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Iron exchange-field penetration into the amorphous interphase of nanocrystalline materials

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In this work an enhancement of the Curie temperature of the intergranular amorphous region in nanocrystalline alloys with respect to amorphous ribbons of the same composition is shown. The Curie temperature reaches a value of 125 °C. The experimental results are discussed in terms of both an inhomogeneous distribution of Nb atoms in the interphase and the magnetic interactions between the Fe ferromagnetic grains and the matrix. Finally, it is proposed that the existence of a molecular field of about 80 T originated by the penetration of the exchange field of α-Fe nanocrystals into the amorphous paramagnetic intergranular region is the main cause of this Curie temperature enhancement. Moreover, the compositional dependence of the Curie temperature in Fe-B-Nb-Cu amorphous ribbons has been reported.

I. INTRODUCTION

Fe-rich soft magnetic nanocrystals are multiphase materials composed of different magnetic and structural phases. They present outstanding soft magnetic properties and they are ideal systems to study magnetic interactions between particles and between the particles and the matrix. They consist of a fine structure of randomly nanocrystallites nucleated in a soft magnetic matrix. The nanocrystalline state is reached after annealing the initial amorphous alloy above its crystallization temperature.[1]

The excellent magnetic properties arise from the fact that the nanocrystalline grains are exchange coupled via the interphase region and the macroscopic magnetic anisotropy becomes negligible as is predicted by the random anisotropy model.[2] Two relevant factors determine the macroscopic soft magnetic behavior. The first is the grain size d (about 10 nm), which is much smaller than the exchange correlation length L of Fe-based nanocrystalline materials, and the second one is the magnetic nature of the intergranular region through which the grains are exchange connected.

The nanocrystalline materials present an enormous area of phase boundary amorphous crystallite which gives rise to an enormous number of magnetic atoms at the interface. Assuming crystallites of cubic shape, the area of the interface per unit volume is roughly given by $6x/d$, where x is the crystallized volume fraction, so that for $x=0.4$ and $d=10$ nm it becomes approximately 2.4×10^8 m^2 for a volume of 1 m^3.

As the Curie temperature of the amorphous matrix T_c^a is smaller than the Curie temperature of α-Fe crystallites T_c^{cr}, the magnetic behavior of the sample can be driven to that of an assembly of single-domain particles by heating at temperatures above T_c^a thus eliminating the capability of the matrix as exchange transmitter. It has been shown that if the crystallized volume fraction is small ($x<15\%$), the nanocrystalline particles become superparamagnetic at temperature well above T_c^a. The experimental blocking temperatures pointed out the expected influence of magnetostatic interactions between grains.[3] More recently, it has been found by measuring the thermal dependence of the coercive force, that the grains are exchange coupled through the interphase at temperature well above T_c^a. The coercive force increases with the temperature, as a consequence of the gradual loss of the exchange coupling between the grains and this increase persists also when T_c^a is reached and exceeded.[4]

The aim of this work is to show the enhancement of the Curie temperature of the intergranular amorphous region in nanocrystalline alloys with respect to amorphous ribbons of the same composition. The experimental results are discussed and finally, it will be proposed as a possible explanation that the exchange field of α-Fe nanocrystals penetrates the amorphous paramagnetic intergranular region. Moreover, the dependence with the composition of the Curie temperature in Fe-B-Nb-Cu amorphous ribbons has been reported.

II. EXPERIMENTAL

Amorphous ribbons, with the following compositions, were obtained by melt spinning technique: (A) $Fe_{96-x}B_xNb_3Cu$, with $x=19$, 20, 22.5, and 25; (B) $Fe_{77}B_{22-x}Nb_xCu$, with $x=3$, 4, 5, 6, and 7; and (C) $Fe_{74.2}B_{20.2}Nb_{4.5}Cu_{1.1}$, $Fe_{70.7}B_{22.9}Nb_{5.1}Cu_{1.3}$, and $Fe_{67.1}B_{25.7}Nb_{5.7}Cu_{1.4}$.

In order to achieve different steps of the nanocrystallization process, samples of $Fe_{77}B_{18}Nb_4Cu$ were submitted to subsequent heat treatments performed under an Ar atmosphere, at temperatures ranging from 455 to 700 °C.

