Domain structures of nanocrystalline Fe$_{90}$Zr$_7$B$_3$ alloy studied by Lorentz microscopy

Youhui Gao$^{a,*}$, Daisuke Shindo$^a$, Teruo Bitoh$^b$, Akihiro Makino$^b$

$^a$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 1-1 Katahira, 2-Chome, Aobaku, Sendai 980-8577, Japan
$^b$Department of Machine Intelligence and System Engineering, Faculty of Systems Science and Technology, Akita Prefectural University, 84-4 Ebino-kuchi, Tsuchiyu-aza, Honjo 015-0055, Japan

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Abstract

As-quenched Fe$_{90}$Zr$_7$B$_3$ alloy has been crystallized at 773, 923 and 973 K, it is found that the specimens annealed at 773 and 923 K have grains with the same size, but the one annealed at 773 K has a thick amorphous matrix and a broad grain size distribution. Big domains and smooth domain walls are observed in the specimen annealed at the optimum condition (923 K), and excellent magnetic softness is obtained. On the other hand, the one annealed at 973 K has very large grains (40 nm). Very small domains with irregular walls are observed, indicating a weak intergranular exchange coupling.

Through in situ Lorentz microscopy, a relaxation of internal stress in the specimen annealed at 773 K is observed at an elevated temperature (333 K). The internal stress observed is considered to be one of the important factors that degrade the soft magnetic properties. Based on the results of differential thermal analysis, a two-step annealing, where the as-quenched specimen is pre-heated at 723 K and subsequently annealed at 773 K, is utilized. The domain structure of the specimen treated by the two-step annealing is analyzed. It is found that the size of the domain is larger than that of the specimen annealed at 773 K, suggesting the possibility of control of the soft magnetic properties.

Keywords: Fe–Zr–B; Nanocrystalline; Soft magnetic materials; Domain structure; Two-step annealing; Lorentz microscopy

1. Introduction

Nanocrystalline FeMB (M = Zr, Hf, or Nb) [1,2] soft magnetic materials prepared by controlled crystallization of amorphous precursors are two-phase systems, consisting of bcc Fe nanocrystalline particles randomly dispersed in a residual amorphous matrix. Such a microstructure gives rise to the outstanding soft magnetic properties, which are generally attributed to the very low saturation magnetostriiction and the dramatically reduced magnetic anisotropy. In addition to the technological relevance, the significance of these heterogeneous materials in fundamental magnetism study has attracted a great deal of attention for a decade.

Fe–M–B alloys have the highest iron concentration in a number of melt-spun Fe-based soft magnetic amorphous alloys, and show much higher $B_S$ (> 1.5 T) than Fe–Si–B systems do [3,4]. The large saturation induction can meet with the requirements of high performance and miniaturization for magnetic devices, such as transformers, inductors, magnetic recording heads and other magnetic sensors. Approaches to further improving intrinsic and extrinsic soft magnetic properties have involved tailoring composition and optimizing the microstructure [5–7]. Excellent magnetic softness has been obtained therefore.

The magnetic behaviors have been understood [8] to result from the decrease of effective anisotropy induced by the refinement of grain size. With strong intergranular exchange coupling, a set of $N$ randomly oriented bcc Fe particles have collective magnetic behaviors with a volume-averaged anisotropy $K_{eff} = K_0/\sqrt{N}$, where $K_0$ is the anisotropy constant of bcc Fe. The reduction of anisotropy further increases the effective exchange correlation length $L_{ex}$. Sixth-power grain size dependence of coercivity has been obtained by the extended random anisotropy model [8]. This behavior has been observed for the systems, where the grain sizes are below 20 nm [9], and indicates the dependence of intergranular exchange coupling upon the grain size and...
the grain boundary structure [8,10,11]. It has also been found that the magnetic natures of amorphous matrix strongly mediate their magnetic softness [12,13]. In order to understand the relations between the microstructure and the soft magnetic properties, the domain structures of Fe₉₀Zr₇B₃ influenced by annealing conditions are systematically studied by Lorentz microscopy. An in situ observation is carried out. According to the results obtained, two-step annealing is proposed in order to optimize the microstructure situation. The evolution of the magnetic structures during the two-step annealing process is observed.

