Structure-related induced anisotropy in metallic glasses

J. M. Riveiro, V. Madurga, and A. Hernando*
Departamento de Física de Materiales, Universidad Complutense, Madrid, Spain
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By using differential scanning calorimetry (DSC) and electrical resistivity measurements, certain kinds of reversible and irreversible anomalies have been observed in $(Co_xFe_{1-x})_{80}B_{20}$ amorphous alloys, with $x=1.00$, 0.94, 0.90, 0.80, 0.40, and 0.00. The measurements indicate that a reversible transformation takes place in the proximities of 600 K, accompanied by another irreversible transformation during the first heating cycles. The reversible and irreversible processes are associated, respectively, with local phase changes and irreversible structural relaxation processes induced by said reversible phase changes. Lastly, these structural changes are related to the possibility of inducing structural anisotropies in metallic glasses.

INTRODUCTION

It is well known that uniaxial magnetic anisotropies are induced in metallic glasses when these alloys are annealed under the action of a magnetic field. For the case of transition metal-metalloid alloys with two types of metallic atoms, a mechanism of pair ordering has been invoked as the origin of the induced anisotropy.[1] In amorphous alloys with only one type of metallic atoms, the origin of the induced anisotropy has been explained as a consequence of the monoatomic directional order where a metalloid occupies the interstitial position.[2]

Suran *et al.*[3] have studied the field-induced anisotropy as a function of composition and deposition parameters on $Co_{1-x}Ti_x$ films obtained by sputtering. They found a compositional dependence which cannot be interpreted by a directional short-range-order mechanism.

It is also now well established that uniaxial magnetic anisotropies can be induced in metallic glasses by annealing under stress.[4] Anisotropies induced in such a way have been found to be surprisingly high, typically one order of magnitude larger than those induced by field annealing. The most relevant characteristics of the stress-induced anisotropy have been thoroughly reviewed by Nielsen.[5] From the earliest studies it was observed that the anisotropy induced by stress annealing consists of two components called anelastic and plastic, because of their similarity to the viscoelastic behavior. The anelastic component is fully recoverable in the sense that it disappears by annealing at the same temperature without applied stress. The plastic component is nonrecoverable. Reversible and nonreversible processes seem to be, respectively, responsible for the anelastic and plastic components. Another important point is that the induced anisotropy reaches a maximum for annealing temperatures of about 600 K. Finally it must be emphasized that studies of compositional dependence performed on (Co,Fe) and (Co-Fe-Ni) alloys[6,7] clearly indicate that pair-ordering mechanisms have to be disregarded in order to account for the observed behavior.[8]

It is worth noting that studies of structural relaxation monitored by differential scanning calorimetry, x-ray diffraction,[9] magnetostriction,[10] resistivity,[11] and Young's modulus[12] have shown a maximum of relaxation at temperatures close to 600 K. Two components, reversible and irreversible, of relaxation were observed.

Recently Suzuki *et al.*[13] have observed, by using diffraction techniques, a bond orientational anisotropy on amorphous ribbon annealed under stress. It seems likely that the anisotropic bond distribution is related to the magnetic anisotropy. Nevertheless, the microscopic mechanism, which gives rise to such anisotropic redistribution, remains to be elucidated.

O'Handley *et al.* have reported the possibility of transforming reversibly from a fairly well-defined local atomic order to another configuration in some metallic glasses.[14] Thermomagnetic hysteresis observed in magnetostriction and magnetic anisotropy in certain Co-rich glasses[15,16] suggested the existence of first-order structural transformations. More recently, Riveiro *et al.*[17] and Riveiro[18,19] have detected reversible and nonreversible structural transformations at low temperatures. The reversible transformation exhibits the characteristics of the martensitic transformations typical of crystalline materials. All these results are evidence that the local structure can be characterized, at least partially, by well-defined local configurations. According to the picture given by Corb *et al.*[15] the amorphous structure of Co-rich glasses is assumed to be built up of clusters with icosahedral, octahedral, and trigonal symmetry. The low-symmetry trigonal units would contribute largely to the magnetic anisotropy. The transformations which occur at certain temperatures consist of a small distortion of a fraction of a type of cluster which takes the configuration corresponding to the other two types of clusters. By using this idea Suran *et al.* have been able to explain the dependence of the anisotropy on deposition parameters on $Co_{1-x}Ti_x$ films.[3]

