Journal of Magnetics 4(3), 84-87 (1999)

Magnetization Processes in Partially Crystallized Co-Based Metallic Glass

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(Received June 21, 1999)

It is shown that progressive crystallization of non-magnetostrictive Co-based metallic glass (VITROVAC 6030) leads to an increase of coercivity by more than three orders of magnitude. The mechanisms responsible for this phenomenon are interpreted showing that the main source for the giant increase of the coercivity is the pinning effect on the domain walls originating from the created crystallites of the size much smaller than the domain width (correlation length for ferromagnetic exchange interactions). It is also shown that gradually devitrified non-magnetostrictive metallic glass is an excellent model material for verification of Néel's theory describing the Rayleigh rule.

1. Introduction

As commonly known, coercivity of magnetic materials strongly depnds on their microstructure, mainly because of the interactions of the domain walls with defects which are generally identified with grains of which a given magnet is composed. Therefore, coercivity scales with the mean grain size. This scaling proceeds differently depending on the mean grain size D compared with the domain wall width δ, the quantity which can be identified with the correlation lengt for ferromagnetic exchange interaction. In the regime where grains are larger than the wall width, $D > \delta$, coercivity decreases with an increase of the grain size according to the well known 1/D - dependence (see, e.g. [1]).

The invention of nanocrystalline magnets [2], known under their trade name FINEMET, has shown that coercivity of these materials scales proportionally to D^6 (see, e.g. [3]). Hence, coercivity rapidly increases with an increase of the grain size contrary to the case when $D > \delta$. The above scaling relations are correct only for materials in which the volume density of crystalline phase is high enough so as the exchange interactions can be effective. Therefore, it would be interesting to recognize the evolution of magnetic properties (coeercivity, inparticular) of magnets obtained by successive devitification of metallic glass in which created nanograins are much smaller than the wall width and in which their volume (TEM) using Philips EM-300 microscope operating with 100 keV. Samples were thinned down by ion-etching. Composition of the crystallites was investigated using X-ray diffraction technique.

2. Results and Discussion

The DSC-curve and magnetic measurements indicate that crystallization of the sample proceeds in two well separated steps and that bot created phases exhibit magnetic behavior. The onset of crystallization takes place around 750 K, whereas, the second step of this process is initiated at about 830 K. An analysis of the X-ray diffraction patterns obtained for all partially crystallized samples shows that the created particles are most probably composed of Co_3B crystalline phase mixed with a very small amount of Co_2Mo_3 phase (the parent amorphous alloy contain only 1% of Mo). Curie temperature of Co_3B equals 760 K [9]. However, the value of this temperature for the crystalline phase grown within the first crystallization step at the time of continuous heating of the parent material is higher than that for Co_3B. It suggests that the composition of the crystallites is more complex than that determined from X-ray diffraction patterns. Heating the sample at the temperatures higher than the onset of the second crystallization step leads to the total crystallization of the sample. For temperature range within the first crystallization peak, tiny nanocrystallites are grown, the size of which and their volume density become larger the higher is the annealing temperature. This effect is seen in Fig. 1 which presents exemplary TEM-micrographs for the samples annealed at successively increasing temperatures.

Fig. 2 presents a dependence of the coercivity on the annealing temperature obtained for a series of samples isothermally heated for 1 hour. As seen in this figure, the change of coercivity exceeds three orders of magnitude,

