

Magnetic properties of amorphous thin films produced by ion mixing

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We have produced several magnetic amorphous alloys by ion mixing of thin multilayer films. Our results show that the ion mixing technique is able to produce amorphous films of the various categories (transition metal-metalloid, transition metal pairs) at the composition appropriate for the appearance of magnetic ordering. A comparison of their saturation magnetization with that of related vapor quenched films suggests similar nearest-neighbor coordination in both kinds of samples.

I. INTRODUCTION

Many amorphous metallic alloys contain large concentrations of transition metals or rare earth elements and are therefore expected to exhibit magnetic ordering. As a consequence, the study of the magnetic properties of metallic glasses has become an important tool for characterizing these alloys. Moreover, it is well known that the combination of outstanding magnetic and mechanical characteristics has made some metallic glasses particularly interesting for specific industrial applications.¹

Standard preparation methods of these systems usually proceed through rapid quenching of the alloy from the liquid (e.g., melt-spinning, splat-cooling) or from the vapor phase (coevaporation, sputtering). A more recently developed technique produces amorphous compounds directly from the solid-state, by ion mixing of thin multilayer films using noble gas atoms as bombarding projectiles.² Several authors have discussed the structural and electrical properties of ion mixed samples, but only recently has attention been paid to their magnetic characteristics.³ In this work, we have prepared several amorphous films by ion mixing and recorded their magnetic parameters. The systems under investigation are representative of two well-known families of amorphous alloys: transition metal-metalloid (Fe-Si, Fe-B) and transition metal pairs (Co-Nb). The alloys were prepared at different compositions, and typical irradiation parameters such as temperature and dose were varied in order to detect their possible influence both on the amorphization process and on the magnetic behavior of the films.

II. EXPERIMENT

Multilayer films of Fe-Si, Fe-B, and Co-Nb were deposited on oxidized Si substrates by electron-gun evaporation of the pure constituents. The vacuum in the evaporation chamber was brought into the 10^{-8} Torr range prior to deposition. The thickness of the alternate individual layers (monitored with a vibrating quartz crystal) was kept below 100 Å in order to maximize the mixing efficiency. The total thickness of the samples varied between 500 and 1000 Å, and was determined as a function of sample composition to match the penetration depth (mean projected range plus one standard deviation) of 300-keV Xe⁺ ions. Irradiation with Xe ions took place at room temperature or liquid nitrogen temperature in a vacuum of about 5×10^{-7} Torr.

The thickness and composition of the samples was ana-

lyzed before and after mixing by backscattering spectrometry, using 2 MeV He⁺ ions. Their lattice structure was checked by x-ray diffraction (Read camera) and transmission electron microscopy (TEM) on selected samples. Magnetization curves were recorded at room temperature with an inductive loop magnetometer operating in the range 10–30 Hz with a maximum driving field of 80 Oe. The magnetic data obtained includes saturation magnetization $4\pi M_s$ and coercive force H_c . Where an in-plane uniaxial anisotropy is developed, the anisotropy field, $H_k = 2K_u/M$, is obtained by extrapolating the low drive magnetization curve in the hard axis to saturation.

III. RESULTS OF ION MIXING

A. Fe-Si and Fe-B

Ion mixing of metallic elements with Si has been reported earlier, both in bilayer and in multilayer configuration.⁴ Mixing of Fe with Si has only been performed on bilayers, and resulted in FeSi formation.⁵ We have mixed multilayers containing between 77 and 30% of Fe at Xe doses varying between 3×10^{15} and 1.2×10^{16} at./cm². At room temperature, Fe lines remained in the diffraction pattern which is typical of incomplete amorphization. Irradiations of 5×10^{15} Xe at./cm² at LN₂ temperature produced amorphous films from all samples, except for Fe₇₇Si₂₃. Due to the extensive solid solubility of Si in Fe, traditional quenching techniques are not able to produce amorphous Fe-Si films below 25% Si concentration⁶; it appears from our results that the limitations of ion mixing are essentially the same. Samples containing less than 60% Fe became amorphous at slightly lower doses than the Fe-rich films. The homogeneity of the amorphous phase was confirmed by TEM and electron diffraction observations on selected samples.

No previous work has been reported on the ion mixing of Fe-B films. We have prepared multilayer samples with nominal compositions of Fe₇₀B₃₀ and Fe₆₀B₄₀. Samples with less than 30% B could not be produced, due to technical difficulties related with controlling the evaporation of very thin boron layers. Since the boron backscattering yield is much lower than that of the Si substrate, the boron signal could hardly be observed in the backscattering spectra. We therefore relied on the calibration of the thickness monitor in the vacuum evaporator for the sample composition. Amorphization of the samples was achieved at liquid nitrogen temperature with irradiation doses of 5×10^{15} Xe⁺/cm² and

