Evidence for Structure-Related Induced Anisotropy in Amorphous CoTi Soft Ferromagnetic Thin Films

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(Received 23 July 1986)

When amorphous $Co_{1-x}Ti_x$ soft ferromagnetic thin films are deposited by rf sputtering in the presence of a dc magnetic field one observes a somewhat bell-shaped variation of the induced in-plane uniaxial anisotropy energy K_u as a function of the pressure of the sputtering gas P_{Ar}. The maximum value of $K_u(x)$, $[K_u(x)]_{max}$, is obtained for the same P_{Ar} for the whole concentration range studied $0.14 \leq x \leq 0.22$. The origin and the overall variations of K_u are interpreted for the first time in terms of the atomic local anisotropies. The continuous decrease of $(K_u)_{max}$ with increasing Ti concentration is explained by the progressive change of the local structure.

PACS numbers: 75.50.Kj, 75.60.Nt, 75.70.−i

It is well established now that a uniaxial anisotropy K_u is induced in ferromagnetic glasses when these alloys are annealed in the presence of a magnetic field. Up until now the experiments were essentially performed on transition-metal (TM)–metalloid alloys (MA). The concentration dependence of K_u was studied in various $(Fe_{1-x}Ni_x)_y-(MA)_{1-y}$ and $(Fe_{1-x}Co_x)_{1-y}-(MA)_y$ binary metallic glasses.[1,2] The variations of K_u were in the range of (1 to 8)$\times 10^3$ erg/cm^3 with a maximum near $x=0.5$, results well explained by a diatomic pair-ordering mechanism via pseudodipolar interaction.[3] In amorphous alloys with only one type of magnetic atom the value of K_u is usually between 1×10^3 and 3×10^3 erg/cm^3. The origin of K_u in this case is related to a monatomic directional order where a metalloid occupies the interstitial position and perturbs the pseudodipolar interaction of the magnetic atom pairs. A theoretical model which takes into account the amorphous structure corresponding to TM-MA alloys permitted us to explain the as-observed value of K_u.[4]

We report here the variation of K_u with composition and deposition parameters obtained on amorphous $Co_{1-x}Ti_x$ films. It is shown that the value of K_u, which is exceptionally high for a soft ferromagnet, and its variation with concentration and deposition parameters cannot be interpreted by a directional short-range-order mechanism. The results are explained by a model where K_u is related to the local anisotropy of Co atoms in accordance with structural investigations, structure which is believed to be specific for Co-metal–type metallic glasses.

The a-$Co_{1-x}Ti_x$ films were deposited by rf diode sputtering onto water-cooled glass substrates by use of Ar as a sputtering gas. K_u was induced by our performing the deposition process in a dc magnetic field of 700 Oe applied parallel to the film plane. The experimental setup of the sample holder has been described in a previous paper.[5] The targets were carefully cooled down by our sticking them to the water-cooled cathode. The results correspond to the central part of the deposit where oblique incidence effects are negligible. The concentration range investigated was $0.14 \leq x \leq 0.22$ on films of thickness in the range of 0.05 to 0.3 μm.

The induced anisotropy field $H_k = 2K_u/M_s$ was determined by three different techniques: (a) The study of B-H loops where H_k was obtained from the saturation field along the hard axis, (b) in-plane ferromagnetic resonance measurements, and (c) sensitive torque magnetometer measurements. The value of H_k was the same within $\pm 5\%$. The measurements revealed also that the dispersion of H_k is negligible.[6] Along the easy axis one obtains a rectangular hysteresis loop and the corresponding coercive field was low, typically in the range of 0.2 to 2 Oe and independent of the magnitude of H_k. These results show that along the hard axis the magnetization change occurs by coherent rotation only, while along the easy axis the magentization reversal takes place by wall movements. Ferromagnetic resonance measurements confirmed the high chemical uniformity of the samples. For perpendicular resonance, the various standing spin-wave modes follow fairly well a quadratic dispersion law.