The structure of the nanocrystalline state was carefully characterized by means of x-ray diffraction and Mössbauer spectroscopy. The heat treatments give rise to an ultrafine structure of α-Fe crystallites, with approximately uniform grain size (10–12 nm) but increase the volume fraction with the annealing temperature from 8 to 40 %. The grain size has been estimated by means of the Scherrer formula from the width of the x-ray diffraction pattern, after correcting the instrumental broadening contribution. The composition of

the crystallites, α-Fe, has been observed by x-ray diffraction and also confirmed from the Mössbauer hyperfine parameters ($B_{hf}=33.1$ and $I_s=0.01$ mm s^{-1}) which are practically those corresponding to the sextet of pure α-Fe ($B_{hf}=33.0$ and $I_s=0.00$ mm s^{-1}). The volume fraction of crystallized Fe, x, is accurately measured from the relative resonant area of the Mössbauer subspectra. The nominal composition of the integranular amorphous region was determined by subtracting the relative number of crystallized Fe atoms, obtained from x, from the composition of the starting amorphous ribbon.

The average distance between Fe grains, Λ, can be derived assuming a cubic shape of the nanocrystals as follows. Let N be the number of nanocrystalline grains per unit volume, with an average grain size d; the following two relations hold:

$$Nd^3=x, \quad N(d+\Lambda)^3=1. \tag{1}$$

These expressions yield the relation of Λ as a function of the experimental x and d

$$\Lambda=d(1/x^{1/3})-d. \tag{2}$$

The thermal dependence of the saturation magnetization M_s has been measured using a Faraday balance, under an applied field of 0.4 T. These curves enable us to estimate the Curie temperature of the integranular amorphous region of nanocrystalline samples and that of the as-quenched amorphous samples with the same composition as the integranular region. The thermal dependence of M_s for nanocrystalline samples exhibits the typical behavior of two-phase systems. The lower Curie temperature, which corresponds to the intergranular amorphous region T_c^a ($<T_c^{cr}$), can be obtained by determining the intersection point of the steepest tangent to the $M_s(T)$ curve, with the T axis and with the magnetization curve of the crystallites extrapolated down to temperatures $T<T_c^a$, respectively.[4] For as quenched samples the Curie temperature is also obtained from the thermal dependence of M_s, which in this case shows the typical behavior of a single magnetic phase. For this case the intersection point of the steepest tangent to $M_s(T)$ with the T axis corresponds to the Curie temperature.

III. RESULTS AND DISCUSSION

As-cast samples. Curie temperatures of the series (A) and (B) are measured from the $M(T)$ curves and also compared with the results of the $Fe_{100-x}B_x$ alloy studied by Hasegawa and Ray in 1978.[5] Figure 1 shows the dependence of the Curie temperature T_c on the relative percentage of Fe:B. IN the series $Fe_{100-x}B_x$, the Curie temperature increases with the boron content. A similar behavior is observed in the series $Fe_{96-x}B_xNb_3Cu$ (with $x=19$, 20, 22.5, and 25): an increase of the B content results in an increase of T_c in accordance with the behavior found in Fe-B alloys. The only appreciable difference is that T_c are more than 100 °C lower than the T_c reported by Hasegawa; this is obviously due to the presence of 3 at. % Nb. The crucial influence of Nb atoms in T_c is evidenced from the results of the $Fe_{77}B_{22-x}Nb_xCu$ (with $x=3$, 4, 5, 6, and 7) series. As can be seen in Fig. 1, an increase of Nb content produces drastic decreasing of T_c and the curves show clear divergences from the Hasegawa and Ray behavior, pointing out that Nb content determines the compositional dependence of T_c.

