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LETTER TO THE EDITOR

Reversible and irreversible structural relaxation in metallic glasses at low temperatures

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Abstract. This Letter describes studies of reversible and irreversible relaxation processes in metallic glasses that take place at low temperatures. The study has been accomplished by measuring the electrical resistivity. We are led by the present results and others published recently to suggest that relaxation is closely related to reversible structural changes that occur in some clusters with a well defined order in the amorphous matrix.

Many of the physical properties of metallic glasses can be seen to change noticeably over a period of time. This is attributed to atomic rearrangements in the amorphous state. No crystallisation is involved in this process, which will be designated structural relaxation.

Structural relaxation is usually observed as an irreversible process, but sometimes appears in a reversible form. The irreversible part is associated with a reduction and redistribution of the free volume, which affects the topological short-range order (TSRO) and an increase in the chemical short-range order (CSRO). The reversible part is associated with the dependency of the CSRO on the temperature. (See, for example, van den Beukel *et al* 1985.)

In order to understand the exact mechanism of the structural relaxation of metallic glasses it is necessary to know the structure of the glass. The idea that this structure simply corresponds to that of the frozen liquid, as Cargill (1970) and Polk (1970) suggested earlier, is not favoured very much today. However, there is evidence that within the short-range order of metallic glass there is a specific, well defined, local order: this is the basis on which Gaskell (1982) drew up a new structural model.

If we consider metallic glasses of the transition metal–metalloid type it is not surprising to find that there is a well defined short-range order, since there is evidence that this order exists even in the molten alloy (Nassif *et al* 1984, Mattern *et al* 1986).

We suggest that, during the process of quenching, the fraction of volume with well defined short-range order can increase, and that the said order may be heterogeneous. That is to say, different well defined short-range orders may be able to establish themselves in different amorphous regions during the quenching process. This would mainly depend on the local CSRO and on the parameters used for obtaining the sample. If indeed this hypothesis were true, there would be an amorphous structural fraction which would be reminiscent of liquids, and another which would be reminiscent of certain crystals (only within the short-range order).

In the structure of a metallic glass it also possible that some of the established

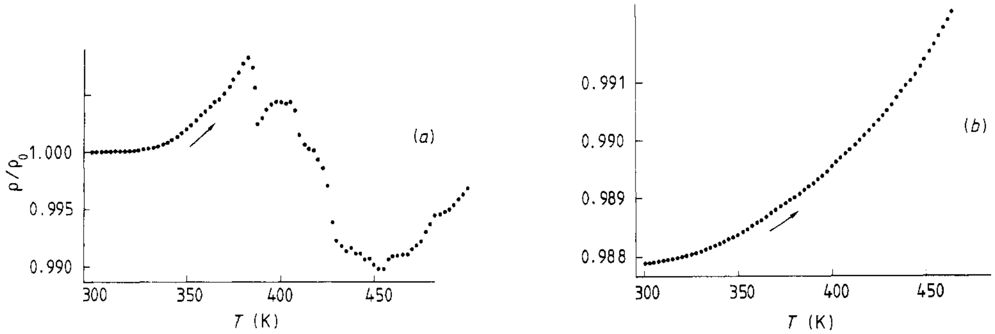

Figure 1. Resistivity, normalised to the resistivity value of the 'as-quenched' alloy at room temperature, against temperature for a commercial $Co_{66}Fe_4Mo_2Si_{16}B_{12}$ amorphous alloy. The figure corresponds to temperatures above room temperature: (*a*) first heating; (*b*) second heating. The heating rate was 1 K min^{-1}.

well defined local orders could turn out to be metastable, within a certain range of temperatures, and that as a result of this a reversible phase change could take place. Structural transformations of this kind have already been described (Corb *et al* 1983, Riveiro and Pareja 1986, Riveiro 1988). The transformations seem to be 'non-diffusive', given the low temperature at which they take place, and in certain ways they are similar to martensitic transformations. The newest aspect of this idea, which we are going to discuss in this Letter, is that it is possible to detect an important acceleration of the relaxation processes near to or in the same range as the temperature at which the reversible transformation takes place (Riveiro 1988). This makes us think that there is a possibility that the main mechanisms of structural relaxation in metallic glasses are connected with the aforementioned reversible structural changes.

