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Magnetic interactions in Fe-Zr-B-Cu nanocrystalline materials at elevated temperatures

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Nanocrystalline samples were obtained by subsequent annealing of the $Fe_{93-x-y}Zr_7B_xCu_y$ metallic glass ribbons either in a conventional furnace or by electric current flowing through the ribbon. The coercive field of the slightly crystallized material shows a drastic increase at temperatures about the Curie point of the amorphous matrix, whereas for samples with high content of the crystalline phase the coercivity increases slowly in the temperature range well above T_C. Temperature dependencies of the coercive field show that at elevated temperatures the magnetic interactions between ferromagnetic particles, most probably of exchange origin, take place through the paramagnetic intergranular matrix.

Beside their outstanding soft magnetic properties, a new group of nanocrystalline magnets produced by crystallization of the amorphous state constitutes a unique object for fundamental studies of magnetism.[1,2] Since the Curie temperature of a residual amorphous matrix is usually much lower than that of the crystallites embedded in this matrix, one can observe in these materials a variety of coexisting magnetic phases at elevated temperatures.[3] One of the interesting features the nanocrystalline materials show, is the occurrence of magnetic interactions between the particles at temperatures above the Curie point of the matrix, as it has recently been reported.[4,5] Though the origin of these interactions is not yet clear enough, one may consider that they are of exchange and/or dipolar nature (see, e.g., Refs. 4 and 5).

The studies hitherto performed were carried out using samples of the conventional composition Fe-Cu-Nb-Si-B, in which the Curie point of the amorphous matrix is relatively high (300–350 °C) and, consequently, the temperature range in which the interparticle interactions can be studied is comparatively narrow. Therefore, for more accurate investigations of the coupling between the grains via the paramagnetic amorphous material, Fe-Zr-B-Cu metallic glasses, with the Curie temperature close to the room temperature, have been chosen.[6]

The main aim of the study undertaken and reported here is to show the existence of magnetic interactions between particles separated by a thin paramagnetic layer even at temperatures well above the Curie point of the amorphous matrix. Additionally, it will be shown that it is a general feature of nanocrystals embedded in an amorphous matrix independently of the composition of the material as well as of the method of heat treatment.

$Fe_{93-x-y}Zr_7B_xCu_y$ ($x=4,6;y=0,1,2$) amorphous ribbons have been obtained by means of the melt-spinning method. The samples were then annealed using either conventional heat treatment, in an inert gas atmosphere furnace, at temperatures $400 \leq T_{\text{ann}} \leq 540\,°\text{C}$ for 1 h or the so-called flash-annealing technique in which samples were heated in air by electric current pulses (1.3 A/30 s) flowing through the ribbon of the cross section of 1 mm×20 μm (for details, see Ref. 7). The nanocrystalline structure resulting from the heat treatments was studied by x-ray diffraction and Mössbauer spectroscopy. The former gives the crystalline phases and grain size, whereas the Mössbauer technique has been used for estimating the relative amount of each Fe containing phase.[7] Heat-treatment conditions of individual samples as well as their crystallization products, obtained from x-ray and Mössbauer spectroscopy, are presented in Table I. Transmission electron microscopy performed by other authors in similar samples,[6] shows a random distribution of nearly spherical nanocrystals after the annealing. The same morphology is assumed to be present in our case.

In order to analyze the magnetic properties of the

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TABLE I. Characterization of the samples and their heat-treatment conditions (p: volumetric fraction of the crystalline phase; T_C (am): the Curie temperature of the as-quenched metallic glass; D: average grain diameter; δ: estimated boundary thickness).

Sample	Alloy	Heat treatment	Crystalline phases	p [%]	T_C (am) [°C]	D [n,m]	δ [nm]
A	$Fe_{86}Zr_7B_6Cu_1$	400 °C, 1 h	α-Fe	1	60	9	32
B	$Fe_{85}Zr_7B_6Cu_2$	420 °C, 1 h	α-Fe	3	50	9	20
C	$Fe_{85}Zr_7B_6Cu_2$	540 °C, 1 h	α-Fe	70	50	12	1.5
D	$Fe_{89}Zr_7B_4$	540 °C, 1 h	α-Fe	75	20	15	1.5
E	$Fe_{86}Zr_7B_6Cu_1$	Flash anneal.	α-Fe, Fe_2B, Fe_3B	85	60	16	0.9

