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RESPONSE OF METALLIC GLASSES $Fe_{40}Ni_{40}P_{14}B_6$ AND $Fe_{80}B_{20}$ TO IRRADIATION WITH 800 MeV PROTONS*

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Metallic glasses with compositions of $Fe_{40}Ni_{40}P_{14}B_6$ and $Fe_{80}B_{20}$ were irradiated in the 800 MeV proton beam at the Los Alamos Meson Physics Facility while the electrical resistance and length changes were monitored. The resistance and the length of the first alloy were both found to increase and saturate with dose to $\Delta R/R \sim 5 \times 10^{-3}$ and $\Delta L/L \sim 2 \times 10^{-3}$. For the second alloy the total dose of 1.1×10^{19} p/cm^2, which was calculated to give roughly 0.12 dpa, was slightly less than that required for saturation. No annealing of these increases was observed for anneals from room temperature to 250°C. These results are interpreted in terms of a model in which collision cascades create small regions of increased atomic disorder which fully overlap each other at saturation.

INTRODUCTION

The newly developed class of materials known as metallic glasses or amorphous metals have special properties which give them potential for technological applications. For instance, it has been proposed that because of their amorphous structure these materials will tend to be resistant to damage in radiation environments and thus could be useful in fission and fusion reactor technologies.

There have been relatively few investigations of the response of metallic glasses to various kinds of irradiation, and to date no written review of these studies exists. It was originally considered that in the pre-irradiated state the atomic structure of an amorphous metal prepared by liquid quenching was so nearly random that the randomizing atomic displacements and rearrangements resulting from particle irradiation would not tend to change the structure and properties. The recent work of Elliott, et al [1,2] and others [3,4] has shown that irradiation can cause significant changes to both the structure and the properties. From these results it is deduced that irradiation is actually causing an increase in the atomic disorder over and above the non-randomness in the pre-irradiated liquid-quenched state.

The present status is that there are still important questions to be answered concerning the magnitude and nature of irradiation effects. In addition, since all but one [5] of the previous investigations have been limited to measurements before and after (as opposed to during) the irradiation, it is desirable to determine the rate at which property changes occur by making in situ measurements of irradiation effects. The purpose of this study is to make such in situ measurements of electrical resistance and length change of two metallic glasses, $Fe_{40}Ni_{40}P_{14}B_6$ and $Fe_{80}B_{20}$, during irradiation with 800 MeV protons. These two alloys were chosen because they were commercially available in ribbon form suitable for this experiment and because their properties were well characterized by prior investigations. Proton irradiation was chosen because of the availability of the Los Alamos Meson Physics Facility (LAMPF) proton irradiation facility and because the penetrating power of the 800 MeV proton beam allowed simultaneous irradiation of several samples.

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EXPERIMENTAL METHOD

Several different sets of samples were irradiated at different dates for irradiation periods of from one to ten days. Both metallic glass alloys were obtained as spool wound ribbon from Allied Chemical Co. The $Fe_{40}Ni_{40}P_{14}B_6$ ribbon was 1.8 mm x 0.061 mm in cross section and the $Fe_{80}B_{20}$ was 1.0 mm x 0.035 mm. Several samples 8 cm long of each alloy were mounted horizontally at various positions in a specimen holder with the ribbon surface perpendicular to the beam. They were carefully aligned so that the proton beam would pass through them sequentially and essentially undegraded in energy [6]. Calculations of the decrease in beam due to multiple scattering showed roughly a 6% decrease between successive samples [6].

The shape of the proton beam for the irradiation was approximately elliptical with a distribution in the vertical and horizontal directions which was close to Gaussian. The full width at half maximum of this Gaussian was roughly 17.5 mm and 6.0 mm for the horizontal and the vertical directions, respectively. With this geometry the 10 mm portion of the sample length over which the resistance measurements were made was radiated relatively uniformly with a decrease of less than 20% of maximum intensity at the end portions along the length of the sample and negligible variation across the thickness.

The beam current during the various irradiations varied from 1 to 8 μamps; however, during a typical 12-hour period, it was usually held constant within 10%. At times not under experimental control the beam was shut off completely for one minute to several hours. The maximum time-averaged beam flux to the sample for the typical beam current of 6 μamps was 5.2 μamps/cm^2 (3.2 x 10^{13} p/cm^2-sec). Based upon best estimates of the damage energy cross section [7] and the threshold displacement energy [8] for these alloys, this proton flux was calculated to produce roughly 6.2 x 10^{-4} dpa/hour.