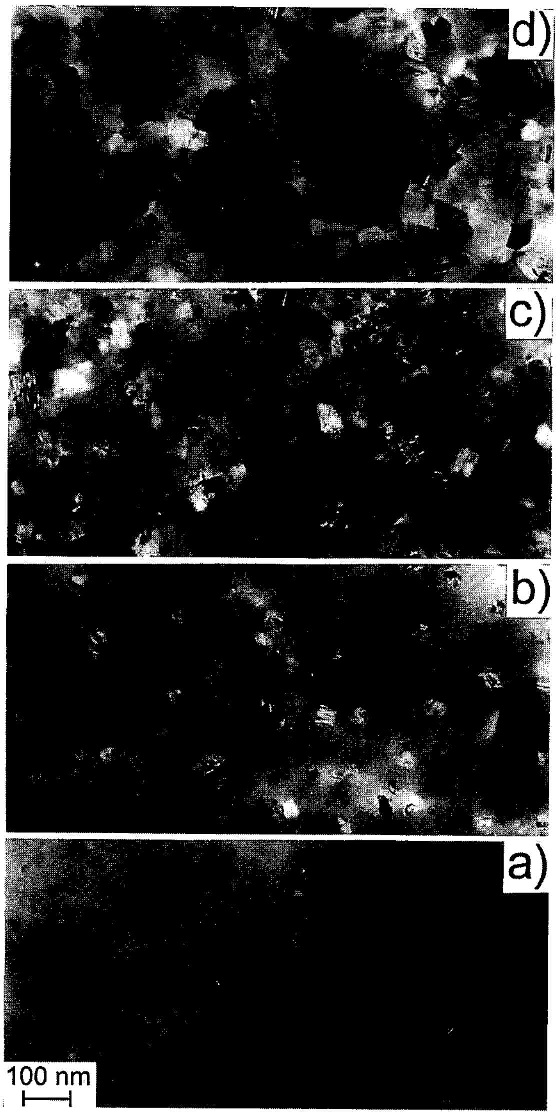

Fig. 1. TEM-micrographs obtained for the samples: annealed at 693 K (a), at 708 K (b), at 753 K (c), and at 873 K (d). Each sample was annealed for 1 h. The magnification is the same for all the micrographs.

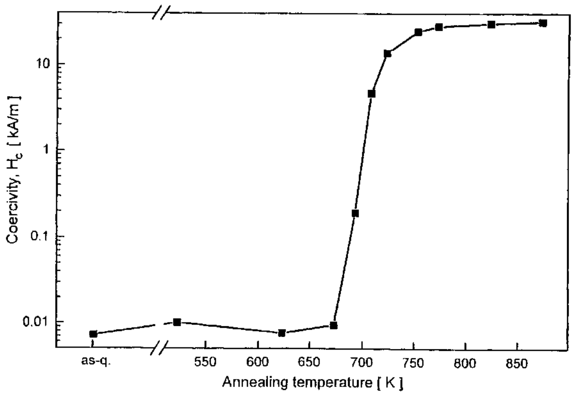

Fig. 2. Dependence of the coercivity on isothermal annealing temperature for a series of Co-Fe-Mo-Mn-Si-B samples measured at room temperature.

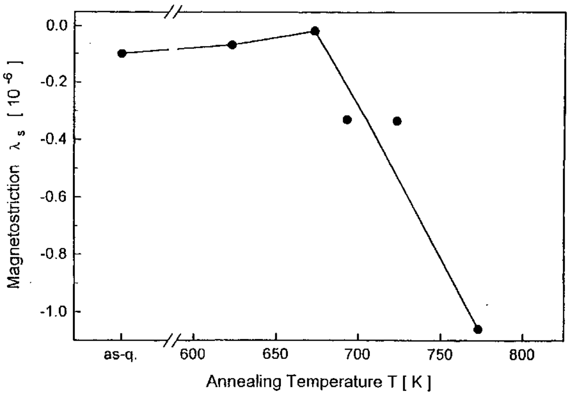

Fig. 3. Dependence of the magnetostriction on annealing temperature for a series of samples (calculated from the data obtained at room temperature using SMFMR-technique).

achieving its "saturation" value of about 32 kA/m for the sample anealed at 873 K. Surprisingly, the lowest value of this parameter, equals 7 A/m, has been obtained for the as-quenched sample on the contrary to the expectation that annealing at relatively low temperature usually leads to a decrease of coercivity owing to stress relaxation. The above result can, however, be explained considering the fact that the parent metallic glass exhibits extremely low magnetostriction (~10^{-7}, as measured usig SMFMR-method, see Fig. 3) and, therefore, magnetoelastic contribution to the coercivity is in this case negligible.

As seen in Fig. 2, the dominant change of coercivity occurs in a relatively narrow range of the annealing temperatures (632-732 K). In this range, initially nucleated tiny crystallites (Fig. 1a) grow up (as seen in Fig. 1b and c) with an increase of the temperature of annealing, occupying more and more of the whole volume of the sample till total crystallization is completed (see, Fig. 1d). Further increase of the annealing temperature generates only small changes of the coercivity.