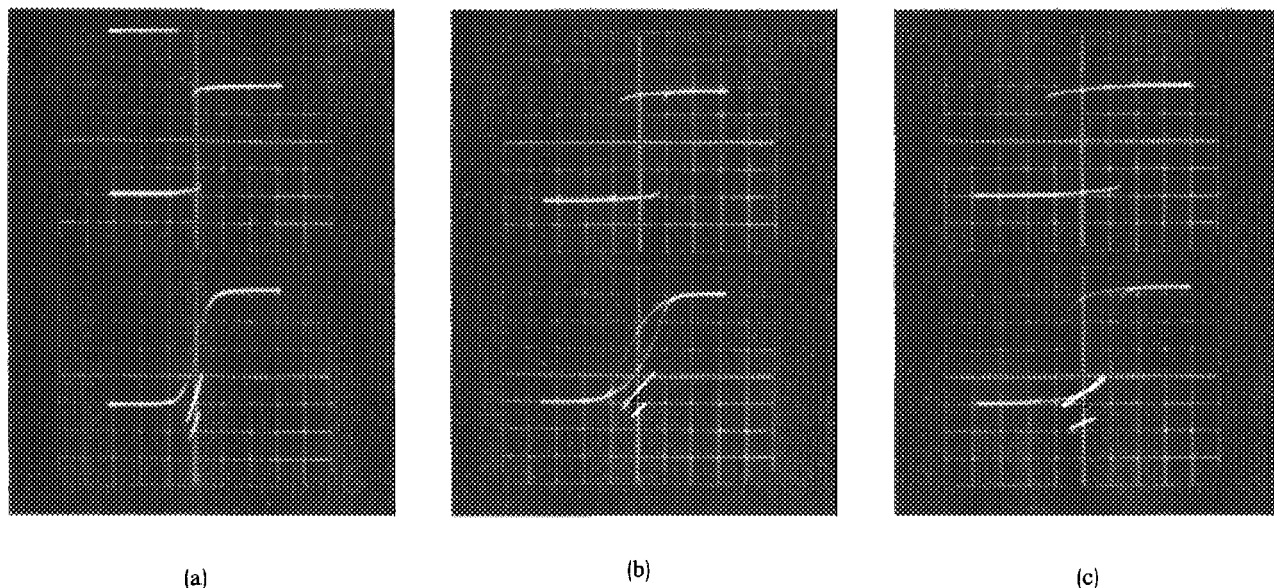


FIG. 1. Magnetization curves of amorphous films. Upper trace: magnetic field applied along easy axis. Lower trace: magnetic field applied along hard axis with three traces at different drive fields. (a) $\text{Fe}_{60}\text{Si}_{40}$, horizontal scale 5 Oe/div; (b) $\text{Fe}_{70}\text{B}_{30}$, horizontal scale 5 Oe/div; (c) $\text{Co}_{85}\text{Nb}_{15}$, horizontal scale 10 Oe/div.

higher. At room temperature evidence for full amorphization was ambiguous. Samples discussed here are those formed at LN_2 temperature.

B. Co-Nb

We made Co-Nb films with compositions corresponding to $\text{Co}_{90}\text{Nb}_{10}$, $\text{Co}_{84}\text{Nb}_{16}$, and $\text{Co}_{75}\text{Nb}_{25}$. Mixed samples were found to be amorphous after irradiation with 3×10^{15} Xe^+ ions/ cm^2 at room temperature; irradiation at low temperatures was therefore unnecessary. Amorphization should be expected according to the structural difference rule⁷: this rule predicts that multilayers consisting of metallic elements with different lattice structure will combine to an amorphous phase after ion mixing. Moreover, Co is known as an anomalously fast diffuser in Nb, a property that has recently been connected with improved mixing behavior.⁸

IV. DISCUSSION OF MAGNETIC MEASUREMENTS

Magnetic parameters were obtained for each composition at various irradiation doses, but no systematic dose dependence was found above the amorphization threshold. We have therefore reported data for the lowest doses at which the films became amorphous. These numbers were not significantly altered by thermal annealing below the recrystallization temperature with the exception of $\text{Co}_{84}\text{Nb}_{16}$. In-plane magnetization curves (hysteresis loops) in both easy and hard axis directions are shown in Fig. 1 for three of the as-mixed samples. Magnetic parameters obtained from curves such as these are given in Table I together with some reference data from the recent literature. Data were chosen from previous work performed on sputtered or evaporated amorphous thin films, since their geometrical similarity to ion mixed films makes them more directly comparable than the corresponding bulk glasses. Moreover, the composition of

TABLE I. Magnetic parameters of ion-mixed amorphous films.

Alloy	Ion-mixed samples			Literature data			References
	$4\pi M$ (kG)	H_c (Oe)	H_k^a (Oe)	$4\pi M$ (kG)	H_c (Oe)	H_k (Oe)	
$\text{Fe}_{77}\text{Si}_{23}$	12.7	1.3	2.5	12			
$\text{Fe}_{70}\text{Si}_{30}$	10	2.1	...	11.5	0.2	4.2	(6,10)
$\text{Fe}_{62}\text{Si}_{38}$	5.5	2.7	4.5	4			
$\text{Fe}_{50}\text{Si}_{50}$							
$\text{Fe}_{30}\text{Si}_{70}$							
$\text{Fe}_{70}\text{B}_{30}$	13.4	3.8	8	11	0.5-1		(12)
$\text{Fe}_{60}\text{B}_{40}$	8.2	3.5	6	10			
$\text{Co}_{90}\text{Nb}_{10}$							
$\text{Co}_{84}\text{Nb}_{16}$	11.4	13.5	30	10	0.2		(14)
$\text{Co}_{75}\text{Nb}_{25}$							

^aBased on slope of magnetization curve in hard direction at low drive field.

liquid quenched glasses is usually restricted to the neighborhood of deep eutectics, whereas both ion mixed and vapor quenched films cover a much wider range.