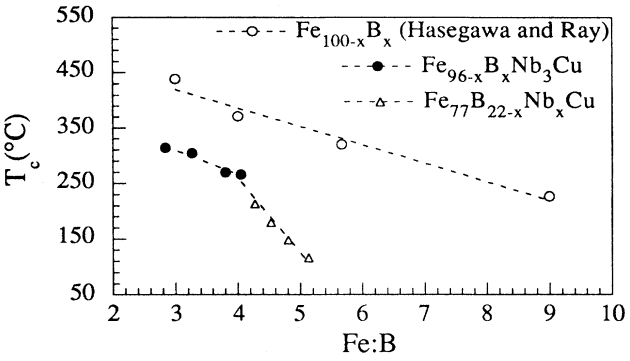

FIG. 1. Dependence of the Curie temperature T_c on the relative percentage of Fe:B of the amorphous series: $Fe_{100-x}B_x$, $Fe_{96-x}B_xNb_3Cu$ (with $x=19$, 20, 22.5, and 25) and $Fe_{77}B_{22-x}Nb_xCu$ (with $x=3$, 4, 5, 6, and 7).

Nanocrystalline samples. The thermal dependence of the saturation magnetization for the as-cast and nanocrystalline $Fe_{77}B_{18}Nb_3Cu$ samples has been measured, after annealing at different temperatures. Figure 2 shows the evolution of the Curie temperature of the amorphous interphase, T_c^a, with the heat treatments. It has been observed that T_c^a increases when the volume crystallized of Fe increases. Taking into account that the Nb and B content of the amorphous matrix grows with the heat treatments as well as considering the drastic influence of Nb atoms in decreasing the Curie temperature of the amorphous alloys, we are not able to explain this result. The numerical values of T_c^a can be found in Table I.

A new experiment was performed in order to resolve this important question: Is the origin of the enhancement of the Curie temperature of the interphase any compositional changes of the amorphous matrix, or is the magnetic nature of the interphase changed by the presence of α-Fe particles?

Amorphous ribbons with the same nominal composition as that corresponding to the integranular amorphous region were prepared (series C) and their Curie temperature T_c^{a*} was measured using the same procedure. Differences were

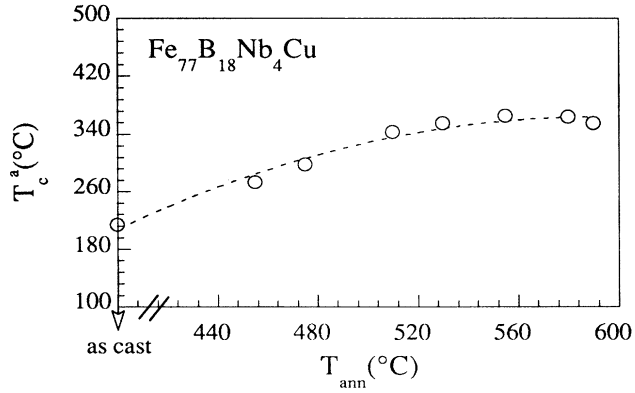

FIG. 2. Evolution of the amorphous interphase. Curie temperature with the annealing temperature.

TABLE I. Estimated amorphous interphase composition and relevant parameters of the $Fe_{77}B_{18}Nb_4Cu$ alloy, in the as-cast state and in nanocrystalline samples annealed at different temperatures.

T_{ann} (°C)	at. % Fe E. Moss	Estimated amorphous matrix composition	d (nm)	Λ (nm)	T_c^a (°C)	T_c^{a*} (°C)	l (Å)
As cast	0	$Fe_{77}B_{18}Nb_4Cu$			214	214	
455	8	$Fe_{75.5}B_{19.2}Nb_{4.3}Cu$	9	12	273	220	5.8
475	14	$Fe_{74.2}B_{20.2}Nb_{4.5}Cu_{1.1}$	10	11	298	225	7.3
510	22	$Fe_{73.5}B_{20.7}Nb_{4.5}Cu_{1.2}$	10	7	343	235	4.4
530	28	$Fe_{70.7}B_{22.9}Nb_{5.1}Cu_{1.3}$	10	5	355	240	5.4
555	32	$Fe_{69.5}B_{23.9}Nb_{5.3}Cu_{1.3}$	10	4	365	235	4.7
580	32	$Fe_{69.5}B_{23.9}Nb_{5.3}Cu_{1.3}$	11	4	364	235	4.8
590	39	$Fe_{67.1}B_{25.7}Nb_{5.7}Cu_{1.4}$	12	4	355	230	4.6

found between the thermal dependence of the saturation magnetization for nanocrystalline samples and that corresponding to an amorphous ribbon of the same composition as the interphase. It is remarkable that the Curie temperature of the intergranular region T_c^a is higher than that corresponding to an amorphous ribbon, T_c^{a*}, of the same composition. The difference is large enough to discard errors in both composition estimation and measuring procedure.

