Tr. J. of Physics
22 (1998) , 481 – 488.

Magnetic Domain Structures in As-Quenched and Annealed $Fe_{78}B_{13}Si_9$ Metallic Glass Ribbons

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Received 04.04.1997

Abstract

Among various soft magnetic materials, ferromagnetic glasses are superior to their crystalline counterparts as they possess no magnetocrystalline anisotropy owing to a non-crystalline structure. However, ferromagnetic glasses carry residual stresses and thus anisotropies of magnetostrictive origin in the as-quenched state. These stresses have an adverse effect on the magnetic softness and should be relieved in order to improve magnetic performance, particularly in magnetostrictive alloys. In the present work, the domain structures of $Fe_{78}B_{13}Si_9$ metallic glass, a highly magnetostrictive alloy, are characterized in the as-quenched and annealed states. The annealing treatments were carried out over a wide temperature range extending from the stress relaxation to the crystallization regimes. The sources of magnetoelastic anisotropies were identified with a consideration of the domain patterns observed at different annealing temperatures.

Keywords: Ferromagnetic glasses, Magnetic domains, Bitter technique.

1. Introduction

Structural elements like grains/grain boundaries and defects such as dislocations and stacking faults which are almost always present in crystalline solids are missing in metallic glasses as they lack the long-range periodicity of crystalline structures. With the exception of some short-range ordering, the amorphous matrix does not reveal any compositional fluctuations either. This structural and chemical homogeneity imparts to metallic glasses some outstanding properties which make those rich in ferromagnetic elements (Fe, Ni, Co) very attractive for various soft magnetic applications [1-4].

Ferromagnetic glasses are magnetized readily as the amorphous state, which has no pinning centers, offers no resistance to the domain boundaries. Furthermore, the magnetocrystalline anisotropy occurs only at atomic scale and is thus negligible. Accordingly, their coercivities are very low, yielding infinitesmal hysterisis losses. However, in spite of a very homogeneous microstructure, metallic glass ribbons carry residual stresses in the as-quenched state which they inherit from the melt-spinning process. These stresses, though low in magnitude, have been shown to result in substantial magnetoelastic anisotropies which affect the domain structure and hence the magnetization process, particularly in magnetostrictive alloys [5]. Therefore, ferromagnetic glasses are invariably annealed in practice to relieve residual stresses and thereby increase magnetic softness [6].

The magnetization behavior of a ferromagnetic material depends on its domain structure which in turn is largely determined by magnetic anisotropies still present or somehow induced [7]. So it is of great practical interest to characterize the domain structures, which are essentially fingerprints of the anisotropy distribution, not only in the as-quenched but also in the annealed state. The present work was undertaken to analyze the magnetic domain structures of the as-quenched $Fe_{78}B_{13}Si_9$ metallic glass, a highly magnetostrictive alloy, and to investigate how they change upon annealing within a range of temperatures extending from the stress relaxation to the crystallization regimes.

2. Experimental Procedures

Characterization of domain patterns were carried out on $Fe_{78}B_{13}Si_9$ metallic glass (Metglas 2605 S2) ribbons, obtained from Allied Corporation in the as-quenched state. X-Ray Diffraction (XRD) and metallographic techniques were employed to make sure that the ribbons were amorphous as received. The XRD spectrum of the wheel-side (the surface of the ribbon which solidifies in contact with the wheel) and the air-side (the opposite surface which solidifies in contact with air) showed the broad halo typical of amorphous solids, but no Bragg peaks. Metallographic analysis of respective surfaces did not reveal any evidence of crystallization either.

Small pieces, 10mm × 5mm × 0.030mm, cut from as received ribbons were annealed in a tube furnace under a vacuum of 10^{-3} mbar. The temperature of the heating zone was controlled to an accuracy of ±2° C. Heat treatments were performed isochronally between 300-450 °C for 1/2 hours. Both stress relaxation [8] and surface crystallization [9] have been reported to take place in this temperature range.