In our opinion, the magnetic anisotropy induced by thermal annealing under stress in metallic glasses could probably be related to some particular "local phase change" such as that proposed by O'Handley *et al.*[14] To support this suggestion it is worth noting that, below 530 K (see Ref. 7) as well as above 670 K (see Ref. 20), no significant anisotropy can be induced by annealing under

stress, indicating that the physical process which gives rise to such anisotropy is actived in a rather narrow range of temperatures, as usually has been observed for local phase changes.[15,18,19] The reversible component of the anisotropy would be explained as a consequence of the macroscopic polarization of the low-symmetry structural units that are stable at low temperatures. The polarization is induced under the bias effect of either field or stress, acting during the high-temperature to low-temperature transformation of the reversible local phase change. To check the idea proposed here we have made a set of experiments over a wide range of temperatures centered at 600 K.

EXPERIMENTAL

Amorphous metallic samples of composition $(Co_xFe_{1-x})_{80}B_{20}$, with $x=1$, 0.94, 0.90, 0.80, 0.40, and 0, about 25 μm thick and 0.8 mm in width, were prepared from the constituent elements by the usual melt spinning technique. Metallic glasses with Co-Fe metallic atoms have been found to exhibit a maximum induced anisotropy by stress annealing particularly for the Co/Fe ratio equal to 3. Differential scanning calorimetry (DSC) has been used to study in detail the region close to 600 K in samples weighing 10 mg.

Figure 1 illustrates the DSC trace corresponding to the first heating process carried out at a rate of 10 K/min. An exothermic process is observed near 600 K for all compositions except for that without Fe atoms. The temperature at which the exothermic peak takes place shows a general tendency to decrease as the iron content increases; composition with $x=0.94$ is an exception to this rule. Unfortunately, cooling down processes cannot be performed since the initial temperature should be very close to the crystallization one. Table I summarizes the onset crystallization temperatures obtained by DSC.

TABLE I. Onset of crystallization temperature of $(Co_xFe_{1-x})_{80}B_{20}$ amorphous alloys, observed by DSC at 10 K/min.

x	Temperature (K)
1.00	683
0.94	716
0.90	728
0.80	748
0.40	753
0.00	721

During subsequent heating processes a wide endothermic peak can be seen in the DSC traces shown in Fig. 2 which correspond to the third and fourth heating processes. The behavior becomes nearly repetitive after the third heating process, as Fig. 3 illustrates for $x=0.80$. Therefore this endothermic peak reflects a reversible transformation centered at 630 K. Note that, in order to get a well-defined anomaly in the DSC traces, the heating rate was increased.

As the irreversible anomaly detected during the first run, the endothermic reversible process tends to spread over a wide range of temperature which increases as the iron content increases. Figure 2 shows that the temperature at which the anomaly starts seems to decrease as the iron content increases.

In order to obtain more experimental evidence for the existence of these reversible and irreversible structural transformations, some resistivity measurements were performed by using a four-probe technique able to detect resistance changes of the order of 10^{-5} percent. As the heating rate must be slow, only those compositions with

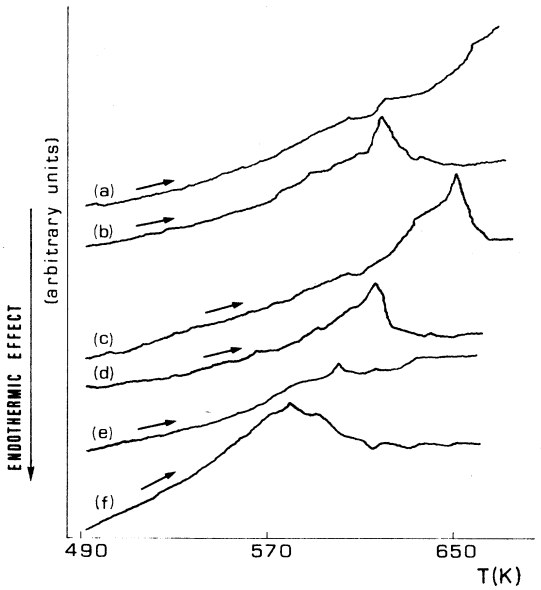

FIG. 1. DSC traces corresponding to the first heating process of samples 10 mg weight, with different compositions. Curves *a*, *b*, *c*, *d*, *e*, and *f* correspond to $x=1.00$, 0.94, 0.90, 0.80, 0.40, and 0.00, respectively. The heating rate was 10 K/min.