Table I summarizes the relevant experimental results corresponding to different nanocrystalline states of the $Fe_{77}B_{18}Nb_4Cu$ alloy, obtained after different annealing temperatures. The volume fraction of crystallized Fe (x), average grain size (d), average matrix thickness (Λ), T_c^a, T_c^{a*}, and the estimated composition of the matrix are shown.

We suggest two different mechanisms as possible explanations of the experimental results: (1) Inhomogeneous spatial distribution of Nb and B atoms at the amorphous interphase. (2) Exchange field penetration of α-Fe molecular magnetic field into the amorphous paramagnetic matrix.

(1) Recently Yavari[6] has proposed that T_c differences between the amorphous grain-boundary phases and the bulk glasses with same compositions can be explained in terms of diffusion layers and the sharp concentration gradient. During the growing of α-Fe nanocrystals, Nb and B atoms are rejected toward the matrix area. The much faster diffusing boron should have a flat concentration profile in the interphase, while the large slow diffusing Nb should exhibit a sharp concentration with Nb accumulation near the α-Fe interface. Assuming that the Nb-rich area is relatively small, the experimental T_c^a will be that of the Nb-poor and B-rich central area, with higher T_c than that of an amorphous alloy corresponding to the global composition.

Using these interesting arguments we have reestimated the nominal composition of the interphase region assuming a Nb percentage constant for all the heat treatments and equal to the initial amorphous ribbon (Nb=4%). Their Curie temperature can be calculated from Fig. 1 by extrapolating the T_c dependence on Fe:B for the samples with 0 and 3 at. % Nb content to our case (4 at. % Nb). The results can be found in Table II. It is interesting to note than the estimated Curie temperatures show large differences with the experimental T_c^a, for instance, 95 °C for the sample annealed at 530 °C.

So, we can conclude that an inhomogeneous distribution of Nb content at the interphase amorphous region could account for an increase of T_c of 25–50 °C, but it is not sufficient to explain all the enhancement observed. Moreover, when the volume fraction of α-Fe increases (>30%), the thickness of the interphase becomes small (<5 nm) and therefore the contribution to T_c from the Nb-poor area cannot be neglected.

(2) Figure 3 shows the enhancement of the Curie temperature of the interphase, $T_c^a - T_c^{a*}$, as a function of the interphase thickness Λ. It was found that $T_c^a - T_c^{a*}$ decreases roughly linearly with Λ. The more probable cause of this difference is the presence of Fe nanocrystals, with higher Curie temperature.

There are in principle two types of interactions which can be invoked to account for this phenomenon, (i) exchange field penetration and/or (ii) magnetostatic field, molecular field, or magnetostatic field, polarizing the matrix above its Curie temperature, giving rise to an apparent increase of the order temperature.

The differences between the exchange-field penetration and the magnetostatic field are their strength and their typical

TABLE II. Estimated amorphous interphase composition, assuming a Nb content equal to 4 at. %, and its Curie temperature for different nanocrystalline samples.

T_{rec} (°C)	Estimated amorphous interphase central region composition (Nb=4%)	Fe:B	T_c (°C)
455	$Fe_{75.7}B_{19.2}Nb_4Cu_{1.1}$	3.9	230
475	$Fe_{74.6}B_{20.3}Nb_4Cu_{1.1}$	3.7	240
510	$Fe_{72.9}B_{21.8}Nb_4Cu_{1.2}$	3.3	255
530	$Fe_{71.5}B_{23.2}Nb_4Cu_{1.3}$	3.1	260
555	$Fe_{70.4}B_{24.2}Nb_4Cu_{1.4}$	2.9	270
590	$Fe_{68}B_{26.5}Nb_4Cu_{1.5}$	2.6	285

