temperature T_0 as the temperature for which the value of H_c increases up to 1 A/m, it is clear that T_0 decreases with the increase of annealing temperature T_a. The influence of annealing temperature T_a on the Curie temperature of the amorphous matrix $T_{C[Am]}$ and the temperatures characterizing the variation of H_c [illustrated in Fig. 2(b)], namely T_0, T_p-peak temperature and T_e-end temperature (defined as the temperature for which the value of H_c decreases down to 5 A/m) are shown in Table I.

The grain diagram l obtained from the width of peaks in the x-ray diffraction pattern and illustrated in Fig. 3 has been shown to be about 15 nm, for this range of annealing temperatures. By taking into account that the anisotropy D in bcc crystallites of α-Fe(Si) is $8\times10^3\ Jm^{-3}$, $A = 10^{-11}\ Jm^{-1}$ and $\mu_0 M_s = 1.1\ T$,[15] we obtain for the reduced wall thickness, through Eq. (2), the relation

TABLE I. Values of enthalpy of crystallization of the first stage of crystallization H_1, the percentage of transformation of the first stage x_1, volume fraction of crystalline phase x, Curie temperature $T_{C[Am]}$ of amorphous phase, and temperatures characterizing the peak of coercive field H_c (T_0, onset temperature; T_p, peak temperature and T_e, end temperature) of the $Fe_{73.5}CuTa_3Si_{13.5}B_9$ alloy in as-quenched state and after one hour annealing at different temperatures T_a (all temperatures are expressed in degrees centigrade).

T_a	H_1 (J/g)	x_1 (%)	x [%]	$T_{C[Am]}$	T_0	T_p	T_e
As-quenched	80.5	0	0	325			
480	64.4	20.0	15	358	312	345	365
500	34.3	57.4	43	367	302	375	365
520				380	292	410	515
540	6.3	92.2	69	326	269	470	548
580	0	100	75	296	225	510	568

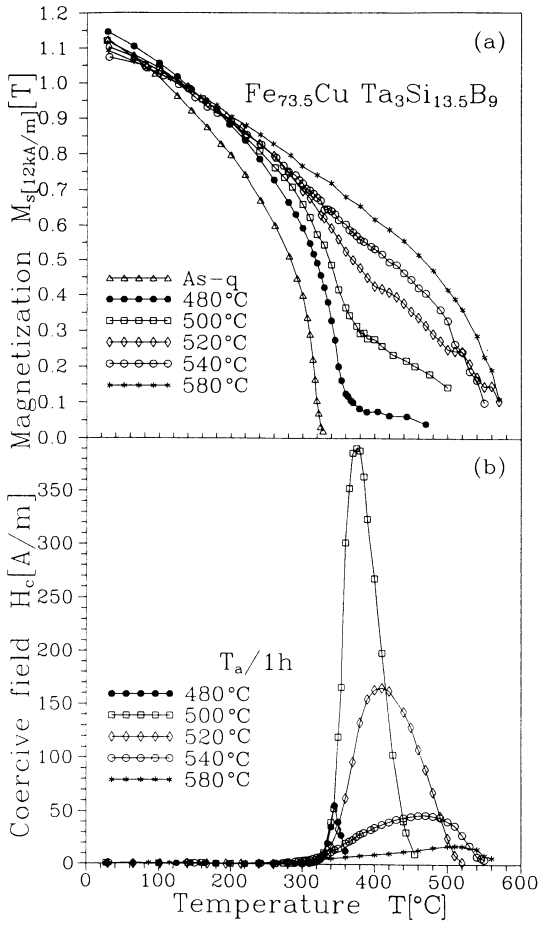

FIG. 2. Temperature dependence of the magnetization $M_{s[12\ kA/m]}$ (a) and the coercive field H_c (b) of the alloy studied in as-quenched state and after one hour annealing at different temperatures.

$$\delta(\gamma)=47\gamma^{3/2} . \tag{3}$$

In the low-temperature range of Fig. 2(b), H_c is negligible in indicating that $\delta(\gamma)$ is larger than 1 or γ larger than 0.1 and the walls can move without hindrances. At T_0 the walls start noting pinning centers which indicates that γ has decreased to 0.1. The ascendant branch between T_0 and T_p can only be explained by the decrease of the domain wall thickness, $\delta(\gamma)$, due to the fast decrease of $\gamma^{3/2}$ with increasing temperature in the neighborhood of $T_{C[Am]}$.

The position of the maximum, T_p, was expected to be located at $T_{C[Am]}$ and that is the case for low T_a, 480 and 500 °C, as illustrated in Table I. Nevertheless, for higher T_a, T_p is shown to be well above $T_{C[Am]}$. $(T_p\text{-}T_{C[Am]})$ increases from 30 to 285 °C as T_a increases from 520 to 580 °C. (Notice that the experimental error for $T_{C[Am]}$ and T_p is not greater than 40 and 10 °C, respectively.) This fact points out that the exchange coupling between grains also takes place above $T_{C[Am]}$. Moreover, the thermal energy $\varepsilon=k_B(T_p\text{-}T_{C[Am]})$, where k_B is the Boltzmann constant, provides information about the strength of the exchange coupling carried through the

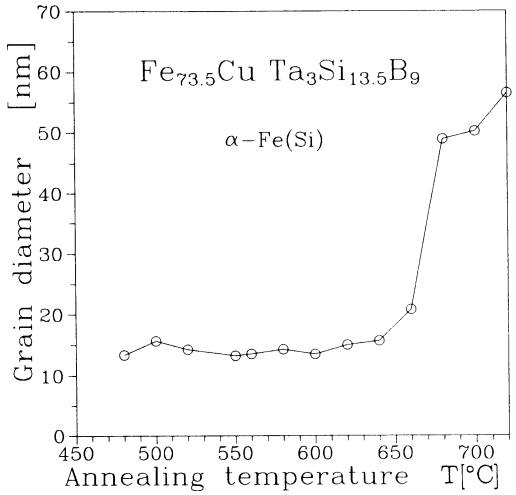

FIG. 3. Dependence of the average grain diameter l on annealing temperature T_a.

paramagnetic amorphous matrix. This strength depends on the average distance between crystallites d, which is the average thickness of the amorphous intergranular region. As both grain size l and α-Fe(Si) volume fraction x are known, an approximate value for d can be immediately found from the relation

$$d=l(1/x^{1/3})-l . \tag{4}$$

According to the values shown in Table I, it is observed that for T_a equal to 520, 540, and 580 °C, ε, within the experimental error, takes the values 0.0024, 0.018, and 0.023 eV, respectively, as d ranges from 4 nm for $T_a=520$ °C to 1.5 nm for $T_a=580$ °C. Just for this range of paramagnetic layer thickness, the existence of ferromagnetic coupling with similar strength has been observed in ferro-para-ferromagnetic multilayers.[16] Notice that for T_a equal to 480 and 520 °C d is 13 and 5 nm, respectively.

In conclusion, the influence of the nature of the intergranular region on the exchange correlation length in multiphase samples has been shown. The experimental determination of H_c as a function of temperature for samples with different crystallized volume fraction has pointed out the existence of exchange interactions between nanocrystals through the paramagnetic matrix in bulk materials. The exchange strength as well as the influence of the spacer thickness are similar to that observed in thin crystalline layers. It is important to emphasize that this effect, observed in amorphous paramagnetic layers, seems to indicate that paramagnetic spacers do not require a crystalline structure to transmit direct exchange. This fact, associated with the ferromagnetic exchange field penetration in paramagnetic metals,[17] should be taken into account in theories.

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