The magnetic etching (Bitter technique) was employed to observe the domain patterns of as-received and annealed metallic glass samples (Fig. 1). A ferrofluid with a very fine dispersion of Fe_3O_4 particles was applied to the surface of the sample to be analysed with a fine point syringe. A small drop was found to be sufficient for each sample. These drops were spread into a thin layer over the surface of the samples by a cover glass. The cover glass also helped to avoid rapid drying of the ferrofluid. The samples thus prepared were examined with a Reichert MeF2 model inverted microscope. A weak field, perpendicular to the plane of the ribbon, was applied in order to facilitate the decoration of domain boundaries with Fe_3O_4 particles. Observations were made on the shiny surface (whell-side) of the ribbons as this surface was smooth enough to allow domain observations by magnetic etching without the need for surface preparation.

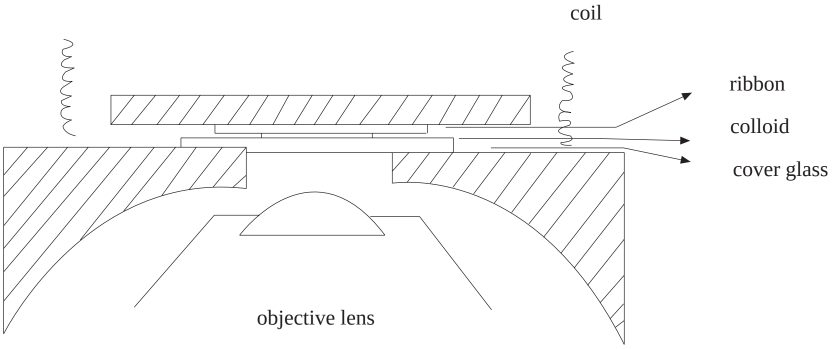
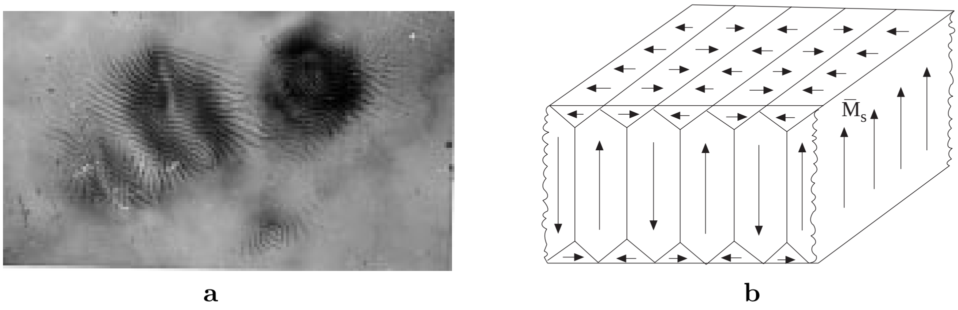


Figure 1. A sketch of the magnetic etching technique.

3. Results and Discussion

Patches of fine, irregular domains, also referred to as 'maze', 'labyrinth' or 'fingerprint' patterns [10], were generally observed in as-received samples (Fig. 2a). The width of the individual domains ranged from 5μ to 10μ. The maze domains are typical of the as-quenched state and imply an out-of-plane magnetic anisotropy [11-13]. When the magnetic easy axis in a metallic glass ribbon is perpendicular to the ribbon plane, demagnetizing fields become important and very fine domain structures are required to reduce the magnetostatic energy. The patterns observed on the surface result from flux closure mechanisms and couple with the domains in the bulk which are magnetized perpendicular to the ribbon plane, as shown in Fig. 2b [11].



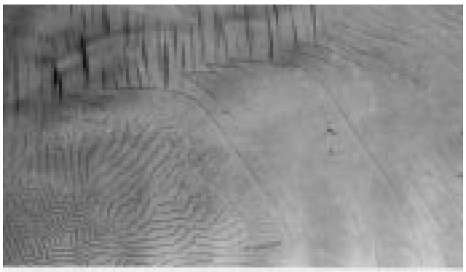


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Figure 2. The magnetic domain patterns of as-quenched $Fe_{78}B_{13}Si_9$ metallic glass ribbons (a,c); Magnification: 100X. Schematic illustration of the through-thickness domain configuration (b).

