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ELECTRON RADIATION DAMAGE OF SOME METAL-METAL AMORPHOUS ALLOYS

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Very few data about the influence of irradiation on the structural properties of metallic glasses are available in the open literature. Furthermore most results deal with the bombardment of amorphous materials with heavy particles, essentially energetic ions, fast neutrons or fission fragments, that is with cascade type damage (Lesueur 1975), Chang 1977, Rechtin 1978, Brimhall 1979, Azam 1979, Audouard 1980). In addition most irradiations in this field were performed up to fluences of several displacements per atom, that is to doses which would result in crystalline solids in a very severe damage. However, interestingly enough, the existing data indicate considerably higher resistance of amorphous alloys, which makes these materials good candidates for applications in radiation environments. The structural changes which were observed in some cases can provide also insight into the nature of the structural anomalies which characterize amorphous solids (Doi 1977, 1979).

From a more fundamental viewpoint, irradiations with fast electrons, which produce simpler defects, appear to be of special interest. In principle, they can help in defining the characteristics of the elemental defects which are inherent to the amorphous state. A further point of interest is the determination of the radiation enhancement of atomic mobility and related phenomena. For both purposes, irradiations at very low temperatures are required, in order that the majority of the created defects are frozen in and their mobility can be analyzed during subsequent anneal sequences. Only recently research was conducted along this line, essentially in metal-metalloid alloys (Audouard 1979, Balanzat 1980 a, Chambron, this conf., Audouard, this conf.).

The present work is intended at obtaining information about the elementary radiation defects in a series of metal-metal amorphous alloys exposed to fast electrons at 20 K. Electrical resistivity measurements were used to monitor the radiation damage and defect behaviour. In this paper, the observed effects are described, with particular reference to resistivity variations evidenced in parallel experiments on the same materials, but in the non-irradiated condition, during alternate heat and quench cycles (Balanzat, this conf.).

Experimental conditions

Ni_{60}Nb_{40}, Cu_{50}Ti_{50}, Cu_{40}Zr_{60} and Cu_{60}Zr_{40} alloys have been prepared by splat cooling, or melt-spinning or else roller quenching (Calvayrac, this conf.), in a controlled atmosphere. The specimens used for the irradiation and resistometric studies were strips 1 mm x 25 mm with original thickness between 40 µm and 70 µm. They were equipped with potential leads by spot welding. Most of them were studied in the as-received condition.

Electron irradiation was carried out at a flux density between 2 and 4 x 10^{12} e cm^{-2}s^{-1}, for 1 to 4 days, with 2.5 MeV electrons, amounting to a total dose in the range 2 x 10^{17} to 1 x 10^{18} e cm^{-2}. During the irradiation, the specimens were immersed in liquid hydrogen under normal pressure. Consequently, irradiation temperature could be kept within a few degrees of 20 K.

Electrical resistivity measurements were carried out during the irradiation or during subsequent anneals at increasing temperatures up to about 500 K. For these thermal treatments, the samples were raised into a furnace placed in the hydrogen vapors about 20 cm above the bath surface and preheated at the appropriate temperature. The duration of every anneal was 10 min.

Results

The different materials exhibited comparable resistivity effects in response to electron bombardment. Resistivity increments were some thousands of the preirradiation resistivity value measured at 20 K. (The room temperature resistivity
is of the order of 150 - 200 µΩcm in all the amorphous alloys studied and the 20 K resistivity differs by only a few per cent from the one at 300 K. It is recalled that in crystalline alloys irradiated at similar dose levels, resistivity increments are some thousandths of the ambient resistivity, but direct comparison in terms of the number of created defects is meaningless, since the specific contribution of a structural defect to resistivity is not known in the amorphous state. In the following, the evolution with temperature of the radiation induced resistivity excess will be considered.

1) Cu₅₀Ti₅₀

The typical pattern of the resistivity variations which were observed on annealing the Cu₅₀Ti₅₀ specimens isochronally is shown in Fig. 1. The values indicated in the figure refer to the initial resistance of the specimen considered. As a result of the electron irradiation, the resistivity was increased by about 0.7 x 10⁻³ of its initial value.

This excess is progressively decreased during the isochronal annealing sequence from 20 K to about 250 K. It is to be noted that this recovery, although partial, is spread out over the entire temperature range indicated, with no clearly defined stages. In addition, the resistivity increment induced by the irradiation is not annealed out before the onset of the resistivity increase which takes place above 150 K. In a parallel study conducted in the same material but with no flux, a similar resistivity increase was found to happen in the same temperature region (Balanzat, this conf.). It was assigned to compositional short range ordering. For the sake of comparison some data points have been plotted in Fig. 1. It can be seen that the two curves for the irradiated and non-irradiated specimens are close to each other. It is inferred that the radiation produced defects have no marked influence on the kinetics of short range ordering, at least for the irradiation dose considered. Con-

![Fig. 1 - Isochronal resistivity variations in a melt-spinned Cu₅₀Ti₅₀ alloy. The results have been normalized to the initial recovery excess induced by the irradiation: (•) first irradiation; (○) second irradiation. The two recovery curves are very similar. In neither case, the preirradiation value was restored.](image1)

![Fig. 2 - Recovery spectra observed in a splat-cooled Ni₆₀Nb₄₀ alloy. The results have been normalized to the initial recovery excess induced by the irradiation: (•) first irradiation followed by isochronal annealing to 340 K; (○) second irradiation. The two recovery curves are very similar. In neither case, the preirradiation value was restored.](image2)
versely, the resistivity increase measured at the time when flux was suppressed is about 20 times smaller than the resistivity effects induced by thermal ordering in the as-quenched specimens, which indicates that no significant ordering occurs during the course of the irradiation.

