September 01, 1990

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V. G. Harris
Northeastern University

S. A. Oliver
Northeastern University

W. B. Nowak
Northeastern University

C. Vittoria
Northeastern University

R. J. Culbertson
U.S. Army Materials Technology Laboratory

See next page for additional authors

MAGNETIC AND STRUCTURAL INVESTIGATION OF HEAT TREATED ION BEAM SPUTTERED AMORPHOUS $Co_{74}Fe_6B_{15}Si_5$ FILMS

V.G. Harris, S.A. Oliver, W.B. Nowak, and C. Vittoria
Northeastern University, Boston, MA 02115
R.J. Culbertson
U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001
W.T. Elam and K.H. Kim
U.S. Naval Research Laboratory, Washington, D.C. 20375-5000

Abstract-**As-deposited and annealed specimens of ion beam sputtered amorphous $Co_{74}Fe_6B_{15}Si_5$ thin films were examined to explore the correlation between changes in magnetic properties and atomic structure. Specimens were characterized magnetically, by traditional ac and dc techniques and structurally, via conversion-electron extended x-ray absorption fine structure analysis. Results show significant ordering of the higher order atomic shells around the transition metal ions well below the crystallization temperature. This ordering evolves into a body- centered-cubic configuration around both the Co and Fe ions. Increases in nearest neighbor peak positions in the EXAFS Fourier transforms were observed to correlate with increasing annealing temperatures. Evidence is presented for the role of the ordering in the observed magnetic changes, but the details remain unclear.**

INTRODUCTION

Over the past decade high energy deposition techniques have allowed for the routine fabrication of amorphous ferromagnetic alloys, typically TM-M (TM=Fe,Co,Ni; M=B,Si,P,C), as high quality soft magnetic thin films. However, in their as-deposited state these films have been found to exhibit metastable behavior requiring further processing to induce the thermal stability necessary prior to application. This additional processing is generally a heat treatment, often performed in a magnetic field. The effects of these procedures on the structure and magnetic properties of these alloys has been unclear. An understanding of the correlation between magnetic properties and the atomic structure of these materials will lead to improved magnetic properties through refined processing techniques. To this end, the $Co_{74}Fe_6B_{15}Si_5$ alloy was selected for investigation of magnetic and structural properties and their response to heat treatment.

Study of the structure of amorphous materials, or materials possessing only short range order (SRO), has always been difficult. This is especially true when the samples are thin films. Analysis of conversion-electron extended x-ray absorption fine structure data gives information about local environments of individual ions in thin films. The basis of this technique is the acquisition of the absorption spectra above the absorption edge by detection of a sample current predominantly composed of Auger electrons[1,2]. Subsequent analysis follows that of traditional EXAFS. With sampling depths well suited for the investigation of thin films [3] this technique has proven effective for structural investigation of thin films supported by thick substrates.[4,5] Although EXAFS results have been obtained for TM-M alloys since the late 1970's [6] the present work represents the first structural exploration of TM-M alloys as thin films, made possible by the sensitivity of conversion-electron EXAFS.

EXPERIMENTAL PROCEDURES

Disc shaped specimens (5 mm diameter) were cored from an amorphous film (t=150 nm) ion beam sputtered (IBS) from a pressed powder target of the composition 74Co-6Fe-15B-5Si (atomic percent). Details of the deposition process and chemical analyses of similar films (including Auger electron spectroscopy and Rutherford backscattering spectroscopy) have been reported elsewhere.[7]

One specimen was incrementally annealed to crystallization in order to determine variation of film coercive field (H_c), loop squareness ($SQ = I_r/I_s$) and saturation magnetization (I_s) values as a function of annealing temperature. Specifically, hysteresis loops were collected at 25°C increments with the specimen maintained at each temperature for approximately 16 minutes (including a four minute loop acquisition time). Although these results, acquired at elevated temperatures, represent both reversible and irreversible magnetic and structural effects we used them qualitatively to select annealing temperatures for other specimens. Specifically, two specimens were annealed at temperatures sufficient for easy-axis reversal and below the observed crystallization temperature (T_x). A third specimen was annealed at a temperature well above the crystallization temperature to intentionally promote long range order (LRO) crystallite formation. Annealing was performed under an argon flow in an oven interfaced to a vibrating sample magnetometer (VSM). A saturation field of 500 Oe was applied in the film plane parallel to the hard axis.