2. Experimental

An ingot of Fe₉₀Zr₇B₃ was initially alloyed by arc melting, and then quenched by a single-roller melt-spinning equipment. The whole process was carried out in argon atmosphere in order to avoid oxidation. The as-spun ribbons with 23 μm in thickness were identified to be completely amorphous by X-ray diffraction analysis. According to the results of differential thermal analysis (DTA) [2], pieces of ribbons were annealed at 773 K (called ZR773, hereafter), 923 K (ZR923), and 973 K (ZR973) for 1 h, corresponding to the initial annealing state, the optimum annealing state and the over-annealing state, respectively. All the heat treatments were carried out with a heating rate of 3 K/s. Their microstructures were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The domain structures were observed with a JEM-3000F TEM installed with a field emission gun. A special pole piece was utilized in order to protect the specimen from the magnetic field of the objective lens. The in situ experiments were carried out with a heating stage. The magnetization curves and hysteresis loops of toroidal specimens were observed by a dc B–H tracer at room temperature. Magnetic spectra were measured at a low magnetic field (0.4 A/m) with frequency ranging from $10^2$ to $10^7$ Hz.

3. Results and discussions

The magnetization curves, hysteresis loops and magnetic spectra of the three specimens are shown in Fig. 1. Some
Table 1
The magnetic properties of the specimens annealed at different temperatures

| Annealing temperature (K) | Permeability | Saturation magnetic induction (T) | Coercivity (A/m) |
|---------------------------|--------------|----------------------------------|------------------|
| 773                       | 2400         | 1.34                             | 38               |
| 923                       | 23,000       | 1.65                             | 5.2              |
| 973                       | 100          | 1.45                             | 1380             |

Typical magnetic properties are summarized in Table 1. It is found that the magnetization curve of ZR923 indicates a linear characteristic when the applied magnetic field is not large enough to saturate the specimen, reflecting a pure magnetization rotation process. ZR773 has similar magnetic behaviors to those of Fe₈₄Nb₇B₉ annealed at 973 K that contains iron boride precipitates [12] and shows fluctuations of exchange coupling. A coercivity of 38 A/m is observed for ZR773, which is much higher than the value of 5.2 A/m for ZR923. However, ZR973 has a very low initial permeability (100) and a huge coercivity (1380 A/m).

From the magnetic spectra (Fig. 1(b)), it is found that all the specimens have the same frequency tendency, but different resonant frequencies. In the low frequency region (<10⁶ Hz), the imaginary part of the complex permeability, \( \mu'' \), increases with observation frequency because of the increase of the eddy-current losses (the structural relaxation losses are negligible). In the high frequency region,
a relaxational domain wall resonance induces a peak on the curves of the imaginary part [14]. Due to the small anisotropy and the low electric resistance, the wall resonance extends to low frequency region as obviously seen in Fig. 1(b) for ZR923. The difference in the resonant frequency indicates the difference in the effective anisotropy, i.e. the lower the frequency is, the smaller effective anisotropy the specimen has. The magnetic spectra of the three specimens evidently indicate that ZR923 has the smallest effective anisotropy and ZR973 has the largest.