nanocrystalline samples, their temperature dependencies of magnetization and coercivity have been measured. For samples B, C, and D these characteristics were obtained using the vibrating sample magnetometer (saturation magnetization in the field of 1.6 T) and a high performance hysteresis loop tracer[8] (coercivity). A conventional furnace, which equipped both instruments, was used for heating. The temperature range for all these measurements was chosen so to avoid further crystallization of the samples. The results obtained are presented in Figs. 1(a) and 1(b). The same dependencies for samples A and E were found from their hysteresis loops observed in a conventional way, applying a triangular-wave drive field of maximum amplitude of about 40 kA/m with its frequency 0.3 Hz.[7] In this case, the sample was heated by an electric current flowing along the sample. The obtained dependencies of magnetization and coercivity vs the intensity of current applied are shown in Fig. 2 (the current 20 mA corresponds to the temperature of 63 °C). The temperature dependencies of the magnetization allowed us to find the Curie temperature of the as-quenched amorphous material as well as to estimate the volumetric fraction of the crystalline phase (p) in the sample. The latter agrees with the Mössbauer measurements. The values found in this way are given in Table I.

As it is seen in Figs. 1 and 2, the coercive field of the slightly crystallized samples A and B rises rapidly (the change of its value is almost three orders of magnitude) at temperatures close to the Curie point of their amorphous matrix, in contrast with the highly crystallized samples C, D, and E, where slow increase in the temperature range well above T_C was observed. In sample C the coercivity reaches the maximum at $T=500$ °C (about 400 °C above the Curie point of the amorphous matrix). In the case of sample D, this temperature range is even larger since for temperatures 500 °C above T_C the coercivity has not reached its maximum value. It is worth noticing that the observed behavior of coercivity seems to be a general feature for the material studied in a sense that different compositions of the amorphous materials and their heat-

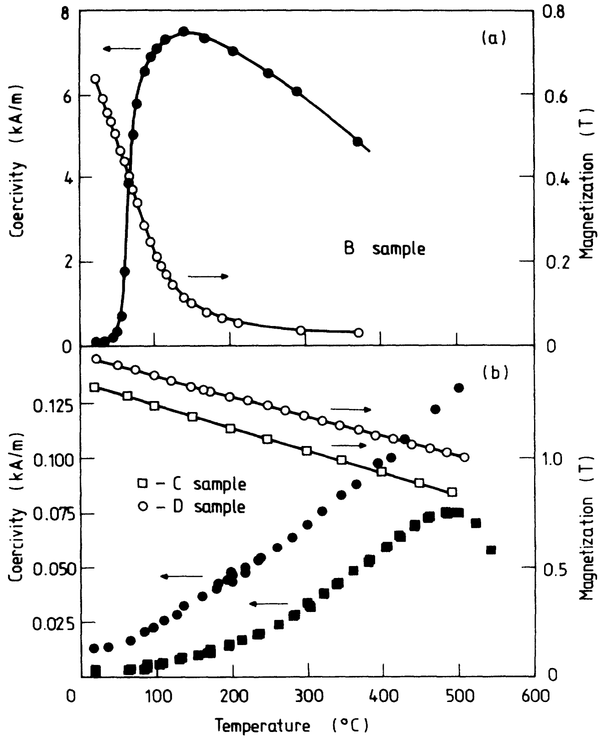

FIG. 1. The temperature dependencies of saturation magnetization (open symbols) and coercivity (closed symbols) in (a) slightly crystallized B sample, (b) nanocrystalline C (squares) and D (circles) samples.