In rf sputtering the main deposition parameters are the pressure of the sputter gas P_{Ar} and the rf input power W_{rf}. W_{rf} determines the deposition rate and the temperature rise of the substrate,[7] which is generally quite important. In the present experiments, because of the special geometry of the sample holder the temperature of the substrate remained close to the room temperature, as revealed by the measurements which used thin-film thermocouples.[8] P_{Ar} determines the average energy of the sputtered particles E^f, as they arrive on the substrate. With increasing P_{Ar} the value of E^f decreases as a result of collisions of ejected atoms with the sputtering gas. E^f was computed for Co and Ti particles by use of the formula of Cadiev and Chencinski[9] for various pressures for the present experimental conditions $E^0_{Co}=3.45$ eV, $E^0_{Ti}=4.05$ eV, $d=75$ mm, $T_G=400$ K where E^0 is the most probable ejection energy as the par-

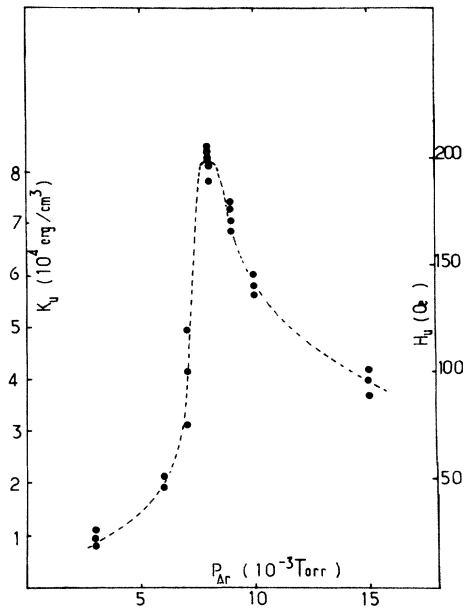

FIG. 1. Variation of K_u as a function of Ar pressure. $x=0.14$; substrate-target distance $d=75$ mm.

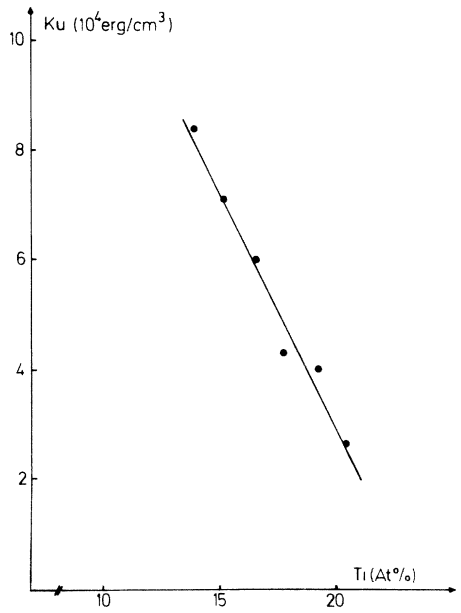

FIG. 2. Maximum induced anisotropy $(K_u)_{max}$ as a function of Ti content in the amorphous $Co_{1-x}Ti_x$ thin films.

ticles leave the target, d the target-substrate distance, and T_G the sputter gas temperature. In the present experiments the values of K_u were essentially related to P_{Ar} and practically independent of W_{rf}. As shown in Fig. 1, for $x=0.14$, K_u presents a well-defined maximum $[K_u(0.14)]_{max}=(8\pm0.5)\times10^4$ erg/cm^3 for $P_{Ar}=8$ mTorr and then decreases more gradually for higher P_{Ar}. The trend of variation of $K_u(x)$ with P_{Ar} is the same for the whole concentration range studied and $[K_u(x)]_{max}$ occurs always for $P_{Ar}=8$ mTorr. The concentration dependence of $[K_u(x)]_{max}$ is reported in Fig. 2.

