Composition-Dependent Crystal Structure and Magnetism in Nanocrystalline Co-Rich Alloy

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1. Introduction

In recent years, ferromagnetic nanocomposite materials consisting of nanocrystals embedded in an amorphous matrix have received both theoretical and experimental attentions because they exhibit unique magnetic, magnetoelectronic, and mechanical properties. Up to now, the magnetic characteristics of isolated magnetic nanocrystals (or nanoparticles) have been well understood [1-3]. However, when the nanocrystals are embedded in an amorphous matrix to form a nanocomposite, the magnetic properties significantly differ from the individual and bulk ones. This is mainly because the magnetic moments of the nanocrystals interact with each other through exchange coupling via the amorphous matrix. In addition, due to strong dependence of nanocrystalline properties on the size and distribution of the nanocrystals as well as the portion of the amorphous matrix in the structure, it is uneasy to characterize the magnetic behaviors of this type of material system both experimentally and theoretically.

Several previous investigations have been reported on the magnetic properties of ferromagnetic nanocrystalline materials [4-8].It has been observed that their magnetic properties were characterized to be either soft or hard, depending on the size and magnetic anisotropy property of the nanocrystals. In addition, the intergranular amorphous matrix also plays a critical role. For example, the behavior of the magnetic nanocrystals in a nonmagnetic intergranular material is governed by a single domain particle model, while that in the magnetic intergranular phase shows much more complicated behavior [9]. Therefore, a thorough understanding of the exchange interaction between the nanocrystal and matrix is necessary for designing a new material for potential device applications. In this paper, we attempt to clarify the correlation between the structural and magnetic properties of CoFeSiB alloy films with various compositions.

We have chosen the $Co_{70.5}Fe_{4.5}Si_{15}B_{10}$ alloy as a model system because it has been employed in the giant magnetoimpedance sensors, and magnetic tunnel junctions for magnetic random access memory devices. When the Co concentration was below 75 at.%, the alloy had an amorphous phase and was magnetically soft. Meanwhile, beyond 75 at.%, the structure consisted of nanocrystals precipitated in the amorphous matrix, and became magnetically hard.

2. Experimental Procedure

A series of CoFeSiB thin films were deposited on Si (100) substrates with 100 nm thick thermally oxidized SiO_2 layers using a six-target dc magnetron sputtering system under a typical base pressure of less than 5×10^{-8} Torr. A magnetic field of 100 Oe was applied during the CoFeSiB film deposition to induce uniaxial magnetic anisotropy. A $Co_{70.5}Fe_{4.5}Si_{15}B_{10}$ target on which small Co chips (5 mm $\times$ 5 mm $\times$ 2 mm) were placed to control the Co concentration

of the CoFeSiB films. Typical film thickness was about 430 nm. The composition of the CoFeSiB thin films was confirmed by energy dispersive x-ray spectroscopy (EDX) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The microstructure was characterized by high-resolution transmission electron microscopy (HRTEM) and x-ray diffraction (XRD). The magnetic properties of the CoFeSiB films at 5 K and 300 K were characterized by using a superconducting quantum interference device (SQUID).

3. Results and Discussion

We have carried out transmission electron microscopy (TEM) and x-ray diffraction (XRD) studies. Both offer complementary (i.e., global and local) information regarding microstructural evolution. A series of in-plane TEM images and selected area diffraction (SAD) patterns is investigated. The films($Co_{70.5}Fe_{4.5}Si_{15}B_{10}$, $Co_{74}Fe_4Si_{14}B_{10}$) with Co < 75 at.% (are in amorphous phase (say, *Region 1).*

, and (d) the SAD pattern of the Co76Fe4Si13B7 film. Unlike previous samples with Co-concentration below 75 at.%, the $Co_{76}Fe_4Si_{13}B_7$ film shows nanocrystalline structures. When a solid solution system is supersaturated, it becomes thermodynamically unstable, and, to avoid that, this system precipitates out the supersaturated solute. In our case, the precipitates are most likely Co nanocrystals.