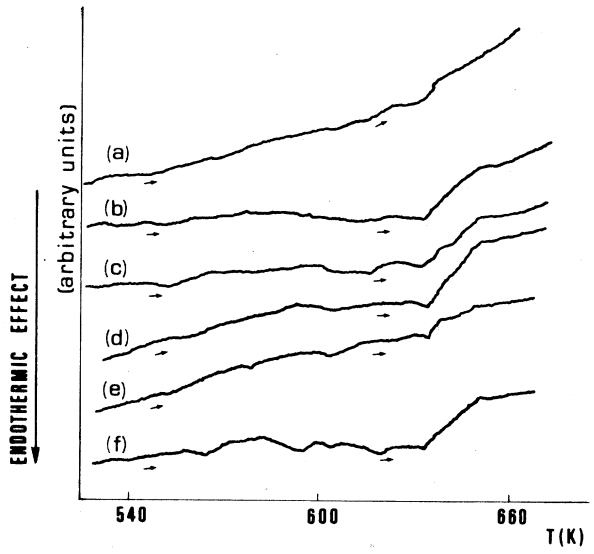

FIG. 2. DSC traces obtained during the third and fourth heating processes for 1.00, 0.94, 0.90, 0.80, 0.40, and 0.00 compositions in Fig. 1. The heating rate was 20 K/min.

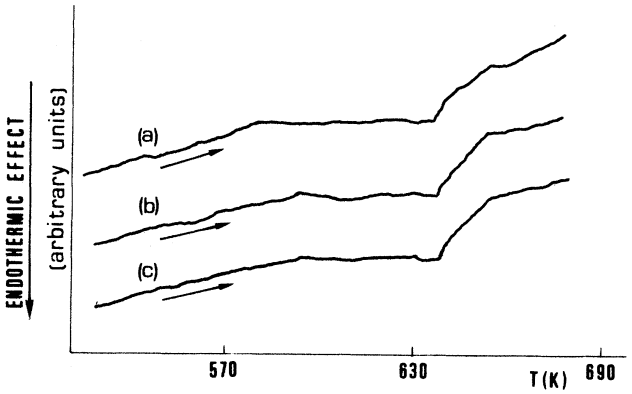

FIG. 3. DSC traces obtained during the third, fourth, and fifth heating of the sample with $x=0.80$ composition. The heating rate was 20 K/min.

high crystallization temperature could be tested. Figure 4 shows the results obtained for the $x=0.8$ composition whose onset crystallization temperature is 748 K (see Table I). The irreversible behavior observed during the first heating process as well as the nearly reversible evolution during the subsequent heating process clearly agree with the results obtained by using DSC. From the results plotted in Fig. 4, corresponding to the nearly reversible

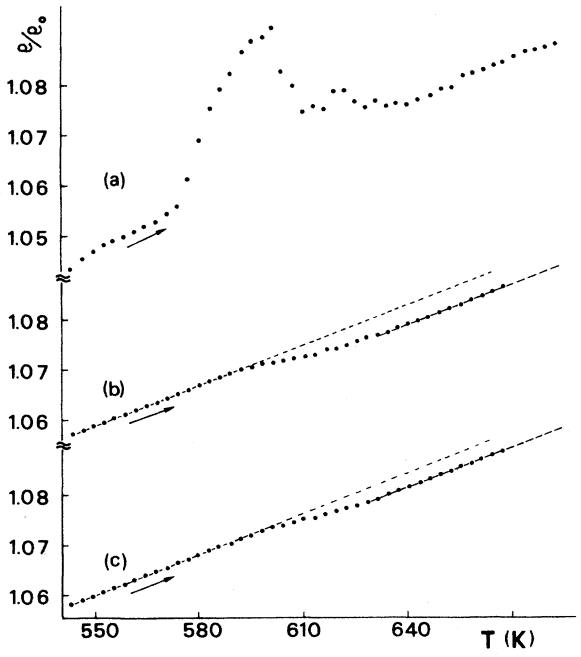

FIG. 4. Resistivity normalized to the resistivity value of room temperature of the "as quenched" $(Co_{0.80}Fe_{0.20})_{80}B_{20}$ alloy plotted vs temperature. Data were obtained during the first (a), fourth (b), and fifth (c) heating processes. The heating rate was 2 K/min.