The maze domains result from residual stresses which develop during the melt-spinning process. Iron-based metallic glasses have a substantial positive magnetostriction and their domain structures are very stress-sensitive. The saturation magnetostriction of the present alloy was reported to be 30×10^{-6} [5]. So, stresses as low as only a couple of megapascals can in some cases be sufficient to produce a dominant magnetoelastic anisotropy and a corresponding maze pattern.

In addition to the fine maze patterns, relatively coarse in-plane domains of varying orientation separated by 180° walls and narrow lamella in a line formation perpendicular to the edge have also been revealed in as-received ribbons (Fig. 2c). The width of the former was sometimes as large as 0.2 millimeters. The magnetoelastic easy axis in such a case is presumed to lie in the plane of the ribbon thus accounting for the comparatively large domain width [14]. This variety of domain patterns is taken to imply a rather complex residual stress distribution in the as-quenched state.

Samples which were annealed at 300° C and 350° exhibit a relatively simple domain structure with many features in common. The stripe domains, which formed a labyrinth-like complex pattern within the patches in as-quenched ribbons, reveal a stacking of a much higher order with slight variations in orientation and cover more or less the entire surface in these samples (Fig. 3). The complex residual stress distribution of the as-quenched ribbons has apparently relaxed to a much more balanced stress state upon annealing in this temperature range. It is inferred from these fine domain patterns that an out-of-plane anisotropy prevails. A 1/2 hour-anneal below 350° C apparently fails to achieve complete stress relaxation in $Fe_{78}B_{13}Si_9$ metallic glass ribbons.

The domain pattern which has developed after annealing at 400° C is in marked contrast to those observed previously (Fig. 4). While patches of maze domains are still present, a larger fraction of the surface reveals domains which are at least an order of magnitude wider. The magnetic easy axis is presumed to lie in the plane of the ribbon in these regions. The wide domains are oriented along the ribbon axis since the demagnetizing fields in a ribbon geometry are minimized with longitudinal anisotropy. Wide domains are typical of stress-free ribbons such as those of as-quenched zero magnetostriction or sufficiently annealed magnetostrictive alloys. So, it is concluded that considerable stress relaxation has taken place during the annealing treatment at 400° C.

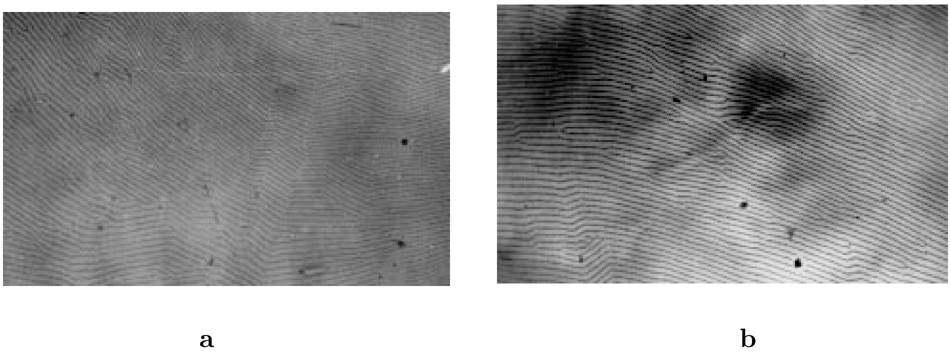

Figure 3. Stripe domain patterns in samples annealed at (a) 300 and (b) 350° C for 1/2 hours; Magnification: 100X.

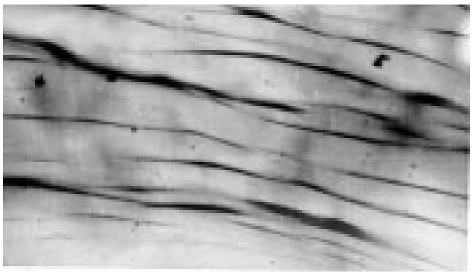

Figure 4. Wide in-plane domains which have formed after annealing at 400° for 1/2 hours; Magnification: 100X.