Typical bright field TEM images and diffraction patterns of the three specimens are shown in Fig. 2(a)–(c). The grain size distributions (Fig. 2(d)–(f)) are obtained by investigating 800 grains. It is found that the mean sizes of nanocrystals are 18 nm in ZR773, 18 nm in ZR923 and 40 nm in ZR973. The grain size does not change so much for the annealing temperatures of 773 and 923 K, but the specimen annealed at 773 K has broad grain size distribution as seen in Fig. 2(d). According to the diffraction patterns, it is confirmed that the crystalline phase is bcc Fe in ZR773 and ZR923, while some Fe2Zr and Fe3Zr compounds are precipitated in ZR973 as indicated by arrows in Fig. 2(c). From HRTEM images of Fig. 3, amorphous layers between nanocrystals are obviously seen in ZR773 and ZR923, but it is not easy to exactly evaluate the thickness due to the overlapped grains. Assuming that the saturation magnetization of amorphous matrix is zero when the temperature is over its Curie point, we can estimate from $M_s - T$ curves that the mean thicknesses of the amorphous layers are less than 3 nm in ZR773 and less than 1.5 nm in ZR923. Zhang et al. [15] reported that Zr was enriched at the bcc Fe–amorphous interface. On the basis of the result, it is considered that the existence of Zr-rich layer resists the grain growth when the annealing temperature is below 973 K. However, with over-annealing, the Zr-rich layer disappears because of the formation of Fe2Zr and Fe3Zr compounds, resulting in the striking growth of nanocrystals in ZR973 as seen in Fig. 2(c).

Fig. 4 is the Lorentz microscope images obtained by the Fresnel mode, which is an out-of-focus technique for identifying the positions of domain walls. Although smooth domain walls are observed in both ZR773 and ZR923, the mean domain size in ZR773 (about 2.3 µm) is smaller than that of ZR923 (about 5.1 µm). Theoretically, one domain can be considered as a unit of exchange coupling. The large domains in ZR923 indicate a strong intergranular exchange coupling. Thus, according to RAM model [8], a small effective anisotropy may be attained for ZR923, which is consistent with the magnetic measurement shown in Fig. 1. The low effective anisotropy and the high saturation magnetization of ZR923 result in the rotation of magnetization vectors being more energy-favorable than domain wall movement in external magnetic field. The magnetic softness of ZR773 is deteriorated by the broad grain size distribution, which enhances the volume-averaged anisotropy as calculated by da Silva et al. [16]. However, ZR973 has much small domains with irregular walls as seen in Fig. 4(c). The size of the nanocrystals in ZR973 is so large that the effective anisotropy no longer obeys the sixth-power law, but $\langle D \rangle^{\frac{1}{6}}$, where $\langle D \rangle$ is the mean grain size [16]. The irregular domain walls are considered to be strongly pinned by the fluctuation of anisotropy induced by the Zr–Fe compounds. The magnetization process dominated by the pinning effect is explicitly shown by the magnetization curve in Fig. 1(a).

Fig. 5 shows the thermal evolution of the domain structure in ZR773, in situ observed by Lorentz microscopy.
with the Fresnel mode. The bright and dark lines indicate the locations of domain walls. The observation temperature increases from room temperature to 393 K, where the residual amorphous matrix becomes paramagnetic. Comparing Fig. 5(a) with (b), it is found that the shift of domain walls occurs at an elevated temperature (333 K). Melt-spinning usually introduces very strong internal stress into as-quenched ribbons. Although the stress is gradually relaxed during the crystallization process, the stress is considered to be still strong at initial annealing state, such as the case of ZR773. At an elevated temperature, the internal stress is relaxed further, and the magnetic energy related to magnetostriction is changed. Thus, the domain walls shifts are driven by minimization of magnetic energy. The fluctuation of internal stress may be one of the key factors that worsen the magnetic softness of ZR773. With further increase of temperature, the straight domain walls disintegrate, which result from the rapid reduction of intergranular exchange coupling due to the paramagnetic amorphous matrix.

In order to refine the microstructure and control the magnetic softness of ZR773, a two-step annealing is employed in this study. It was reported that a reaction in Fe–Zr–B system involved a process of redistribution of Zr and B atoms before crystallization started [17]. Therefore, a pre-heating process is expected to improve spatial distribution of Zr and B, which is important to obtain fine microstructure because Zr can improve the glass-forming ability of Fe–Zr alloys and B can bring about an increase in the nucleus density of the primary bcc Fe phase. According to the DTA results reported in previous paper [2], two temperature points are chosen in the two-step annealing, i.e. 723 and 773 K. Firstly, the as-quenched specimen is pre-heated at 723 K for 60 min and then held at 773 K for 30–60 min in microscope. The heating rate is 3 K/s. The domain structures of the specimens at the two

Fig. 4. Lorentz microscope images of three specimens, (a) ZR773, (b) ZR923 and (c) ZR973. DW stands for ‘domain wall’.

