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Study of the induced anisotropy in field annealed Hitperm alloys by Mössbauer spectroscopy and Kerr microscopy

J. S. Blázquez[1*], J. Marcin[2], F. Andrejka[2], V. Franco[1], A. Conde[1], I. Skorvanek[2]

[1] Departamento de Física de la Materia Condensada, ICM-SE CSIC, Universidad de Sevilla, P. O. Box 1065, 41080, Sevilla, Spain

[2] Institute of Experimental Physics, Slovak Academy of Sciences, SK-040 01 Kosice, Slovakia

* Corresponding author: Javier S. Blázquez

e-mail: jsebas@us.es

Abstract

Samples of $Fe_{39}Co_{39}Nb_6B_{15}Cu_1$ alloy were nanocrystallized under zero field annealing (ZF) and transverse field annealing (TF) conditions. A reduction in coercivity for TF samples with respect to ZF sample (16 and 45 A/m, respectively) is observed. Kerr microscopy images show a well-defined parallel domain structure, transversally oriented to the ribbon axis for the TF sample unlike for the ZF sample, for which a complex pattern is observed with large and small domains at the surface of the ribbon. Although Mössbauer spectra are clearly different for the two studied samples, Mössbauer studies confirm that there is no significant difference between the hyperfine field distributions of TF and ZF samples but only the relative intensity of the 2nd and 3rd lines A_{23} (related to the angle between the gamma radiation and the magnetic moments, α). Whereas for TF annealed samples α=90º (A_{23}=4), indicating that the magnetic moments lay on the plane of the ribbon in agreement with the well-defined domain structure observed by Kerr microscopy, ZF annealed samples show A_{23}=1.8. This value is close to that of a random orientation (A_{23}=2) but smaller, indicating a slight preference for out of plane orientations. Moreover, it is clearly smaller than that of as-cast amorphous samples A_{23}=2.8, with a preference to in plane orientations. The application of the law of approach to saturation yields a larger effect of the inhomogeneities in ZF sample with respect to TF one.

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Keywords: Soft magnetic alloys; Hitperm alloys; Magnetic field annealing; Magnetic anisotropy; Domain structure

1 Introduction

Nanocrystalline alloys with a general composition $Fe_{100-x-y-z}ETM_xMET_yCu_z$, with ETM an early transition metal (Nb, Zr, etc.) and MET a metalloid (Si, B, P, etc.) [1] owe their excellent soft magnetic properties to the magnetic coupling between α-Fe type nanocrystals, which are embedded in an amorphous matrix also ferromagnetic. This particular microstructure leads to averaging out the magnetocrystalline anisotropy [2], although the magnetic coupling is lost above the Curie temperature of the amorphous matrix, T_C^{am} [3]. In this sense, Hitperm alloys, in which Co is partially substituted for Fe, were proposed as candidates to keep magnetic coupling at elevated temperatures [4] as T_C^{am} is enhanced even beyond the onset temperature of the crystallization. This implies that, in order to nanocrystallize the sample, it has to be annealed below its T_C^{am} leading to domain walls stabilization due to pair ordering mechanism [5] and unwanted magnetic hardening [6,7,8].

The stabilization of domain walls can be overcome by annealing under the application of a magnetic field large enough to saturate the sample. In this case, magnetic softening can be achieved even in comparison to as-cast amorphous samples [9,10,11,12]. However, there are induced magnetic anisotropies, which imply a preferential orientation of the magnetic moments. In this work, we explore the relationship between the orientation of the magnetic moments and the annealing procedure by using ^{57}Fe Mössbauer spectrometry and Kerr microscopy. The studied sample was a $Fe_{39}Co_{39}Nb_6B_{15}Cu_1$ Hitperm-type alloy, for which a minimum 3 A/m in coercivity was obtained after annealing under longitudinal field [12].

Hitperm-type alloys have been characterized using Mössbauer spectroscopy [13,14,15,16,17,18], or other nuclear resonant techniques [19]. These studies describe the evolution of the hyperfine parameters as nanocrystallization progresses. However, Mössbauer studies on Hitperm-type alloys submitted to field annealing processes are scarce (e.g. Kanuch et al. studied the effect of field annealing on the Mössbauer spectra of $Fe_{38}Co_{38}Mo_8B_{15}Cu_1$ [20]).