If a simple thermally activated process, or processes, were involved in the structural relaxation, we could come close to the ideal glass, by raising the temperature of the sample (with the condition that the crystallisation temperature is not reached). Once we were able to consider the amorphous structure to be 'stable', such stability would become even greater on lowering the temperature. We intend to demonstrate, using two experimental examples, that this does not always happen in this manner, leading us to the conclusion that the mechanisms of relaxation are more complex.

The experiments were carried out with samples obtained by different procedures. The amorphous nature of the samples was determined by x-ray diffraction both before and after the experiments were done. We employed the electrical resistivity (ρ) as a sensitive parameter that could detect small structural changes in the amorphous alloys. Using a sensitive four-probe technique, resistivity measurements were made on a sample while it was heated or cooled. Measurements were taken using two different sets of equipment: (i) using a furnace with an inert atmosphere, for temperatures that were above room temperature; and (ii) for lower temperatures, using a metallic 'finger' that could be introduced into liquid nitrogen.

First we present the results obtained with a Goodfellow ML commercial sample ($Co_{66}Fe_4Mo_2Si_{16}B_{12}$) with a thickness of 25 μm. Figure 1 shows the resistivity (normalised to the room-temperature value of the as-quenched alloy) versus the annealing temperature for temperatures above room temperature. The graphs correspond to the first and second heatings. There are considerable differences between the two graphs. It is

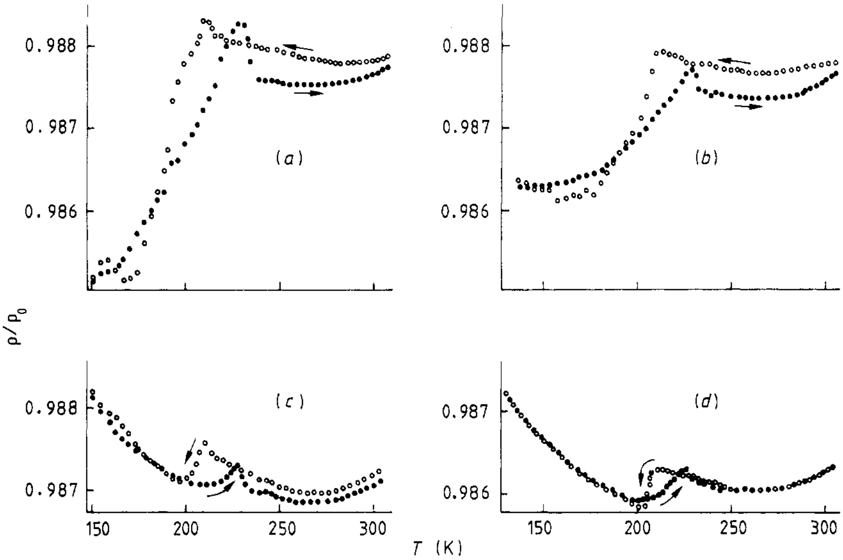

Figure 2. First- (*a*), second- (*b*), sixth- (*c*) and thirteenth- (*d*) loop cycles (ρ–T) obtained at low temperatures for the $Co_{66}Fe_4Mo_2Si_{16}B_{12}$ sample (ρ is normalised to the corresponding value at room temperature at the beginning of the first cycle). The cooling and heating rates were 3 and 1 K min^{-1} respectively.

possible to reproduce the second heating in consecutive heatings made in the temperature range of figure 1, indicating that irreversible behaviour is only present in the first heating. It is important to notice that the irreversibility is most pronounced in the range close to 400 K. As can be seen in figure 1, the reversible behaviour is non-linear and $\rho(T)$ appears to have a relative minimum for a temperature somewhat below room temperature. The sample seemed to be structurally relaxed for temperatures below those of the given treatment and in these conditions the experimental arrangement was changed in order to observe the minimum for $\rho(T)$. The results at low temperatures are shown in figure 2. Surprisingly, we were able to detect new irreversible changes in $\rho(T)$ at low temperatures. The thermal cycles at low T have a marked hysteresis, as can be seen in figure 2. The anomalous behaviour in $\rho(T)$ observed in figure 2(*d*) is reversible. Figure 2(*d*) is well reproduced in later thermal cycles (not illustrated in figure 2). The results of figures 1 and 2 are reproduced qualitatively with other samples from the same material.