In order to explain these results we must first consider the mechanisms of induced anisotropy that are usually proposed. The contribution to $K_u(x)$ of the magnetoelastic interaction via stresses is negligible since the magnetostriction in a-CoTi is fairly low ($\lambda_s=2\times10^{-6}$), being independent of concentration, and the easy axis of the anisotropy is always parallel to the applied field. The theory corresponding to monatomic directional order predicts that K_u should increase with increasing nonmagnetic atomic concentration, a result effectively observed on a-TM-MA alloys.[10] However, in the present case K_u decreases with increasing Ti concentration. When monatomic directional order is the basic mechanism, the corresponding K_u is generally fairly small.[10] In the present experiments the values of $[K_u(x)]_{max}$ are exceptionally high and $[K_u(0.14)]_{max}$ is by far the largest ever obtained on a soft amorphous (or crystalline) ferromagnetic material.

We believe that our experimental results can be understood by consideration of the particular local structure of CoTi amorphous films. In an amorphous material the local magnetic anisotropy is related to the local symmetry seen by the magnetic atoms. If the local symmetry is low and highly directional the magnetic atoms see a local uniaxial anisotropy which can be oriented along the applied field if some thermomagnetic conditions are satisfied. Let us recall here the experiments reported on $Co_{80}Nb_{14}B_6$ amorphous alloys,[11] the structure of which is believed to be similar to a-CoTi films. Corb *et al.*[11] observed a thermomagnetic hysteresis in the magnetic anisotropy which they related to a structural transformation as a function of temperature. The structural short-range order was assumed to be built up of clusters with icosahedral, trigonal, and octahedral symmetry, where the trigonal and the octahedral clusters are related, respectively, to the hexagonal-compact (hcp) and to the face-centered-cubic (fcc) phases of crystalline Co-rich alloys. The transformation was centered around a critical temperature T_c and required a well-defined activation energy Q. The lower and higher anisotropy states were observed for $T>T_c$ and $T<T_c$, respectively. These results were explained by a small distortion of a fraction of the icosahedral clusters, which take, respectively, an octahedral and trigonal configuration, and are stable in these two temperature regions. Based on these results we propose for the origin of K_u and its variation with P_{Ar} the following mechanism.

In a-$Co_{1-x}Ti_x$ thin films, the high value of K_u is essentially related to the local anisotropy K_l corresponding to Co atoms located in trigonal clusters, $K_u(x)$ being

maximum when the probability is the highest that these clusters are oriented along the applied field.

In order to verify the validity of this hypothesis we performed a detailed structural study by electron-microscope observation as a function of concentration and P_{Ar} on $Co_{1-x}Ti_x$ thin films. In the microcrystalline region ($x < 0.14$) one observes a transmission-electron diffraction pattern (TEDP) where reflections corresponding to hcp phases are clearly detected. The microcrystallites could be directly visualized by transmission-electron microscopy (TEM); as an example, for $Co_{91}Ti_9$ the average grain size is typically 50 Å.

On amorphous samples ($x \geq 0.14$) TEM appears to have weak contrast, the largest distinct details being smaller than 10 Å. The TEDP on the amorphous samples exhibit three diffused halos characteristic of an amorphous structure. The diffraction pattern exhibits a shoulder after the second maximum for $s \approx 0.95$. This shoulder is the most marked for $x = 0.14$ and becomes progressively attenuated with increasing Ti concentration. We also observe, for a given concentration, a small but significant change of the TEDP as a function of P_{Ar}. A typical evolution of the experimental scattered intensities obtained for $x = 0.14$ and for three different characteristic pressures are reported on Fig. 3. One observes a slight shift of the second peak toward lower values of s and simultaneously the shoulder on the peak becomes more marked when the induced anisotropy increases.[12]

The experimentally observed scattered intensities were reproduced by a computed model based upon the following hypothesis: (a) The structure of a-CoTi alloys is formed of a random continuous matrix of clusters with trigonal (hcp-like), octahedral (fcc-like), and icosahedral symmetries. (b) The octahedral, trigonal, and icosahedral clusters are built up of, respectively, 19, 19, and 25 atoms. The number of atoms was determined from the size of the corresponding clusters which should be smaller than 10 Å as was shown by TEM. (c) The various clusters are correlated by a threefold symmetry axis. However, we suppose that a fivefold and not a threefold symmetry axis exists among the icosahedral clusters. (d) In order to reproduce the density of amorphous alloys we inserted between the various clusters, except between the icosahedral-icosahedral ones, high-density two-dimensional layers formed of seven atoms. (e) The scattered intensities were computed by the assumption of a random distribution of Co and Ti atoms and by the use of an average atomic scattering factor.