For a magnet build up from an amorphous medium containing non-directly interacting randomly distributed nanocrystallites, Porteseil and Goeffroy have shown that its coercivity can be estimated from simple statistical arguments [10]. Applying these arguments, they have derived the following expression which describes the influence of domain wall pinning arising from the anisotropy energy of the crystallites inside the wall on the coercivity of the material

$$H_c = n^{1/2}\delta^{-3/2}K_1\upsilon/12J_s \qquad (1)$$

where: n is the volume density of the nanocrystallites, δ - the wall width, K_1 - the anistotropy constant of the crystallite, υ - its mean volume, and J_s - the saturation polarization of the sample.

The samples studied fulfil the assumptions under which eq. (1) has been derived, therefore, this expression can be used to interpret the observed changes of coercivity.

A direct use of eq. (1) to compare the calculated and experimental values of coercivity is, unfortunately, not pos-

Table 1. Dynamics of the Variation of Coercivity

T_{ann} [K]	D [nm]	$n \times 10^{-21}$ [m^{-3}]	$n^{1/2}\upsilon \times 10^{14}$ [m$^{-1/2}$]	k_{exp} –	k_{cal} –
693	20	1.38	15.5	1	1
708	50	2.33	315.7	25.0	20.4
753	70	1.58	710.6	131.0	45.8

sible since the values of the magnetocrystalline anisotropy of the crystallites and that of the wall width are unknown. However, this equation can be used to compare the dynamics of an increase of coercivity with the annealing temperature, observed in the experiment with that calculated from this equation. Assuming that the anisotropy, wall width and saturation polarization do not change significantly with the temperature of annealing, then, according to eq. (1), coercivity should scale with the product $n^{1/2} \times \upsilon$ (its values, estimated from TEM-micrographs for samples annealed at 693 and 708 K, are given in Table 1). Two last columns in this table display the introduced parameters k_{exp} and k_{cal}, equal to the values of the experimental and calculated coercivity, respectively, both normalized in relation to the values of the coercivity of the sample annealed at 693 K. Both parameters give a measure of the dynamics of the rise of coercivity with the annealing temperature.

As it is seen in Table 1, the divergence between the calculated and exprimental values of both parameters increases with the temperature of annealing. Since the volume content of the crystalline phase increases with the rise of this temperature, the effective anisotropy seen by the wall becomes larger, and, consequently, its width decreases inconsistently with the earlier assumption that the wall width does not change at these conditions. This effect which is, however, difficult to be controlled, is the most probable source of the observed large discrepancies when using eq. (1) to interpret the experimental results.

Fig. 3 shows the dependence of magnetostriction as a function of the annealing temperature as measured by SMFMR-technique, assuming the values of the g-factor and of Young modulus equal 2.2 and 220 GPa (a typical value for metallic glasses), respectively. As seen in this figure, magnetostriction displays extremely low values (~10^{-7}) for samples annealed in the range of temperatures lower than that at which the onset of crystallization occurs. In the range of higher annealing temperatures, within which primary crystallization takes place, magnetostriction rises almost linearly in its absolute value becoming more and more negative, achieving the value of 10^{-6} for the sample heated at 773 K. For still higher temperatures of annealing, in the range of the second step of crystallization, the observed resonance spectra are so smeared that calculation of magnetostriction becomes quite unreliable. As claimed in [11], at the early stages of crystallization of the CoFe-based metallic glasses, iron-rich crystal-like clusters are formed which act as nucleation sites in the glass to crystal transformation. Thus, the growing crystallites may contain some amount of iron causing that the amorphous matrix becomes poorer of this element and, consequently, magnetostriction grows more negative. The observed very low magnetostriction confirm the anticipation made earlier that magnetoelastic interactions have negligible influence on coercivity. This conclusion is additionally confirmed by observation of domain structure in the as-quenched sample which do not display complex and irregular pattern typical for magnetostrictive samples in which magnetoelastic interactions due to the quenched-in stresses play a significant role. The observed domain pattern for this sample in its demagnetized state is as simple as possible, consisting of two domains separated by the straight wall aligned with the length of the ribbon sample (see, Fig. 4a). However, the number of walls increases (see, Fig. 4b and c) with an increase of the annealing temperature. This effect is not surprising since the force pinning the walls becomes stronger the larger volume density of the crystallites.