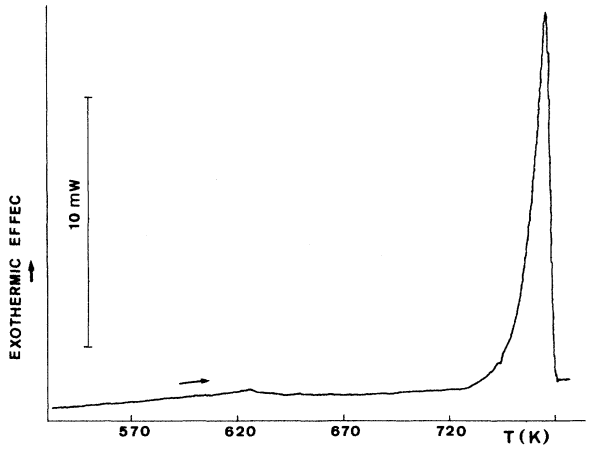

FIG. 5. DSC trace obtained during the first heating process, for a $(Co_{0.80}Fe_{0.02})_{80}B_{20}$ amorphous alloy (weight is 8.46 mg). The heating rate was 10 K/min.

behavior, a reversible transformation is suggested to take place at 620 K.

The irreversible process could be associated to some incipient crystallization phenomenon. However, the DSC plot shown in Fig. 5 points out that the exothermic peak corresponding to crystallization for $x=0.8$ takes place at 765 K, well above 625 K which is the temperature at which the irreversible process discussed here is centered for $x=0.8$. The noticeable difference of temperatures suggests that the possible relation between the crystallization and the irreversible process can be disregarded. On the other hand, if the irreversible transformation were connected to a macroscopic transformation, the transformed phase should be detected by x-ray diffraction. X-ray studies show that the transformation associated to the exothermic peaks in Fig. 1 does not produce any type of crystallinity, except for the composition $x=1.0$, so in this case (see Table I) the irreversible process and the crystallization process take place at quite close temperatures. As an example, the results shown in Fig. 6 illustrate these ideas. Figure 6(a) shows the x-ray diffraction pattern of an "as cast" sample of composition $x=0.8$. Subsequently, this sample was annealed at (640±5) K during 5 min. Figure 6(b) shows the lack of crystalline order traces in the pattern of the annealed sample. The small changes on the shape of the spectrum suggest that some short-range-order transformations might take place. Consequently, it seems likely that the exothermic peak at 625 K in Figs. 1(d) and 5 is not due to a macroscopic process.

Finally, the influence exerted by the transformation on the magnetic properties of the material is illustrated in Fig. 7, where the hysteresis loop of the $x=0.8$ composition is shown for different temperatures. The amplitude of the ac field (50 Hz) is 100 A m^{-1}. A noticeable change in the shape of the hysteresis loop starts at 570 K. The variation consists of a drastic reduction of the coercive force, as can be seen in the hysteresis loop obtained at 630 K.