The variation of the TEDP as a function of P_{Ar} was simulated by our changing the amount of the various clusters. If one changes the respective number of trigonal and octahedral clusters and keeps constant the icosahedral ones, the as-computed interference function and the scattered intensities remain practically unchanged. If the amount of icosahedral clusters is increased progressively with respect to the trigonal and/or octahedral ones, the second peak shifts towards lower values of s and the shoulder becomes more marked as shown on the inset of Fig. 3. In conclusion: (a) The position and intensity ratio of the experimental scattering intensities can be fairly well reproduced by our assuming the existence of the three types of clusters, but the model does not permit us to distinguish between the octahedral- and trigonal-type clusters. (b) The amount of icosahedral clusters is the largest for $P_{Ar} = 8$ mTorr, i.e., where K_u is maximum. One can point out that the concentration $x = 0.14$ corresponds to the lower limit of the amorphous phase, so that the probability is large to find fcc-like and hcp-like sites, both of which exist in Co-rich crystalline alloys.

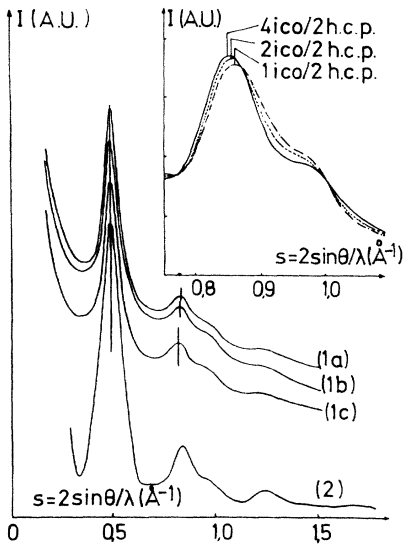

FIG. 3. Microdensitometer recording of experimental TEDP $s = 2\sin\theta/\lambda$ corresponding to a-$Co_{86}Ti_{14}$ obtained at various pressures: (1a) $P_{Ar} \approx 3$ mTorr, $K_u \approx 8\times10^3$ erg/cm^3; (1b) $P_{Ar} \approx 15$ mTorr, $K_u \approx 3.5\times10^4$ erg/cm^3; (1c) $P_{Ar} \approx 8$ mTorr, $K_u \approx 8\times10^4$ erg/cm^3; (2) computed scattering intensities for elastic diffusion. Inset: The as-computed second peak for three amounts of icosahedral clusters, the trigonal and/or octahedral amounts remaining constant.

By use of the present structural model the variation of $K_u(0.14)$ as a function of P_{Ar} can be explained as follows. P_{Ar} determines the energy E^f of the sputtered atoms and the corresponding effective temperature when they arrive at the substrate. The deposit is instantaneously quenched down to room temperature. The energy required for this gas-solid transformation is negligible so that E^f can be considered as the activation energy Q available in the solid state. Let us consider E^f for three characteristic values of P_{Ar}, i.e., $P_{Ar} = 3$, 8, and 15 mTorr. When $P_{Ar} = 3$ mTorr E^f is respectively $E^f_{Co} = 1.17$ eV and $E^f_{Ti} = 1.09$ eV. As a result the effective temperature of the particles and Q are fairly high so that