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On the other hand, domain structure has been observed for different Hitperm-type systems after either conventional annealing or field annealing. Several studies used Lorentz microscopy to observe magnetic domains in samples prepared for transmission electron microscopy [21,22,23], which differs from the expected pattern in the ribbon samples. Kerr microscopy was used to study the domain structure and its relation to induced anisotropy in $Fe_{44.5}Co_{44.5}Nb_7B_{12}$ [24] and in Co-rich Finemet-type ribbons [25]. However, no Mössbauer results were supplied in these studies. On the other hand, although few studies explore the relationship between Mössbauer spectroscopy results and domain structure in nanocrystalline ribbons, these studies correspond to Co-free compositions [26,27,28], for which T_C^{am} is below the annealing temperature. The aim of this work is to correlate the Mössbauer spectra and the domain structure observed for a Hitperm-type alloy submitted to different field annealing processes.

2 Experimental

Amorphous $Fe_{39}Co_{39}Nb_6B_{15}Cu_1$ alloy was produced by melt-spinning in the shape of a ribbon 4.75±0.05 mm wide and 26.3±0.5 μm thick. The density of the samples was 8.1 g/cm^3. This amorphous alloy experiences a primary crystallization leading to the development of a nanocrystalline microstructure. Samples were annealed during 1 h at 739 K (466 ºC) (peak temperature of the nanocrystallization process at 10 K/min [29]) under zero magnetic field (ZF sample) and applying a magnetic field of 640 kA/m transversal to the axis and in the plane of the ribbon (TF sample). For Mössbauer and Kerr microscopy experiments, 30 mm long samples were prepared, whereas for hysteresis loops, 60 mm long samples were used in order to reduce the demagnetizing factor.

The local environment of Fe atoms was analyzed at room temperature by Mössbauer spectrometry in a transmission geometry using a ^{57}Co(Rh) source. The values of the hyperfine parameters were obtained by fitting with NORMOS program [30] and the isomer shift (IS) was quoted relative to that of a α-Fe foil at room temperature.

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Domain structure images were acquired using a magneto-optic Kerr microscope. Hysteresis loops were acquired in a Forster type B-H loop tracer using flux-gate sensors. A vibrating sample magnetometer was used to measure the saturation magnetization.

3 Results

Figure 1 shows the hysteresis loops of 6 cm long TF and ZF samples. A shared loop with good linearity up to the anisotropy field is observed for TF sample, indicating that for this sample a clear anisotropy field can be defined at H_k=1200 A/m with an induced anisotropy constant K_u~850 J/m^3 [31]. However, ZF sample shows a rather curved loop and analysis of the perpendicular magnetic anisotropy yields a broad maximum centered at 800 A/m [32]. Although conventional annealing in ZF sample yields a clear magnetic hardening with respect to the as-cast sample (H_C=45 A/m and 10 A/m, respectively), coercivity remains low after TF (H_C=16 A/m), as annealing in saturation state prevents magnetic hardening due to pair ordering mechanism [32]. No difference is observed between the saturation magnetization of the two samples, which increases with respect to the amorphous as-cast alloy (from 113 to 122 Am^2/kg).

Ribbons 30 mm long (this size is limited by the sample holder of the microscope) were annealed as described in the experimental section to produce TF and ZF samples. These very samples were also studied by Kerr microscopy and Mössbauer spectroscopy without changing their shapes in order to avoid any effect on domain configuration. Domain patterns of both ZF and TF samples observed by Kerr microscopy are shown in figure 2. Clear differences are observed between them. In the case of ZF sample, the domains are irregularly shaped and sized. However, in the case of TF sample, the domain pattern is regular and perpendicularly aligned with respect to the ribbon axis. From the value of the magnetic anisotropy, K_u=850 J/m^3, and the width of the ribbon w=4.75 mm, the width of the perpendicular domains can be predicted from [33]:

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$$D = \left(\frac{64 A w^2}{K_u} \right)^{1/4} \quad (1)$$

A value D=64 μm (assuming the exchange stiffness, A=10^{-11} J/m) is in rough agreement with the observed structure of figure 2.