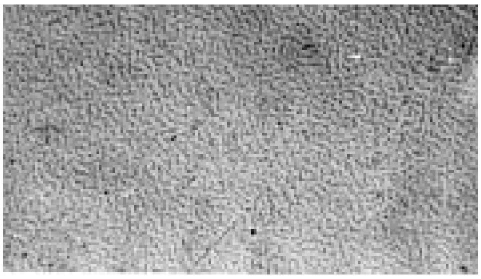

Figure 5. The magnetic domain structure of the sample submitted to a 1/2 hour-anneal at 450° C; Magnification: 100X.

At still higher temperatures (T=450° C) the annealing treatment has produced a domain structure with a cellular network configuration (Fig. 5). The average cell size is estimated to be approximately 5 microns. Cellular domain patterns are attributed to balanced biaxial compression [7] which in turn leads to a perpendicular anisotropy. The mentioned stress-state, which is responsible for the perpendicular anisotropy in this case, should be an induced rather than a residual state as quenching stresses were shown to have already relaxed at lower temperatures. Densification of the surface layers by some structural and/or chemical change during annealing, for instance, would put the bulk of the ribbon under compression leading to such an anisotropy distribution and the observed domain patterns. Two mechanisms which could give such localized densification at the surface are surface crystallization [15-17] and surface oxidation [18]. The latter appears to be out of question in this particular case as the samples kept their metallic luster following the annealing treatment. While the crystallization point of the present glass was estimated by thermal analysis to be 540° C, its ribbons were shown to undergo surface crystallization well below this temperature [9]. Hence, surface crystallization may be responsible for the biaxial compression and for the perpendicular anisotropy which has developed after the 1/2 hour-anneal at 450° C. This appears to be a plausible account of the observed domain structure since a similar iron-rich metallic glass has been reported to be %1 denser in the crystalline state [19].

Optical metallography and x-ray diffraction techniques were employed to identify the source of the perpendicular anisotropy in this sample. The transverse cross-section and the air-side surface were both featureless after etching with a %5 Nital solution (Fig. 6a,b).