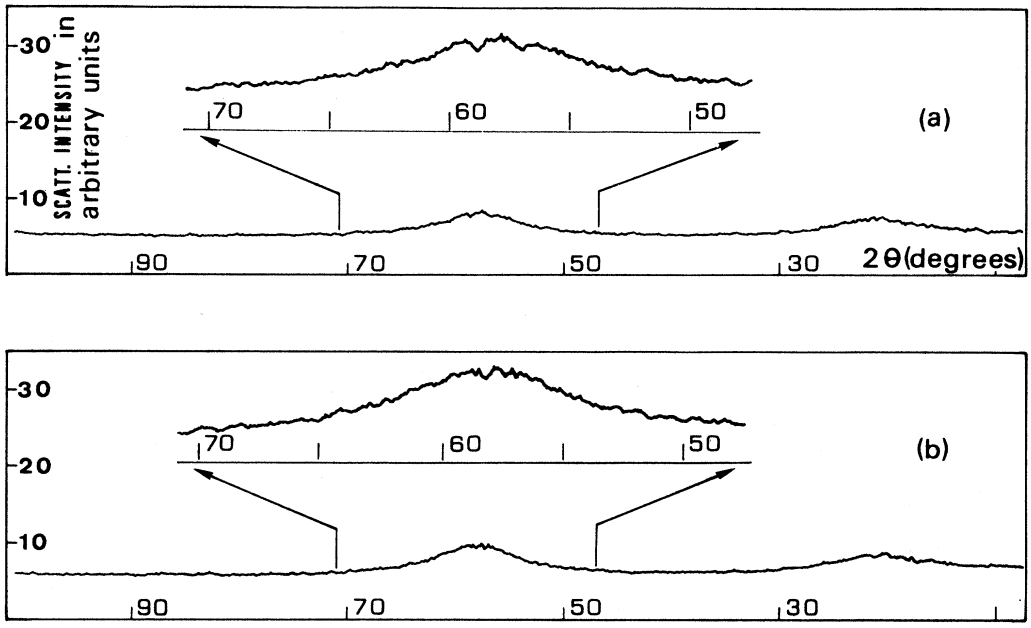

FIG. 6. X-ray diffractograms (Fe $K\alpha$ radiation) for a $(Co_{0.80}Fe_{0.20})_{80}B_{20}$ amorphous alloy: (a) "as cast"; (b) after annealing for 5 min at (640±5) K.

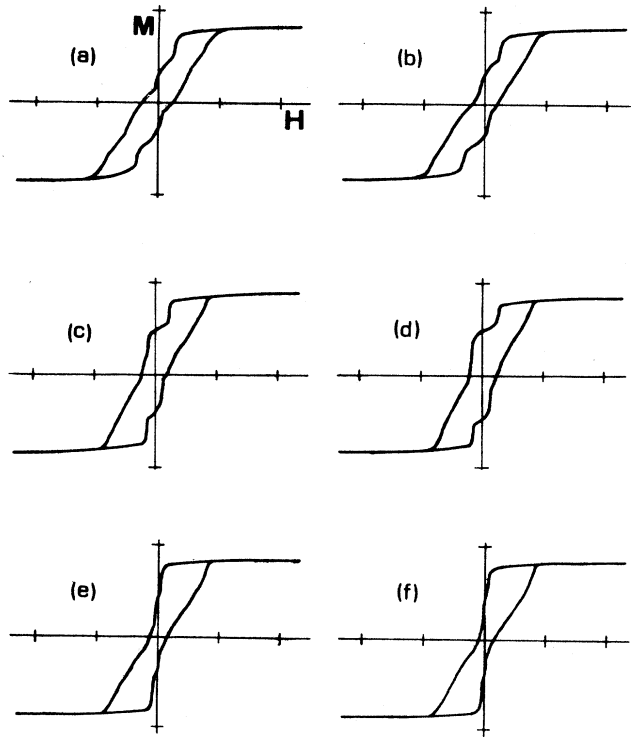

FIG. 7. Hysteresis loops M-H observed at different temperatures for $x=0.80$ composition. Curves a, b, c, d, e, and f correspond to 510, 540, 565, 590, 630, and 635 K, respectively. The maximum amplitude of the 50 Hz ac field was 100 A m^{-1} and the heating rate was 4 K/min.

DISCUSSION

The experimental results described in this work suggest that some structural transformation, centered around 600 K, takes place. The characteristics of such a transformation are similar to those exhibited by the transformations previously detected in metallic glasses at low temperature.[14,17,18,19] According to the well-established interpretation given in these references, the reversible (to some extent) transformation corresponds to a structural transformation between two fairly well-defined local atomic configurations. The irreversible component, which is clearly observed only during the first heating, seems to be due to irreversible rearrangements of atoms in the neighborhood of the transformed units or at the interstitial positions.