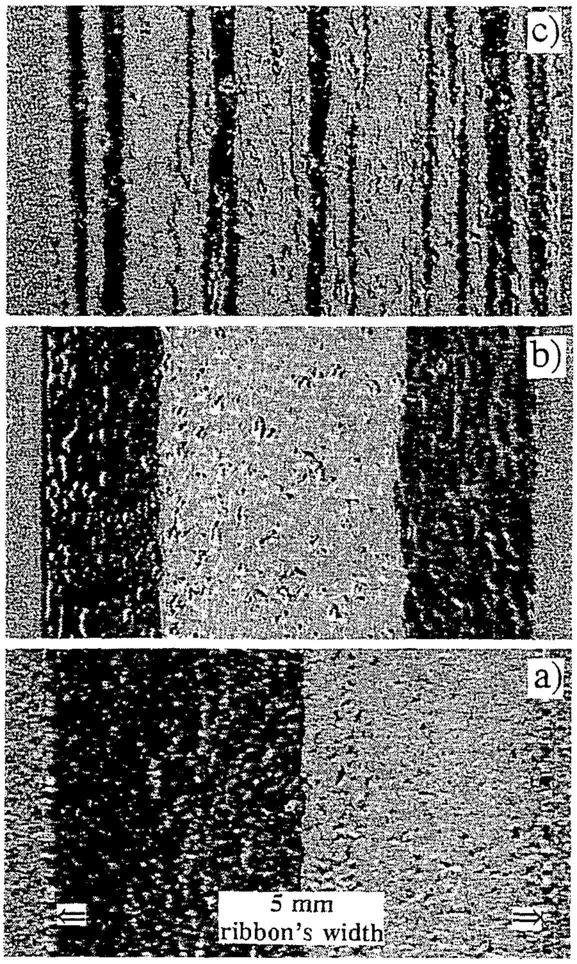

Fig. 4. Kerr-effect images of domain structure observed for samples: in as-quenched state (a), annealed at 673 K (b), and at 693 K (c). The patterns (b) and (c) were taken after demagnetization of the samples by an a.c.-field.

It has been turned out that the studied series of partially crystallized metallic glass is an excellent model material for

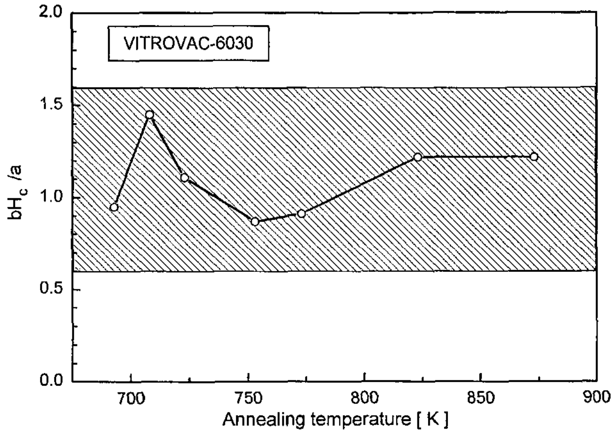

Fig. 5. Annealing temperature dependence of the parameter p (hatched area shows theoretical limitation of the p-parameter).

the experimental verification of the old Néel's theory [12] which describes the empirical Rayleigh rule representing the initial part of the virgin magnetization curve. In this theory, Néel shows that the introduced dimensionless parameter $p = bH_c/a$, where a and b are the coefficients of the commonly known quadratic polynomial expressing the Rayleigh rule and H_c the coercivity, should range between 0.6 (hard magnets) and 1.6 (soft). To the best our knowledge the values of the parameter p obtained from the experiments for numerous magnets are highly greater than those expected. As it is seen in Fig. 4, the values of p, calculated for a series of the samples in queston, comprise within the range anticipated by Néel's thèory (for the details of these calculations and interpretation of the obtained results, see [13]).

3. Conclusions

It has been shown that the observed giant increase of the coercivity of Co-based metallic glasses with the temperature of annealing is mainly due to the pinning effect on the domain walls coming from the created crystallites of the size much smaller than the wall width. It has also been shown that the studied series of the samples is an excellent model material to verify Néel's theory of the Rayleigh empirical rule describing the initial part of the virgin magnetization curve.

Acknowledgements

The work was supported in part by the State Committee for Scientific Research (Poland) under grant No.8 T11B 048 10. The authors are greatly indebted to Dr. G. Herzer (Vacuumschmelze, GmbH, Hanau, Germany) for supplying the Vitrovac 6030 amorphous ribbon.

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