2) Ni$_{60}$Nb$_{40}$

Fig. 2 is to illustrate in some detail the low temperature recovery spectrum of a Ni$_{60}$Nb$_{40}$ alloy. First the specimen was irradiated at a dose which resulted in a resistivity increment of $1.6 \times 10^{-3}$. It was then given a series of isochronal anneals up to 300 K. At this temperature, only 40% of the initial resistivity increment were annealed. A second irradiation at 20 K was then triggered, until an additional resistivity increase of $2 \times 10^{-3}$ was obtained. A new annealing sequence was started up to 500 K. It can be seen in the figure that the shape of the second recovery curve is quite similar at subambient temperatures, to the one for the first irradiation. Three maxima are detected in the recovery rate, located around 60 K, 150 K and 250 K, respectively. On the other hand, the recovery is observed to increase above 400 K, just like in the CuTi alloy, a phenomenon supposedly linked to short range ordering.

3) Cu Zr alloys

In Cu$_{40}$Zr$_{60}$ alloys, the same features are observed. The resistivity is decreased progressively down to 300 K and no stage can be distinguished in the recovery curve. Above room temperature, just like for the previous cases, resistivity starts

![Fig. 3 - Recovery curves in irradiated alloys of the CuZr system, for two compositions: (●) Cu$_{40}$Zr$_{60}$, splat cooled. Initial resistivity increase was $0.7 \times 10^{-3}$. (○) Cu$_{60}$Zr$_{40}$ prepared by roller quenching. Initial increment was $1.2 \times 10^{-3}$. Both specimens were freshly produced ones.](image)

![Fig. 4 - Recovery curves for two Cu$_{60}$Zr$_{40}$ specimens exposed to the same irradiation: (●) rolled, 'fresh'; (○,▼) rolled, aged at room temperature; (●,▲) rolled, aged at room temperature and annealed for 30 min. at 200°C, in hydrogen under normal pressure; (+) splat cooled and aged. The full symbols are for the first irradiation run. Open symbols are for the second irradiation. All initial increments were between 0.7 and $1.9 \times 10^{-3}$.](image)
increasing again. Preliminary experiments have shown the existence of the same trend, in non-irradiated specimens cycled thermally between ambient and 500 K (Balanzat 1980 b).

For the Cu\textsubscript{60}Zr\textsubscript{40} composition, the situation is more complex. On one hand, 'fresh' specimens exhibit a normal behaviour, in as for the recovery curve is rather smooth, with only a slight change in the recovery rate around 150 K (fig. 3). Again 50% of the initial increment are left after anneals at 400 K. By contrast, specimens which have been aged at room temperature over periods of one month or longer exhibit very different recovery profiles, namely (i) two well defined stages are present, (ii) the resistivity excess is totally annealed as early as a temperature of 250 K is attained. Incidentally, if the post-irradiation annealing sequence is stopped at 250 K, that is when the resistivity of the virgin specimen is restored, and a second irradiation is started, the recovery spectrum on second heating is identical to the first one (iii) above 250 K, the resistivity still decreases below its preirradiation value. At the moment, there is no simple interpretation for the observed influence of aging on the irradiation behaviour. However the aging process itself has been analyzed in some detail and explained in terms of oxide formation leading to a decomposition in which fcc copper precipitates in a zirconia-like matrix (Calvayrac, this conf.). It is interesting to note that reactivity to hydrogen is enhanced as a result of aging and that crystallization temperature is lowered by 150°C when aged specimens are heated in an hydrogen atmosphere under normal pressure (Balanzat unpublished). Finally, Cu\textsubscript{60}Zr\textsubscript{40} appears to be a peculiar case, since the other amorphous alloys studied seem to be much less sensitive to room temperature aging.

Concluding remarks

The general picture which emerges from the present results is one in which the defects created by the electron irradiation are annealed progressively over the entire temperature range explored with no sharp peak in the recovery rate. A striking feature is that in those alloys in which a short range ordering process has been evidenced by electrical resistivity measurements after quenching, Cu\textsubscript{50}Ti\textsubscript{50} and Cu\textsubscript{60}Zr\textsubscript{40}, no significant enhancement of the ordering rate was detected as a result of the irradiation. This means possibly that the number of defects created by the impinging particles is much smaller than the one originally present in the specimens as retained by the quench from the melt. An alternate explanation is that the produced defects undergo only a small number of diffusional jumps before getting eliminated, which restricts their contribution to ordering. Indeed this would be quite a different situation from the one in crystalline alloys, in which electron irradiation leads to the advent of short range ordering at temperatures much smaller than those at which thermal diffusion is operative. Next question is whether the radiation created defects have the critical size above which they can participate in the atomic mobility (Turnbull 1961). These points are essential keys to elucidate the atomic transport processes in amorphous metallic alloys.

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