In the case of Mössbauer experiments, as the width of the ribbon is smaller than the diameter of the radiated area in the spectrometer, the 30 mm long piece of ribbon was centered between two pieces of lead to block the beam. Figure 3 shows the Mössbauer spectra of both ZF and TF samples along with the hyperfine field distribution used to fit them. The as-quenched sample is also shown for comparison. In this latter case, a single *HF* distribution is used to fit the spectra, which extends from 0 to 40 T (in order to use the same distribution as the one used for nanocrystalline samples) although contributions below 9 T and beyond 36 T are negligible. A very important parameter in this study is the ratio, A_{23}, between the 2nd and 3rd lines (5th and 4th) of the sextets (either discrete ones or those forming a distribution). For each ^{57}Fe magnetic moment (assumed to be parallel to the hyperfine field) this parameter is related to the angle α between the gamma radiation and the magnetic moment of Fe through the following expression:

$$\cos(\alpha) = \sqrt{\frac{4 - A_{23}}{4 + A_{23}}} \quad (2)$$

For a magnetic moment perpendicular to the γ radiation (in the plane of the ribbon) A_{23}=4 and for a magnetic moment parallel to the γ radiation (perpendicular to the ribbon) A_{23}=0. Moreover, a value of A_{23}=2 corresponds to a homogeneously random distribution of the orientations of hyperfine field directions.

In the case of single phase amorphous as-cast sample, A_{23}=2.79±0.02 for the distribution used to fit the experimental data, which indicates that magnetic moments are preferentially in the ribbon plane. This result is in agreement with recent results on anisotropy distribution for this composition, which shows a certain degree of induced longitudinal magnetic anisotropy in the as-cast state [33].

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For nanocrystalline samples, both phases (nanocrystals and amorphous matrix) are well coupled and the average angle between the gamma radiation and the magnetic moment of Fe atoms must be independent of the phase where the Fe atoms are placed (domains are much larger than the structural units). Therefore, a first fitting was done using a single distribution from 0 to 40 T for both ZF and TF samples in order to obtain an average value for the A_{23} parameter, which should be used and fixed in a second fitting consisting of two *HF* distributions (amorphous matrix and interface region) and four sextets (to take into account the presence of different Fe sites depending on the number of Co neighbors [34]). Both results from single distribution and from the two distribution plus the sextets are plotted in figure 3. Table 1 collects the data results from Mössbauer spectroscopy.

4 Discussion

Despite the different experimental profile of the spectra, both fitting leads to the same *HF* distribution for both ZF and TF samples. The differences in the shape of the spectra are explained simply by the different value of A_{23} without significant difference in the other hyperfine parameters, unlike results reported by Kanuch et al. for Mo-containing Hitperm-type alloys [20]. In the case of TF samples A_{23}=4, which is the maximum value achievable by this parameter, and leading to α=90º. This indicates that the magnetic moments are in the plane of the ribbon, in agreement with the well defined domain pattern observed by Kerr microscopy. In the case of the ZF sample, A_{23}=1.80±0.05. This indicates that magnetic moments slightly rotate out of the ribbon plane after nanocrystallization under zero field in agreement with previous results [18,21]. The out of plane component leads to the complex domain structure observed in the Kerr microscope.

Both ZF and TF annealed samples were analyzed in the frame of the law of approach to saturation. It is established that at high enough applied fields magnetization can be written as a power series of the inverse of field [35].

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$$M = M_S\left(1-\frac{a}{H}-\frac{b}{H^2}\right) \tag{3}$$

Where a is the Neel constant and is related to the presence of inhomogeneities in the system (e.g. non-magnetic voids or stresses) [36], which pin the domain walls. On the other hand, b is related to the anisotropy energy as [36]:

$$b = \frac{1}{2}\frac{\left(\left.\frac{\partial E_a}{\partial\theta}\right|_{\theta=0}\right)^2}{\left(\mu_0 M_S\right)^2} \tag{4}$$

Where, E_a is the anisotropy energy and θ is the angle between the magnetization and the applied field. The derivative of the anisotropy energy is related to both the orientation of the magnetization with respect to the field, θ, and to the easy axis, ϕ.