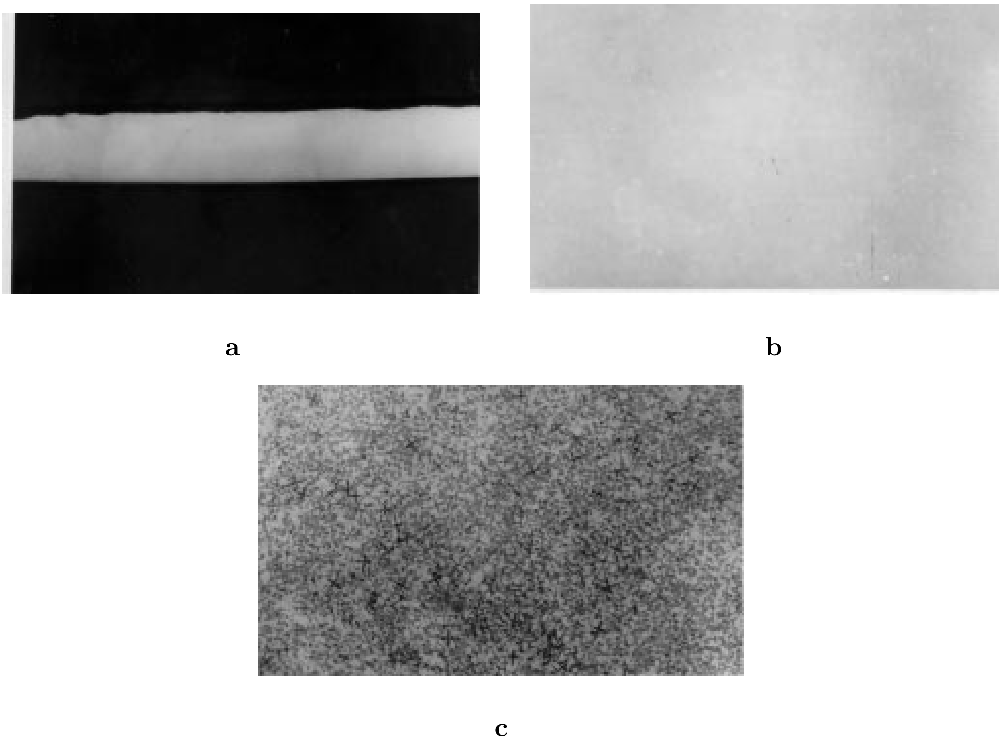

Figure 6. Optical micrographs of the transverse cross-section (a) and the air-side surface of the ribbon annealed at 450° C for 1/2 hours (b), for 2 hours (c); Magnification: 350X.

However, the same sample revealed some crystallinity when annealed further at 450° C. Dendritic α (Fe) crystals with 3- and 4-fold symmetries can be readily identified in Fig. 6c. Considering that the crystallization reactions are dominated by growth processes at temperatures well below the crystallization point, it is presumed that the sample annealed at 450° C for only 1/2 hours also contained α(Fe) crystallites which were too small to be resolved with the optical microscope. This is confirmed by the results of the XRD analysis (Fig. 7). The diffractograms of the samples which were annealed below 450° C are identical and reveal only a broad halo, typical of the amorphous state. This broad halo is somewhat pointed in the case of the sample annealed at 450° C, implying the presence of some very fine crystals.

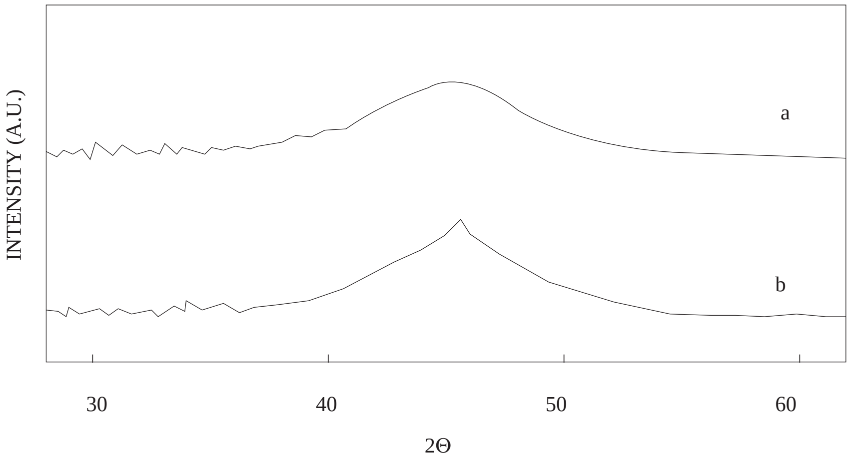

Figure 7. Typical XRD patterns of samples annealed at 400° C (a) and at 450° C (b).

4. Conclusions

Magnetoelastic anisotropies dominate in as-quenched $Fe_{78}B_{13}Si_9$ ribbons due to residual stresses which are inherited from the melt-spinning process. Patches of maze domains associated with an out-of-plane anisotropy and wider domains in between with an in-plane magnetization are typical of the as-quenched state. The variety of domain patterns imply a complex stress distribution which gradually relaxes to a much more balanced stress state upon annealing between 300-350 ° C. A narrow stripe pattern of a much higher order develops at these temperatures. When annealed at 400° C for 1/2 hours, the metallic glass ribbons exhibit domains which are at least an order of magnitude wider. These domains are oriented along the ribbon axis and indicate an in-plane longitudinal anisotropy. Considerable stress relaxation apparently takes place at 400° C. At still higher temperatures (T=450° C), a perpendicular anisotropy develops once again and is believed to be induced by surface crystallization.

Acknowledgements

It is a pleasure to thank E. Atar and H.K. Zeytin for their help in magnetic etching experiments. The financial support of TÜBİTAK is gratefully acknowledged.

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