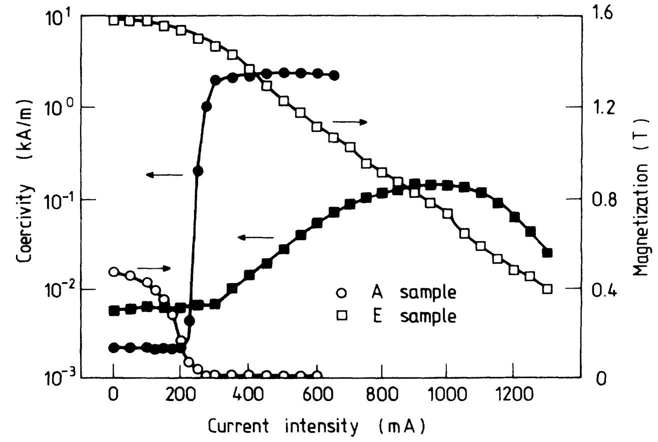

FIG. 2. The evolution of saturation magnetization (open symbols) and coercivity (closed symbols) vs the intensity of the current flowing along the ribbon in A (circles) and E (squares) samples.

treatment methods lead to the same results (see also Ref. 4).

It is well known that the outstanding magnetic softness of nanocrystalline materials is due to the extremely low effective anisotropy they show as well as near-zero effective magnetostriction.[9] For particle dimensions much smaller than the ferromagnetic exchange correlation length, the coupling between randomly oriented particles tends to average out the macroscopic anisotropy. Thus, owing to this mechanism, the effective anisotropy may become extremely small (several orders of magnitude smaller than that of an isolated particle). According to this picture, the effective anisotropy should rise very rapidly when the exchange coupling between the grains is interrupted. Such an effect should be of a dramatic measure when the temperature reaches the close vicinity to the Curie point of the amorphous matrix.[9] The coercivity of the amorphous materials scales roughly with the ratio of the effective anisotropy to the saturation magnetization. For a single-phase magnet, its anisotropy usually decreases with the temperature faster than the saturation magnetization and, consequently, the coercivity diminishes as the temperature is risen. Therefore, it can be expected that the coercivity of the nanocrystalline Fe-Zr-B-Cu magnets should increase very steeply when the temperature reaches the Curie point of the amorphous matrix and then, with a further increase of the temperature, slowly diminish (except for very small isolated particles which at elevated temperatures show superparamagnetic behavior leading to a very rapid decrease of coercivity).

The expected temperature dependence of coercivity has experimentally been observed but only in the slightly crystallized samples A and B [see Figs. 1(a) and 2]. However, in the samples with high content of crystallites a slow increase of coercivity was observed well above T_C. This fact can be recognized as a strong evidence that the coupling between particles takes place through paramagnetic amorphous layer separating them. An increase of coercivity is caused then by a progressive decrease of the interparticle coupling. In order to estimate the thickness of the paramagnetic layer δ, we used the very simple expression[2,4] (valid for a regular array of cubic crystals of side D):

$$\delta=D(p^{-1/3}-1) .$$

The values so obtained are presented in Table I for all the samples except the last one, which shows the presence of several crystalline phases, making difficult the estimation. The change from isolated grains to the coupling through the paramagnetic interlayer corresponds to a decrease in the mean layer thickness from around 3 to only 1.2 nm. This latter distance seems to be short enough to allow the magnetic interaction between the grains.

In a real material, due to a certain distribution of the grain sizes and the distances between them, the strength of the coupling should also be distributed in a certain way within the volume of the sample. Therefore, the magnetic isolation should first be achieved by particles from the regions where the coupling strength is the lowest. According to this, in sample C, where the volumetric fraction of the crystalline phase is slightly lower than in sample D and, moreover, containing smaller grains (due to the presence of Cu, which is known to enhance the nucleation rate for crystallization) the decoupling between particles can be observed at lower temperatures.

It has already been shown in thin multilayer systems[10] as well as in magnetically hard granular alloys[11] that the exchange interactions between ferromagnetic materials occur through a nonmagnetic spacer. Similarly, in the case of soft nanocrystalline materials, obtained by annealing the metallic glasses, the coupling between the grains seems to be of the exchange nature. The exchange field produced by ferromagnetic particles penetrates into the paramagnetic intergranular space a distance which decreases with an increase of the temperature. Thus, the temperature dependence of coercivity results from the competition of two effects, namely, an increase of the effective anisotropy of the material caused by a lessening of the exchange interactions with temperature and a simultaneous decrease of the local magnetocrystalline anisotropy of each grain due to the rise of temperature (the latter is especially important within the regions where particles become isolated from the exchange coupling). The coercivity should, therefore, increase in the temperature range within which the first effect dominates and then decrease with a further rise of temperature, since the second effect becomes the prevailing one.

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