Samples were irradiated in air at ambient temperature (~ 30°C) in a closed target box; however, there was sample heating due to the beam. This was roughly 6°C/μamp and 1.6°C/μamp for the $Fe_{40}Ni_{40}P_{14}B_6$ and $Fe_{80}B_{20}$ samples, respectively. Because this heating varied with the beam current for each irradiation, the resistance and the length change measurements were corrected to a constant beam current using measured temperature variation constants. The specimen holder was mounted on a motor driven elevator platform that allowed the samples to be remotely raised or lowered in or out of the proton beam. This allowed the annealing behavior to be investigated at various times during the irradiation.

Conventional 4-lead resistance measurements were made on the samples and a standard resistance using a measuring current of 100 milliamp. This current was reversed for each measurement to correct for thermal emf's. The emf leads, which were of the same material as the sample, were spot-welded 10 mm apart so that this portion was in the center of the beam. Resistance measurements were made with a reproducibility of 10^{-5} ohm; however, the uncertainty due to variations in specimen temperature was greater than this by at least an order of magnitude. The length change measurements were made using a linear variable differential transformer (LVDT) with the core attached to one end of the sample and spring loaded to be lightly in tension. The LVDT signal was amplified, and with the emf's for the resistance, was measured, analyzed and stored at periodic intervals using an automated data processing station. Typically each datum point was obtained from the averaging of twenty emf measurements.

RESULTS

Fig. 1 and Fig. 2 show the results of the change of resistance with time during the same irradiation of the $Fe_{40}Ni_{40}P_{14}B_6$ and the $Fe_{80}B_{20}$ alloys, respectively. In addition, shown at the bottom of the figures is the position of the sample in or out of the beam. Both figures show two different kinds of data, lower resistance results for the sample at ambient temperature because the beam is off or the sample is removed from the beam and higher resistance results with the sample at above ambient temperature due to beam heating. The sample resistances at above ambient temperature have been corrected for variations of the beam current from the nominal value for this irradiation of 6 μamps. Based upon our measured values of 1/R dR/dT for amorphous $Fe_{40}Ni_{40}P_{14}B_6$ alloy and literature values for $Fe_{80}B_{20}$ [9], the resistance differences between ambient temperature (beam off or out of beam) and above ambient indicate that the 6 μamp beam caused the two samples to be respectively, 35°C and 10°C above ambient. The greater temperature above ambient for the $Fe_{40}Ni_{40}P_{14}B_6$ sample was because it was more massive, having

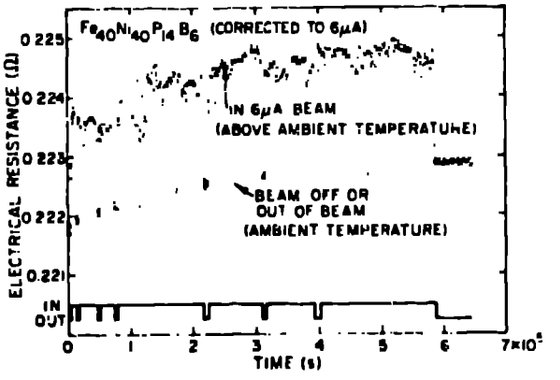

FIG. 1
Electrical resistance vs time for a $Fe_{40}Ni_{40}P_{14}B_6$ alloy irradiated in a 6 μamp beam of 800 MeV protons. The upper set of data points are for the sample in the beam and thus heated to above ambient temperature, while the lower set are either with the beam off or out of the beam and thus are at ambient temperature.

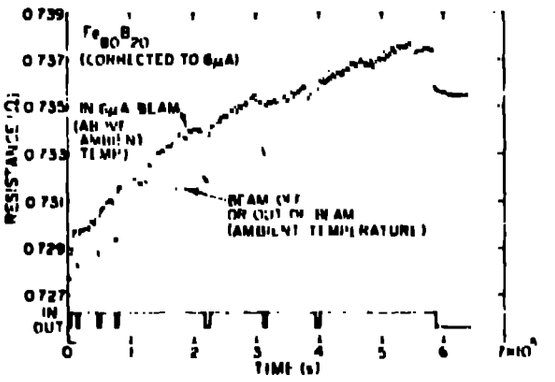

FIG. 2
Same irradiation as in Fig. 1 but for a $Fe_{80}B_{20}$ alloy.

roughly three times the cross sectional area of the $Fe_{80}B_{20}$ sample. Also, because the former sample was at higher temperature in the proton beam, it had wider short-time temperature variations due to variable convective cooling during irradiation and thus showed more fractional scatter in the as-irradiated resistance values.