Room temperature VSM measurements were made on specimens after annealing. Hysteresis loops were obtained with the applied field parallel to both easy and hard axes (±1°). This allowed determination of the coercive field (H_c), saturation ($I_s, 4\pi M_{sat}$) and remanence moments (I_r), and loop squareness ($SQ = I_r/I_s$). A value for the in-plane anisotropy (H_k) was obtained by superimposing the hard axis loop over the easy axis loop. The values of H_k were corroborated by ferromagnetic resonance (FMR) measurements.

Room temperature FMR measurements were taken using an X-band cavity with the applied field both parallel and perpendicular to the film plane. These results allowed calculation of in-plane anisotropy field (H_k), effective magnetization ($4\pi M_{eff}$), g-factor (g), and FMR line width (ΔH). Spin wave resonance (SWR) spectra, observed in perpendicular FMR results, were used in determining the exchange stiffness constant (A).

The atomic environment of TM ions was investigated by conversion- electron EXAFS for specimens in the as-deposited state and those which had undergone magnetic field annealing. X-ray absorption spectra were collected from measurements of helium gas ionization currents while increasing the incident photon energy from 100 eV below the ion's K-edge to 500 eV above the edge. Because the sample current, normalized to the incident x-ray flux, faithfully reproduces the x-ray absorption spectrum, traditional EXAFS analysis [8] can be applied. The oscillations

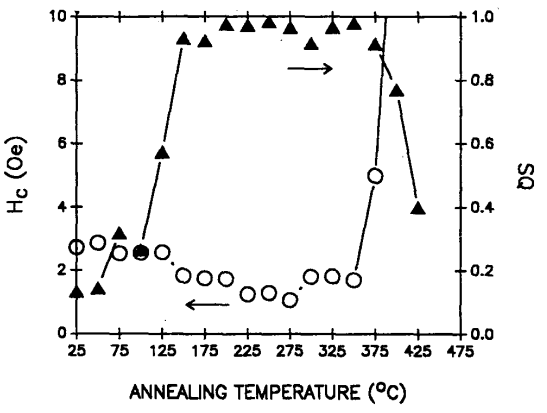

Figure 1. Variation of film coercive field (H_c) and hysteresis loop squareness (SQ) with annealing temperature for an IBS Co74-Fe6-B15- Si5 film (t=150 nm). Data was extracted from hysteresis loops acquired at annealing temperatures (annealing time approx. 16 min.) via VSM.

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above the edge were isolated and converted from energy space to photoelectron wave vector (k) space. A cubic spline background was removed, followed by Fourier transformation. Resulting Fourier transforms were compared to those of crystalline films of single element iron and cobalt, generated as thin film standards from the same IBS system. The conversion-electron EXAFS spectra were collected using the Naval Research Laboratories' (NRL) materials analysis beam line (X23B) at the National Synchrotron Light Source (at Brookhaven National Laboratories, Upton, N.Y.). The x-ray capabilities of this beam line have been presented elsewhere.[9]

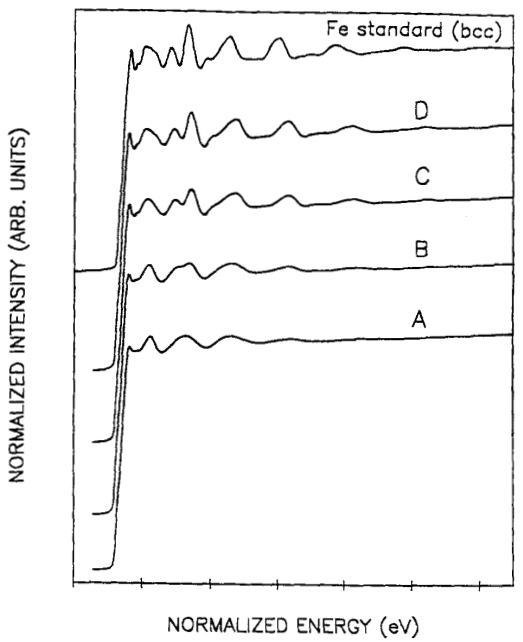

Figure 2. Conversion-electron x-ray absorption fine structure spectra for as-deposited and annealed specimens of amorphous IBS Co74-Fe6-B15-Si5 (specimens A,B,C,D) and for IBS Fe film.

RESULTS

Figure 1 illustrates the variation of film coercive field and loop squareness as a function of annealing temperature for a film (t = 150 nm) sputtered from the 74Co-6Fe-15B-5Si target (data was acquired at the annealing temperature). Full easy axis reversal occurs when loop squareness approaches 1.0, signifying that a near-saturated state exists at remanence along the applied field direction. This occurs at approximately 150°C (see Fig.1). The rapid increase in coercivity at approximately 375°C is accompanied by a reduction in SQ and signifies the development of impediments to domain wall movement. This indicates LRO crystallites exists in the film. This approximate value of T_x is consistent with results from annealing studies performed on ribbons of similar compositions by differential thermal analysis (DTA) [10].