The noticeable influence of the metalloid content on the low-temperature transformations[18] has not been observed for this structural transformation at 600 K. It is therefore suggested that metallic atoms are particularly involved in this process.

The structural transformation observed and reported in this work occurs over a wide range of temperature. The temperature at which the transformation is centered and the tendency to decrease the onset of the transformation, as the iron content increases, indicate that the process may be a putative or similar $\alpha \rightleftarrows \beta$ Co transformation as that well known in Co and Co-Fe crystalline alloys. This suggestion would explain the remarkable influence of the transformation on the magnetic properties. Let us consider the trigonal and octahedral clusters, related, respectively, to the hexagonal-close-packed (hcp) and to the face-centered-cubic (fcc) phases of crystalline Co-rich al-

loys. The phase at low temperature is then characterized by a higher fraction of trigonal clusters than the phase at high temperature. Consequently the capability of inducing a macroscopic structural anisotropy is remarkably larger at the low-temperature phase where the uniaxial structural units, to be polarized along any direction, are present in a large fraction.

With regard to the relationship between the experimental results reported here and the anelastic and plastic components of the stress-induced magnetic anisotropy, some considerations are outlined. In a systematic set of experiments carried on (Co,Fe) and (Co,Fe,Ni) composition, reviewed in Refs. 6 and 7 it was observed that the plastic anisotropy strongly depends on the thermal history of the sample, whereas the anelastic component is almost unchanged by previous thermal treatments. By preannealing the samples at a temperature higher than the temperature at which the subsequent stress annealing is performed, the plastic component is not observed. This result suggests that the nonrecoverable plastic anisotropy is related to the irreversible processes which give rise to the irreversible exothermic anomaly shown by both DSC and resistivity measurements. The anelastic anisotropy is clearly associated to the nearly reversible phase transformation.

Although the influence of composition on the induced anisotropy strength[8] indicates a correlation between chemical and topological short-range order which must be analyzed,[21] the discussion of the experimental test allows us to outline some conclusions.

CONCLUSIONS

The exothermic anomaly observed in the proximity of 600 K during the first annealing process of quenched samples reflects the irreversible atomic rearrangements which give rise to the maximum change of many physical variables[10–12] during relaxation. When these processes are activated under the action of a tensile stress a permanent structural anisotropy appears. For some compositions the structural anisotropy results in a magnetic anisotropy (plastic anisotropy).

Underlying the exothermic anomaly an endothermic process has been detected which can be fairly well associated to a local reversible phase transformation. Thermal characteristics of such transformation show its relation with the anelastic anisotropy. Therefore the anelastic component of the stress-induced anisotropy is thought to be due to a macroscopic polarization of structural units with local uniaxial anisotropy, produced by the stress during the fcc to hcp-like transformation of the units. The reversibility of the transformation is reflected in the reversibility of the induction of anelastic anisotropy.

An important point is the coincidence of temperature for structural relaxation and reversible transformation, which has been previously observed in transformations occurring at low temperatures.[17–19] It suggests that relaxation processes are actived by the onset of structural transformations. According to this picture, the cooperative redistribution of atoms involved in the short-range order of the reversible transformation would drastically decrease the activation energy of atom relaxation in the neighborhood of these transforming clusters, where there is a high local fictive temperature.

The quite wide range of temperatures for which reversible and irreversible transformations have been observed is the more striking characteristic of these processes. Two following explanations are tentatively proposed.

(a) The temperature at which the reversible transformation occurs would presumably depend on the characteristics of the local environment through a thermoelastic coupling energy term. Fluctuations of the short-range order would lead to a spectrum of critical temperatures which may account for the amplitude of the transition temperature range as well as for the sharpness of the exothermic peaks in Fig. 1 and the resistivity peak in Fig. 4(a).

(b) In Co-Fe crystalline alloys with 0.8–1.2 at. % Fe, the hcp structure transforms into the double-hexagonal-close-packed (dhcp) phase at (540–670) K on heating, and then to the fcc at about 670 K.[22] The large thermal transition in the hcp to dhcp transformation depends on the Fe content of the alloy. These results agree very well with our data. Therefore, the respective transformations could be similar.

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*Also at Laboratorio de Magnetismo RENFE-UCM. Las Matas, Madrid, Spain.

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