The SAD pattern of $Co_{76}Fe_4Si_{13}B_7$ film shows a six-fold symmetry meaning that the nanocrystal structure is most likely the *hcp* Co. The lattice structure of the nanocrystals is important in terms of determining the magnetic properties because the *hcp* Co structure has higher magnetic anisotropy (related with higher coercivity) compared to the *fcc* one. In overall, the films with Co-concentration above 75 at.% (say, *Region 2*) can be regarded as nanocomposites consisted of a mixture of precipitated nanocrystals embedded in the amorphous matrix. The TEM result suggests that, therefore, the crystal structure of CoFeSiB samples varies from an amorphous to a nanocrystal one when the Co concentration exceeds a certain critical value (Co > 75 at.%). In order to estimate the grain size, at least semi-quantitatively, we used the Scherrer equation. According to this equation, the estimated sizes of Co nanocrystals in the $Co_{76}Fe_4Si_{13}B_7$, $Co_{78}Fe_3Si_{12}B_7$, and Co81Fe2Si10B7 films were 20 nm, 24 nm and 25 nm, respectively. By increasing the Co concentration, therefore, the precipitates Co nanocrystal size is increased.

Now we discuss the magnetic responses of the films in two different regions.

The H_c values, in the magnetic hysteresis of the films measured at RT for (a) $Co_{70.5}Fe_{4.5}Si_{15}B_{10}$ and (b) $Co_{74}Fe_4Si_{14}B_8$, appears to be very low ($\leq$ 5 Oe) because the magnetic anisotropy arises from the short-range order. The soft magnetic properties of amorphous materials were explained by Herzer within the framework of so called the random magnetic anisotropy model [6]. According to this model, when the exchange correlation length (L_{ex}) exceeds the orientation fluctuation length, the magnetic moments are strongly exchange-coupled via the amorphous matrix. Because of this, the anisotropy energy of the Co-rich phase can be transmitted to each other. Hence, excellent soft magnetic properties have been observed due to the fact that all of the magnetic anisotropies were averaged out in the amorphous system [6-8]. Moreover, the Co-based amorphous alloys exhibit near zero magnetostriction [10].

The magnetic characteristics of the Region 2 (nanocomposite where nanocrystals are embedded in the amorphous matrix) are discussed. The M-H hysteresis of the nanocrystal $Co_{76}Fe_4Si_{13}B_7$ sample has a different shape from that of the amorphous one in Region 1. The M-H curve represents a linear magnetization switching part with an abrupt increase in H_c. The magnetic hysteresis curves of the $Co_{76}Fe_4Si_{13}B_7$ sample shows high and low field sweeps, respectively. The saturation field of this sample is around 2.5 kOe. This large saturation field is presumed to be due to an antiferromagnetic exchange coupling between the Co nanocrystals and residual amorphous matrix at the interface.

In this case, the exchange forces are not able to overcome the magnetocrystalline anisotropy, resulting in the magnetic decoupling (broken of the nanocrystal-amorphous matrix-nanocrystal coupling chain). And, as a

consequence, it brings a significant increase in the H_c. The magnetic decoupling was also observed at temperatures above the Curie temperature of the residual intergranular amorphous phase [11]. Another origin of the increase in Hc may also be due to magnetoelastic effect resulted from precipitation of Co nanoparticles. The presence of internal stress along with a large magnetostriction constant of Co (-62×10^6) results in the development of magnetoelastic anisotropy [9].

4. Conclusion

We have investigated the microstructural evolution and change in the relevant magnetic properties upon the addition of Co to an amorphous ferromagnetic CoFeSiB alloy. The crystal structure evolved from amorphous to nanocrystal-embedded two-phase mixture system when the amount of Co addition exceeded the critical amount (~ 75 at.%). Very low coercivity values took places in the amorphous state due to the averaging out of magnetic anisotropy. Meanwhile, a drastic magnetic hardening and antiferromagnetic exchange coupling effects appeared for higher Co concentration samples due to the precipitation of highly anisotropic Co nanocrystals.

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