Fig. 5. Thermal variations of the domain structures of ZR773 for (a) room temperature, (b) 333 K, (c) 353 K, and (d) 393 K. Some of walls arrowed show the shift between (a) and (b).
steps are observed by Lorentz microscopy at room temperature as shown in Fig. 6. In the pre-heated specimen (Fig. 6(a)), no domain walls are observed indicating that it is a paramagnetic state at room temperature. By heating at 773 K for 30 min, large domains with straight walls appear. With a further increase in the holding time, the domains become larger, and the mean domain size is estimated to be about 4 µm in Fig. 6(c). The magnetic properties of ZR773 are expected to be controlled by this two-step annealing because magnetic domains with a larger size generally correspond to the improved soft magnetic properties. The detailed analysis of the effects of the two-step annealing on the microstructure and magnetic properties is under progress and the results will be published elsewhere.

4. Conclusions

We summarize the experimental results as follows

1. The specimen annealed at 773 K has a thick amorphous matrix and broad grain size distribution, while the specimen annealed at 923 K having the excellent soft magnetic properties has a uniform microstructure. Also, the specimen annealed at 973 K has precipitates of Fe–Zr compounds.

2. Through in situ Lorentz microscopy, the relaxation of internal stress is observed in the specimen annealed at 773 K. In addition to the microstructures with broad grain size distribution, the internal stress is also considered to degrade the magnetic softness of the specimen.

3. The domain size of the specimen annealed at 773 K is found to become larger by the two-step annealing process, i.e. by pre-heating at 723 K and subsequently annealing at 773 K.

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References

[1] K. Suzuki, A. Makino, A. Inoue, T. Masumoto, J. Appl. Phys. 70 (1991) 6232.
[2] A. Makino, A. Inoue, T. Masumoto, Mater. Trans. JIM 36 (1995) 924.
[3] Y. Yoshizawa, S. Oguma, K. Yamauchi, J. Appl. Phys. 64 (1988) 6040.
[4] Y. Yoshizawa, K. Yamauchi, Mater. Trans. Jpn Inst. Metals 31 (1990) 307.
[5] S. Ohnuma, M. Nose, K. Shirakawa, T. Masumoto, Sci. Rep. Res. Res. Inst. Tohoku Univ. A 29 (1981) 254.
[6] K. Suzuki, N. Kataoka, A. Inoue, A. Makino, T. Masumoto, Mater. Trans. JIM 31 (1990) 743.
[7] K. Suzuki, A. Makino, N. Kataoka, A. Inoue, T. Masumoto, Mater. Trans. JIM 32 (1990) 93.
[8] G. Herzer, IEEE Trans. Magn. 26 (1990) 1397.
[9] I. Skorvanek, S. Skwirblies, J. Kotzler, Phys. Rev. B 64 (2001) 184437.
[10] A. Hernando, M. Vazquez, T. Kulik, C. Prados, Phys. Rev. B 51 (1995) 3581.
[11] S. Suzuki, J.M. Cadogan, Phys. Rev. B 58 (1998) 2730.
[12] Y. Gao, D. Shindo, T. Bitoh, A. Makino, J. Appl. Phys. 93 (2003) 7462.
[13] Y. Gao, D. Shindo, T. Bitoh, A. Makino, Phys. Rev. B 67 (2003) 172409.
[14] W. Zhong, Ferromagnetism, Science Press, Beijing, 1998.
[15] Y. Zhang, K. Hono, A. Inoue, A. Makino, T. Sakurai, Acta Mater. 44 (1996) 1497.
[16] F.C.S. da Silva, M. Knobel, D. Ugarte, D. Zanchet, IEEE Trans. Magn. 36 (2000) 3430.
[17] K. Suzuki, A. Makino, A. Tsai, A. Inoue, T. Masumoto, Mater. Sci. Engng A179/A180 (1994) 501.