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ScienceDirect
Journal of Non-Crystalline Solids 353 (2007) 777–781
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Magnetic behavior and microstructure of *Finemet*-type ribbons in both, surface and bulk

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Available online 9 February 2007

Abstract

Different kinds of magnetic anisotropies have been induced during the nanocrystallization process of Co- and Ni-rich amorphous ferromagnetic (*Finemet*) ribbons using diverse procedures like the application of a constant stress or an axial magnetic field during the annealing process. Magnetization measurements have evidenced the anisotropy of the treated samples. The main goal of this work has been the structural and microstructural analysis of the treated ribbons using X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM), detecting substantial differences in the crystallization state and grain size of the samples depending on the treatment that was carried out. Moreover, AFM measurements revealed in all the treated samples a strong nanocrystallization of the surface without evidences of amorphous matrix, which contrast with XRD measurements that have shown a high content of amorphous phase in the bulk of the ribbons. Magneto-optical Kerr effect measurements have been performed with the aim to elucidate the complex magnetic behavior that is expected for the surface of the ribbons, measuring surface hysteresis loops that show much higher coercive field values than in the bulk.

PACS: 75.30.Gw; 75.50.Kj; 81.07.Bc

Keywords: Alloys; X-ray diffraction; Magnetic properties; Atomic force and scanning tunneling microscopy; Microcrystallinity; Nanoparticles

1. Introduction

Soft ferromagnetic nanocrystalline alloys with trademark *Finemet* reveal superior soft magnetic properties as consequence of their microstructure, composed of an ultrafine grain structure of bcc Fe–Si grains with typical sizes around 10–15 nm embedded in an amorphous matrix. The grains are produced by devitrification of the amorphous Fe–Cu–Nb–Si–B alloy after thermal treatment, being the reduced grain size compared with the ferromagnetic correlation length (35 nm) the key for the extremely low effective magnetocrystalline anisotropy of these materials. This fact leads to a small coercivity (around 1 A/m) and high initial permeability values, which are decisive factors that, together with their mechanical properties and their resistance to corrosion, have triggered enormous interest in both scientific and industrial community. Important works have been performed by the controlled introduction of several anisotropies in the amorphous alloys in order to tailor the shape of the hysteresis loops according to the demand of the technical applications. It should be considered that in these materials a small induced anisotropy can be of relative importance, because there is practically not magnetocrystalline anisotropy to compete against it. Several procedures, like the application of magnetic field or tensile stress during thermal treatment of the

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doi:10.1016/j.jnoncrysol.2006.12.039

amorphous alloy are commonly used for the induction of anisotropy in the samples. In the case of magnetic field annealing, it is induced an uniaxial anisotropy where the easy axis is given by the direction of the applied magnetic field. This behavior has been explained by some authors in terms of thermally activated local atomic motions below the Curie temperature, occurring a directional-ordering process [1]. This phenomenon is the so-called 'atomic pair ordering' that, in case of nanocrystallized alloys, is thought to occur mainly in the Fe–Si grains [2,3]. The field annealed samples show slightly smaller coercivity than the samples treated without field. On the other hand, the introduction of anisotropy by the application of a tensile stress induces an easy axis perpendicular to the applied stress. Two possible microstructural mechanisms try to explain the experimentally observed induced anisotropy: the first is the inelastic deformation of the amorphous matrix which creates internal stresses in the two-phase material [4], and the second one is an atomic rearrangement with more bonds oriented in the direction perpendicular to the axis of the applied stress than along this axis [5]. The induced anisotropy by tensile stress is found to be several orders of magnitude higher than the one induced by field annealing [6]. Multiple works dealing with the effects of the induced anisotropies on the magnetic properties of the nanocrystalline ribbons have been published. However, the microstructural or magnetic state of the surface of the ribbons stays completely unexplored. In the present work, the grain nucleation and growth mechanism in the bulk and at the surface of Co-rich *Finemet*, $(Co_{77}Si_{13.5}B_{9.5})_{90}$-$Fe_7Nb_3$ (COF), and Ni-rich *Finemet*, $Ni_5Fe_{68.5}Nb_3$-$Si_{13.5}B_9Cu$ (NIF), alloys under the application of a magnetic field or a constant tensile stress during thermal treatment is studied. A structural analysis has been performed by X-ray Diffraction (XRD), providing information about the crystallization state in the bulk of the ribbons and the size of the grown nanocrystals, while Atomic Force Microscopy (AFM) has been used with the aim to elucidate the crystallization state in the surface of the ribbons. Finally, magneto-optical Kerr effect measurements have been carried out and compared to the obtained ones from fluxmetric method concerning the bulk.

2. Experimental

2.1. Sample treatments

Amorphous ribbons were prepared by melt-spinning technique with dimensions: 3.1 mm wide and 20 μm thick. The amorphous character of the as-cast ribbons was confirmed by both, XRD and Transmission Electron Microscopy analysis. It was found that thermally treated ribbons show the formation of bcc-(Fe, Co[Si]) and fcc-Co phases for COF samples and bcc-(Fe, Ni[Si]) for NIF ones [7]. The thermal treatments on the as-cast ribbons were carried out in air by Joule-heating during short time (always below 5 min). The samples were submitted to the same annealing current (≈32.5 A/mm^2), applying simultaneously an external tensile stress (50 or 95 MPa), or an axial magnetic field (750 A/m) during annealing and cooling down process to room temperature. The sample treated with stress will be identified as sample SA, and the one treated with magnetic field will be called FA. A third sample (CA) was submitted to the same annealing process with the application of neither an external magnetic field nor an external tensile stress. This ribbon was used as reference for the SA sample. Fluxmetric measurements carried out on the treated samples have evidenced the presence of an induced anisotropy, revealing completely different hysteresis loops depending on treatment [6].

2.2. Structural analysis

The structural analysis of the ribbons was carried out by XRD and AFM measurements in order to respectively analyze the bulk and the surface of the ribbons.

XRD patterns have been normalized in the high q-range where the intensity cannot vary between the different samples owing to the very short structural distances responsible for the scattering in this q region. In the case of crystallized samples, the evaluation of the crystalline phase has been performed by the subtraction of the amorphous halo of the as-cast sample (Ia) to the measurement performed on the crystallized ribbon (I). The resulted intensity pattern can be used to estimate the crystallinity ratio, χ, defined as following:

$$\chi = \frac{\int q^2(I - Ia)\,\mathrm{d}q}{\int q^2 I\,\mathrm{d}q}, \quad q = \frac{4\pi \sin\theta}{\lambda}, \tag{1}$$

where $(I - Ia)$ denotes the resulting intensity pattern that corresponds to the crystalline fraction of the sample, q is the scattering vector and 2θ is the scattering angle. Additionally, the crystallite size, D, has been evaluated from the Scherrer's formula.

3. Results and discussion

3.1. XRD and AFM structural results

Usually, the X-ray reflections of the amorphous ribbon become higher and narrower with longer time and temperature treatments, indicating the beginning of the crystallization process. Differences in the diffraction patterns of the treated samples are detected depending on the kind of annealing process that has been performed. Fig. 1 shows an example of XRD patterns corresponding to COF and NIF samples with different treatments and compared to the as-cast ones. SA samples present an incipient but remarkable crystalline peak corresponding to the crystallization of the bcc-(Fe, Co[Si]) phase (or bcc-(Fe, Ni[Si])) that is overlapped with the amorphous halo of the still present amorphous matrix. A relative crystalline volume of 6% and grain size of 9 nm are obtained for COF-SA rib-