The as-deposited specimen (A) displays static and microwave magnetic properties (Table I) comparable to those previously reported [11].

Specimen B, field annealed at 300°C, displays decreases in coercive field values, indicating that domain wall mobility has increased. The increase of in-plane anisotropy, seen in both FMR and VSM results, is attributed to stresses induced by the cooling rates occurring incidental to the annealing process.

Significant increases in coercivity were observed in specimen C, relative to specimen B. This may be attributed to crystallite formation, possibly at the surface, causing significant retardation of domain wall mobility.

Specimen D (T_{ann} = 450°C) shows marked deterioration of soft magnetic properties. This was expected since this specimen was intentionally field annealed well above the crystallization temperature. All annealed specimens have increased saturation magnetization values corresponding to increased annealing temperature (Table I). Similar results have been reported for annealed Fe-Ni-B-Si sputtered films [12]. FMR measurements show all annealed specimens have disrupted SWR spectra and additional absorption modes above the mainline resonance.

X-ray absorption spectra encompassing the Co K-edge for the as- deposited and annealed films along with the Fe K-edge spectrum of the Fe standard are shown in Fig. 2. For comparison purposes the spectra have been normalized for both edge step height and energy with a pre-edge linear background removed. Although structural comparisons are best performed using Fourier transformed data these spectra clearly show the extended fine structure of the annealed specimens evolving towards the profile of the body-centered-cubic (bcc) Fe-standard. Figure 3 displays the Fourier transforms of the spectra presented in Fig. 2. Profile A of Fig. 3 shows the TM-TM nearest neighbor (NN) peak, intentionally uncorrected for electron phase shift, dominating the profile with little contribution from the constructive scattering of local metalloids or higher order TM shells. This is representative of an amorphous material. Peaks appearing below the NN peak are to be disregarded as residual of the background removal operation. Higher order TM shells become progressively more pronounced in Fourier transforms as specimen annealing temperatures are increased. The TM-TM NN Fourier transform peak position was found to increase with progressive annealing from the as-deposited 1.96 Å (specimen A) to 2.02 Å, (specimen B) and attain a final value of 2.12 Å (specimens C and D). Simi-

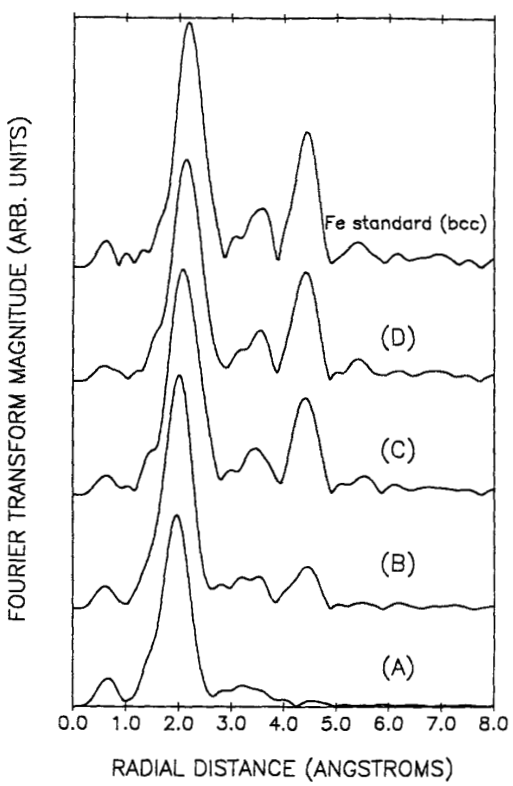

Figure 3. Fourier transforms of conversion-electron EXAFS spectra of specimens in the as-deposited and magnetic field annealed states. The Fourier transform of the Fe standard is included for

lar expansions were observed with respect to the Fe ion obtained from the same specimens (Table I). The environment of the Co ion is seen to be conclusively that of a bcc structure by comparing the relative position and amplitude of the peaks above 3 angstroms with the Fe standard (Fig. 3). The environment of the Fe ion in the sputtered alloy specimens show the same pattern.