the sample is built up essentially of icosahedral and low-anisotropy octahedral clusters. For $P_{Ar}=15$ mTorr, $E_{Co}^{f}=0.053$ eV and $E_{Ti}^{f}=0.04$ eV. Now the sputtered atoms are practically thermalized to the temperature of the plasma $T=400$ K. The effective temperature of the particles is low, a condition corresponding to the development of a significant amount of trigonal clusters, a result which explains the fact that for this pressure the value of K_u is much higher than for 3 mTorr. However, Q is fairly low and out of the range for which a significant phase transformation occurs so that the probability of trigonal-like clusters to be oriented along the applied field is small. When $P_{Ar}=8$ mTorr, conditions for which K_u is maximum are $E_{Co}^{f}=0.24$ eV and $E_{Ti}^{f}=0.15$ eV. These values are close to the activation energy $Q=0.15$ eV determined by Corb *et al.* for which the phase transformation is the largest. As the sample is cooled down, some of the octahedral clusters will be transformed to icosahedral or trigonal ones. During this transformation the trigonal clusters will be oriented along the applied field in order to minimize the total energy acting on the film. This mechanism is more probable because of the structure of the icosahedral clusters which possess 10 axes of threefold symmetry. A small amount of trigonal clusters oriented along the easy axis explains the value of $(K_u)_{max}$. If one supposes that for $x=0.14$ the value of K_l corresponding to trigonal clusters is close to the magnetocrystalline anisotropy K_1, corresponding to hcp Co, then the number of trigonal clusters oriented along the applied field is $n=0.04n_T$, where n_T is the total number of clusters.

For samples where the Ti concentration is higher the attenuation of the shoulder on the second peak is believed to be related to a more disordered local structure. This effect could be simulated in the model by the addition of atoms on the triangular faces of trigonal and octahedral clusters in order to progressively destroy the symmetry of these sites. The decrease of $[K_u(x)]_{max}$ with increasing Ti concentration is believed to be related to this effect. The various clusters, in particular the trigonal and octahedral ones, progressively lose their bond orientational order; the corresponding value of K_l decreases so that the total induced anisotropy $K_u=\sum_i K_l^i$ diminishes.

In conclusion, *a*-CoTi thin films with soft amorphous ferromagnetic properties were obtained which exhibit an exceptionally high field-induced uniaxial anisotropy. The results are explained by our assuming that K_u is related to the local anisotropy of Co atoms in accordance with structural investigations. The variation of K_u as a function of the pressure of the sputter gas is explained by a structural transformation of the local order which occurs for a limited range of activation energy.

The authors acknowledge J. Sztern for technical assistance and M. Rivoire for discussions.

[1]F. Luborsky, IEEE Trans. Magn. **13**, 853 (1977).

[2]T. Miyazaki and M. Takahashi, Jpn. J. Appl. Phys. **17**, 1755 (1978).

[3]J. C. Slonczewski, in *Magnetic Annealing,* edited by G. Rado and H. Suhl, *Magnetism Vol. I* (Academic, New York, 1963), p. 205.

[4]P. Allia and F. Vinai, IEEE Trans. Magn. **14**, 1050 (1978).

[5]G. Suran, K. Ounadjela, J. Sztern, and C. Sella, J. Appl. Phys. **55**, 1757 (1984).

[6]G. Suran and K. Ounadjela, J. Magn. Magn. Mater. **54–57**, 237 (1985).

[7]S. S. Lau, R. H. Mills, and D. G. Muth, J. Vac. Sci. Technol. **9**, 1196 (1972).

[8]K. Ounadjela, G. Suran, and J. Sztern, to be published.

[9]F. J. Cadieu and N. Chencinski, IEEE Trans. Magn. **11**, 227 (1975).

[10]T. Miyazaki, M. Takahashi, and K. Hisatake, J. Appl. Phys. **57**, 3575 (1985); J. Riviero, G. Rivero, and M. S. Sanchez, J. Magn. Magn. Mater. **31–34**, 1551 (1983).

[11]B. W. Corb, R. C. O'Handley, J. Megusar, and N. J. Grant, Phys. Rev. Lett. **51**, 1386 (1983).

[12]K. Ounadjela, thesis, Université de Paris, 1986 (unpublished).