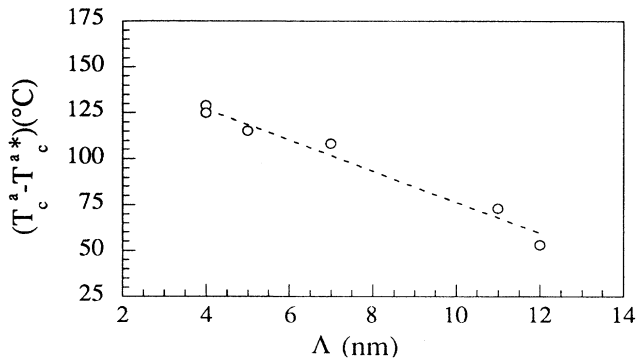

FIG. 3. Difference between the Curie temperatures of the intergranular region in nanocrystalline samples and the Curie temperatures of the amorphous sample with the same composition as the interphase, $(T_c^a - T_c^{a*})$, versus the interphase thickness.

length range. The magnetostatic field is a long-range field which may reach maximum values close to 2 T in the whole volume of the matrix. On the other hand, the effective molecular field within α-Fe particles is closed to 1000 T but is expected to decay exponentially, along the perpendicular direction to the interface and inwards toward the matrix, in one or two atomic distances.[7] Hence, if we consider the molecular field at the matrix atomic layer adjacent to the Fe atomic layer to be 500 T, the volume average of both fields in the matrix would take the same value for a typical matrix thickness Λ, corresponding to 500 interatomic distances. For shorter Λ the molecular-field average, even decaying so fast, becomes much larger than the magnetostatic one. Moreover, the observed increase of T_c^a larger than 100 °C which corresponds to an effective increase of the molecular field of 80 T, can only be produced by the presence of a molecular exchange field.

According to these arguments, the following explanation for the enhancement of T_c^a, is proposed. The exchange coupling between the ferromagnetically ordered atoms of the crystallites and the atoms of the matrix induces ferromagnetism on the layers of the matrix adjacent to the interface, and through the exchange coupling the magnetic order propagates inwards toward the matrix, giving rise to a spontaneous magnetization above its Curie temperature. We can define phenomenologically an effective exchange penetration length l. The meaning of l is found from the average of the Curie temperature in the matrix volume limited by two parallel crystallite surfaces located at $z=0$ and $z=\Lambda$, respectively. The Curie temperature of the matrix enhanced from T_c^{a*} to T_c^a can be expressed as the lineal average of T_c^{cr} between 0 and l, a uniform T_c^a between l and $\Lambda - l$, and a uniform T_c^{cr} between $\Lambda - l$ and Λ according to

$$T_c^a = T_c^{a*} + (T_c^{cr} - T_c^{a*}) 2l/\Lambda. \quad (3)$$

The experimental results indicate that T_c^a obeys an average procedure as that described by (4) and this rough approximation leads to values of l mainly comprised between 4.5 and 5.5 Å, see Table I.

IV. CONCLUSION

In conclusion, a noticeable enhancement has been found of the Curie temperature of the amorphous matrix mainly due to the interaction with the ferromagnetic particles with higher Curie temperature. It has been shown that this enhancement decreases with the increase of the average distance between grains. In particular it has also been shown that the experimental Curie temperature of the matrix can be obtained by averaging the Curie temperature of an amorphous alloy of the same composition and that corresponding to Fe grains.

The Curie temperature enhancement has been explained as a consequence of the α-Fe exchange-field penetration into the amorphous matrix that gives rises to an increase of the matrix average effective molecular field. The relevant parameter is the ratio between the exchange penetration length and the interphase thickness, $2l/\Lambda$, for nanocrystalline sample ranges between 0.1 and 0.25. For these values the effect of the exchange-field penetration is probably much larger than that corresponding to magnetostatic interactions. However, magnetostatic interactions as well as the inhomogeneous distribution of Nb at the interphase can also be invoked, and surely contribute, as causes of the Curie temperature enhancement but in a much smaller amount than the exchange-field penetration.

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