Table I

	A	B	C	D
Annealing Temperature (°C)	AD	300	350	450
Coercive field (Oe) (easy axis)	1.96	1.72	9.30	12.95
Anisotropy field (Oe)	33	42	13	45
Saturation magnetization (kOe) (as $4\pi M_{sat}$)	11.3	11.4	12.2	12.5
Electrical resisitivity ($\mu\Omega$ – cm)	167	128	97	74
Fe nearest neighbor (Å) peak position*	1.96	2.02	2.15	2.15
Co nearest neighbor (Å) peak position*	1.96	2.02	2.12	2.12

*Extracted from Fourier transformed data uncorrected for electron phase shift.

Note: All annealed films were annealed for 60 minutes at listed temperatures with a saturation magnetic field of 500 Oe applied parallel to the in-plane hard axis.

DISCUSSION

Fourier transforms of conversion-electron EXAFS spectra of these specimens conclusively show the existence of order in higher TM shells in all annealed specimens, including those annealed below the crystallization temperature (Fig.3). The relative amplitude and position of all Fourier peaks (above 3 Å) of annealed specimens correspond most closely to those of a bcc atomic configuration. This is reflected in both the conversion-electron fine structure spectra (Fig. 2) and in their Fourier transforms (Fig. 3). Concurrent with the appearance of the higher order shells is an increase in NN peak distance. Neither the apparent increase in TM NN distance nor the evolution of the Fourier transforms to a bcc symmetry have been reported in previous studies of $TM_{80}M_{20}$ alloy ribbons.[6] The observed ordering may be attributed to incipient crystal growth which was shown by EXAFS to be the mechanism of amorphous-to-crystalline transition in amorphous Ge. 13

Coercive field, being particularly sensitive to specimen structure, may reflect the progressive ordering observed in the Fourier transforms. Specimen B exhibits a decrease in coercivity from the as-deposited state. This is attributed to an ease in domain wall mobility induced by the reduction of free volume trapped within the film during deposition. Secondly, it indicates that the degree of ordering that exists in this specimen is not sufficient to retard domain wall mobility. Alternatively, the significant increase of coercivity seen in specimen C, relative specimen B, indicates that sufficient ordering has occurred to hinder domain wall mobility. It is unclear if this hindrance is due to direct domain wall pinning by incipient crystallites or by related stress effects. Crystallite formation is also reflected by increases in saturation magnetization (Table I). These increases are believed to have resulted from the precipitation of TM-based crystal phases, possibly TM_2B,ϵ-cobalt and poly-(Fe-Co). These products were determined to result from crystallization of an Fe-Co-B-Si alloy ribbon [14]. The cumulative total of this mixed phase appears to possess a higher saturation magnetization value than the as- deposited amorphous ternary. The magnetic deterioration occurring in specimens C and D may be attributable to the increase in NN distance or to the ordering of higher shells.

CONCLUSIONS

We present the first analysis of amorphous thin films by conversion-electron extended x-ray absorption fine structure analysis. The results obtained by conversion-electron EXAFS and ac and dc magnetic characterization of heat treated IBS $Co_{74}Fe_6B_{15}Si_5$ are summarized as follows:

(1) Fourier transforms of conversion-electron EXAFS spectra revealed ordering of higher TM shells in all annealed specimens. Incipient crystal growth may be the mechanism of amorphous-to- crystalline transition of this alloy.

(2) The relative amplitude and position of all Fourier transform peaks above 3 Å for annealed specimens correspond to the bcc configuration seen in the Fourier transform of the IBS Fe film standard.

(3) An increase in nearest neighbor Fourier transform peak distance was observed to correlate with increased annealing temperature.

(4) Magnetic properties of annealed specimens show increases in saturation magnetization values with annealing temperature. Specimen C and D show significant increases in coercivity, possibly due to growth of incipient crystals.

We have attempted to correlate these observations to specimen magnetic properties. We visualize a model relating the specimen coercive field to local structure. However, anisotropy appears to be dominated by stress effects of the annealing technique. A more detailed study of the crystallization behavior is necessary in order to correlate quantitatively the magnetic property changes with the progressive ordering induced by heat treatment.

ACKNOWLEDGEMENT

The authors would like to thank S. Bushnell and M. El Rayess for assisting in the collection of conversion-electron EXAFS spectra. The authors are indebted to J.P. Kirkland and R. Neiser for their assistance in the operation of NRL's material analysis beam line X23B at NSLS. This research was carried out (in part) at the National Synchrotron Light Source, which is sponsored by the U.S. Department of Energy (Division of Material Science and Division of Chemical Sciences of the Office of Basic Energy Sciences). One of the authors (K.H.K.) is supported by the National Research Council.

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