Amorphous Fe-Si films have been prepared by both coevaporation⁹ and sputtering.^{6,10} Their saturation magnetization is nearly independent of the preparation method and is mainly determined by composition. The magnetization decreases gradually with increasing Si content, and disappears at room temperature between 40 and 50% Si concentration. Coercive fields are currently lower than 1 Oe, and both planar or perpendicular anisotropy has been reported for as-deposited films.

rf-sputtered Fe-B films have been studied over a broad range of compositions.¹¹⁻¹³ Both saturation magnetization and coercivity are comparable in magnitude to the Fe-Si system up to 30% metalloid concentration. Perpendicular anisotropy observed after thermal treatment has been associated with the development of compressive stress.¹¹

$\text{Co}_x\text{Nb}_{1-x}$ films have been prepared by dc sputtering in the range $70 < x < 90$.¹⁴ The films are magnetically soft, a substantial drop in H_c being achieved by thermal annealing. The as-deposited films show an in-plane anisotropy, and the observed magnetostriction is very low.

Our ion-mixed films of $\text{Fe}_x\text{Si}_{1-x}$ were clearly magnetic for $x > 0.6$ and had nearly zero magnetic moment for $x < 0.5$. Both films of Fe-B were magnetic, and $\text{Co}_x\text{Nb}_{1-x}$ was magnetic for $x = 0.84$ and nonmagnetic for $x = 0.9$ and 0.75 . These ranges are quite similar to those found for films prepared by sputtering and coevaporation. Comparing the references values of magnetic parameters listed in Table I with our own measurements of ion mixed films, we also notice an overall similarity between saturation magnetization values of the corresponding alloys. The largest discrepancies occur for the Fe-B system, and may be related to errors in the determination of the B concentrations, for reasons explained above. The meaning of this agreement in terms of structural similarities must be considered with some caution. The sensitivity of the bulk magnetization of amorphous alloys to their microscopic structural arrangement is well established, in particular for metal-metalloid glasses. Models for magnetization based on percolation theories¹⁵ predict a connection between the threshold concentration for magnetic ordering and the nearest-neighbor coordination number. Similarly, the nearest-neighbor coordination model¹⁶ assumes the Fe moment to depend on the number of Fe and metalloid nearest neighbors. According to these models, the magnetization trend of our Fe-Si and Fe-B films would imply close similarity in short-range order between ion-mixed and vapor-quenched films. On the other hand, models based on the itinerant electron theory¹⁷ relate the change in the Fe moment with composition to the transfer of electrons between metalloid atoms and the Fe 3d band. This mechanism would be less sensitive to local structure effects.

All films show some degree of in-plane anisotropy. Since the deposition and mixing processes only differentiate between in-plane and perpendicular directions, there is no obvious source for the in-plane anisotropy, but this same problem has been long recognized in almost all methods of preparing thin polycrystalline films as well. It is plausible

that in analogy to polycrystalline films, the orientation of this in-plane anisotropy could be controlled by an in-plane magnetic field during the ion-mixing process, but this has not been verified experimentally.

The values of coercive force given in Table I correspond to flux reversal in the easy direction. The coercivity is usually smaller in the hard axis direction as shown in Fig. 1. The values of coercive force are comparable to or smaller than those normally observed in polycrystalline films, but are larger than those reported in the literature for evaporated or sputtered amorphous films. However no efforts have been made to optimize or minimize H_c . In contrast to what usually happens with vapor-quenched alloys, the coercive force did not change significantly after thermal annealing.

V. CONCLUSION

For the binary alloys considered here, composition is the single most relevant parameter that affects the magnetic properties of the resulting films. The deposition process (such as ion mixing, sputtering, or coevaporation) is of relatively minor importance. In ion mixing, this fact is reflected in the observations that irradiation beyond the threshold dose required for amorphization changes the magnetic properties little. The exception is that the coercive force of ion mixed films changes less than films produced otherwise, suggesting that ion mixed samples are structurally and electronically more rigidly bound than other samples. A simple interpretation of this insensitivity to the deposition process is that magnetically the amorphous phase must be a fairly well-defined state. In practice, this also means that future experimental investigations of amorphous magnetic alloys may use whatever process is convenient, and ion mixing offers a new alternative to improve flexibility and rapidity in sample preparation. The promising approach for future studies of amorphous magnetic alloys thus is the variation of sample composition in the pursuit of optimal properties, using multilayered evaporated films and ion mixing or codeposition to carry out systematic searches.

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