$$\left(\frac{\partial E_a}{\partial\theta}\right)^2 = \left(K_u \sin\left[2\left(\phi-\theta\right)\right]\right)^2 \tag{5}$$

For TF sample, close to saturation $\phi=\pi/2$ and $\theta=0$ and thus K_u can be obtained as:

$$K_u = \mu_0 M_S\sqrt{2b} \tag{6}$$

Figure 5 shows the plot of $(M/M_S\text{-}1)H$ vs $1/H$ from which a is obtained as the intercept with the axis of abscisa and b as the slope of the curve. These plots are very sensitive to the value of M_S. In order to determine it more accurately, we use as M_S the value that leads to the best linear fitting. Results leads to M_S=1.002M_{max} and 1.0325M_{max} for TF and ZF respectively, where M_{max} is the magnetization observed at the maximum applied field used. The intercept a is clearly larger for ZF than for TF sample, implying a larger effect of inhomogeneities in ZF sample in agreement with the domain wall pinning effect occurring after conventional annealing and prevented after saturating field annealing. On the other hand, application of Eq. (6) to TF sample leads to K_u=823 J/m^3 for the TF sample in good agreement with our previous estimation of 850 J/m^3 [32].

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4 Conclusions

In this study, $Fe_{39}Co_{39}Nb_6B_{15}Cu_1$ amorphous alloy was nanocrystallized by zero field annealing and by transverse field annealing, using a magnetic field large enough to saturate the sample in order to avoid domain wall stabilization.

Kerr microscopy images show a well defined parallel domain structure, transversally oriented to the ribbon axis (in the direction of the annealing field) for the TF sample unlike for the ZF sample, for which a disordered pattern is observed with large and small domains at the surface of the ribbon.

Although Mössbauer spectra are clearly different for the two studied samples, differences in the hyperfine field distributions are negligible. The only significant difference is the ratio between the 2nd and 3rd lines, A_{23}. Whereas for TF annealed samples A_{23}=4 (α=90º), in agreement with the well defined domain structure observed by Kerr microscopy, ZF annealed sample shows A_{23}=1.8, closer to a random orientation (A_{23}=2) and much smaller than that of as-cast amorphous samples (A_{23}=2.8), indicating that moments change their orientation to out of the ribbon plane during ZF annealing unlike during TF annealing.

Application of the law of approach to saturation to both samples indicates a more important effect of inhomogeneities in the case of ZF sample, possibly due to the domain wall pinning effect occurring during conventional annealing. Moreover, the anisotropy constant obtained from this analysis for TF sample is in agreement with that determined from hysteresis loop.

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Table 1. Results from Mössbauer analysis

		<IS>	<HF>	<A23>	Fraction
Distribution	as-cast	0.06	24.2	2.8	100
1st distribution	ZF	0.07	14.3	1.8	28.3
	TF	0.06	14.3	4	28.3
2nd distribution	ZF	0.09	26.6	1.8	26.8
	TF	0.07	26.5	4	28.7
Crystalline sites	ZF	0.013	33.0	1.8	4.3
	TF	-0.003		4	4.1
	ZF	0.031	34.5	1.8	23.4
	TF			4	21.4
	ZF	0.014	35	1.8	12.9
	TF			4	13.9
	ZF	0.041	37	1.8	4.2
	TF			4	3.7

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Figure captions.

Figure 1. Hysteresis loops of 6 cm long samples.

Figure 2. Domain structures obtained from Kerr microscopy for the zero field (left) and transverse field (right) annealed samples showing domains perpendicularly oriented to the ribbon axis.

Figure 3. Experimental and fitted Mössbauer spectra. Components of the fitting spectra are also shown for nanocrystalline samples (two *HF* distributions and four sextets). Red lines in *HF* distributions correspond to results fitting using a single *HF* distribution from 0 to 40 T as used for as-cast sample.

Figure 4. Plot of $(M/M_S\text{-}1)H$ versus $1/H$. Following the law of approach to saturation, the intercept *a* is related to the inhomogeneities of the sample and the slope *b* is related to the anisotropy constant.