Secondly, results obtained in a Co–P amorphous alloy, obtained electrolytically by using pulsed current, are shown in figures 3 and 4. The sample was obtained two years before being used in this experiment, and during this time in storage it was kept at room temperature. The characteristics of the sample have previously been published (Riveiro and Rivero 1981). The sample is a multi-layer, made with layers with low P concentrations (20 at.% P, 300 Å thick), alternated with others of high P concentration (30 at.% P, 30 Å thick). Above room temperature, $\rho(T)$ exhibits an almost linear behaviour with a very small temperature coefficient (4×10^{-6} K^{-1}). At low temperatures, anomalies less pronounced than but similar to those observed and discussed in figure 2 may be seen in figures 3 and 4.

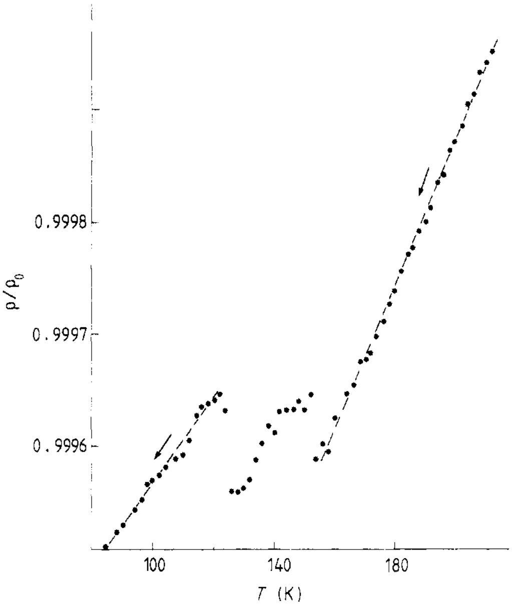

Figure 3. Resistivity normalised to the resistivity value of the 'as-obtained' alloy at room temperature against temperature, for a multi-layered Co–P amorphous film.

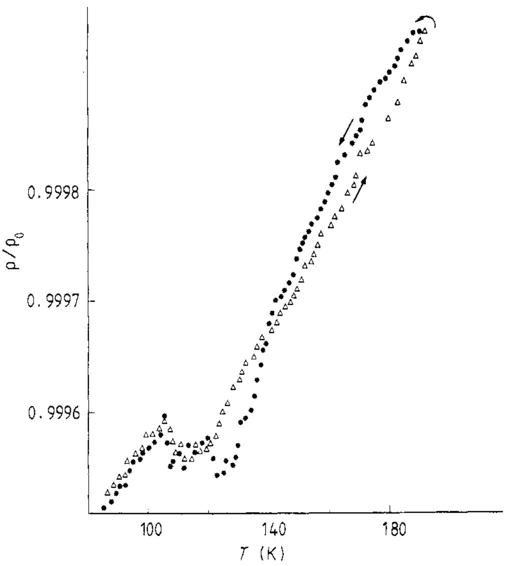

Figure 4. Resistivity against temperature for a complete thermal cycle, in the multi-layered Co–P amorphous film (after the first cooling of figure 3).

We believe that the reversible anomaly that we have observed in $\rho(T)$ at low temperatures reflects the same physical phenomenon as other reversible anomalies seen in metallic glasses at higher temperatures (Scott and Kursumovic 1982, Balanzat *et al* 1985, Komatsu *et al* 1986), which, as we have already mentioned, have usually been attributed to changes in the CSRO. Nonetheless, both the reversible and irreversible anomalies, especially those which are found at low temperatures, can be interpreted by taking into account only certain changes in the TSRO. In this way, for example, the reversible anomaly could be a reflection of the reversible structural transformation, which has already been discussed. The transformation could simply change the symmetry of the well defined local order, without there being changes in the CSRO. Let us suppose that the said transformation really exists in metallic glasses. The transformation temperature that corresponds to a certain cluster will depend on the surroundings of the cluster and, given the heterogeneity of the amorphous structure, it is understood that the cooperative effect of all the same clusters present in the amorphous matrix gives rise to a wide range of transformation temperatures. This idea will account for the wide temperature range of the reversible anomaly, as shown in figure 2(*d*).

Let us assume that this reversible transformation takes place in a certain cluster of atoms. When the transformation occurs, it will facilitate the relaxation of the atoms surrounding the cluster. The transformation could provoke a deep and complex change in the local activation energy of the relaxation process within the surroundings of the cluster. We believe that in this way a sufficient activation energy reduction can be produced to enable irreversible structural relaxation at low, and even very low temperatures.

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