As can be seen from the data for both ambient temperature and above ambient, each of the two metallic glasses shows an increase in resistance with irradiation. The $Fe_{40}Ni_{40}P_{14}B_6$ alloy exhibits an increase of roughly 0.5% ($\Delta\rho$ = 1.2 μΩ-cm) up to an irradiation time of roughtly 2 x 10^5 sec (56 hours). The average proton flux during this time (corrected for sample out of beam and for the shape of the beam) was 2.1 x 10^{13} p/cm^2-sec. Thus the fluence at saturation was roughly 4 x 10^{18} p/cm^2. In addition to the above, it may be observed that this alloy does not show appreciable annealing effects at room temperature when removed from the beam, e.g., the resistance remained constant when the sample was withdrawn from the beam at various times during the irradiation and at the end of the run (5.8 x 10^5 sec).

The resistance of the $Fe_{80}B_{20}$ alloy, on the other hand, did not saturate during this irradiation, although the shape of the curve indicates that it is approaching saturation. It showed roughly a 1.0% increase ($\Delta\rho$ = 2.6 μΩ-cm) during the 5.8 x 10^5 sec of irradiation which gave a fluence of 1.1 x 10^{19} p/cm^2. This amounts to a resistivity increase per unit of fluence of 2.4 x 10^{-19} μΩ-cm/cm^2 which may be compared with the value of 3.0 x 10^{-19} μΩ-cm/cm^2 for the results in Fig. 1 for the $Fe_{40}Ni_{40}P_{14}B_6$ alloy.

The annealing results when the samples were lowered out of the beam are not appreciably different for the two alloys. The significant finding is that the irradiation-induced contribution to the resistance was stable at room temperature. This was determined to be true for longer periods of time than indicated, i.e., after two weeks at room temperature, the resistance was still unchanged. Also, it was true for annealing at up to 250°C for 3 hours done in situ using Joule heating of the $Fe_{40}Ni_{40}P_{14}B_6$ sample. The small decrease in resistance in Fig. 2 for the $Fe_{80}B_{20}$ sample, which occurs roughly over the first hour after moving the samples from the beam, was determined to be a transient due to decreasing sample temperature as the ambient temperature in the target box surrounding the samples decreased (by roughly 3°C) to room temperature after the beam heating was stopped. The effects of this transient were obscured by the error of the measurement for the other alloy.

In Fig. 3 are shown the length change results for the $Fe_{40}Ni_{40}P_{14}B_6$ alloy for a subsequent irradiation to the one in Figs. 1 and 2.* The proton beam current for this irradiation was 2 μamps with the sample again moved in and out of the beam as indicated in the lower portion of the figure. Also, as indicated in the figure, during the middle of this irradiation the beam was off for 17 hours. In order to cancel the length change effects of variable beam heating of the sample, the length change results which are reported are differential measurements with respect to an aluminum wire sample which was also in the beam. It was determined in this and previous irradiations that aluminum and platinum did not show irradiation-induced length changes, at least within the experimental error of the measurement.

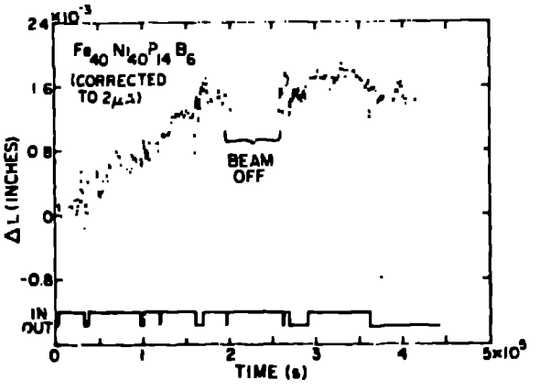

FIG 3
Length change vs time of a $Fe_{40}Ni_{40}P_{14}B_6$ alloy irradiated in a 2 μamp beam of 800 MeV protons with the sample in and out of the beam as indicated.

The length change results appear to be similar to the resistance results for this alloy. The increase in length saturates after roughly 2 x 10^5 sec. This is somewhat unexpected since it is roughly one-third the saturation fluence in Figs. 1 and 2. The magnitude of the length increase at saturation is $\Delta L/L \sim 2 \times 10^{-3}$. As with the resistance measurements there was no apparent annealing effect on the length change other than a short transient due to decreased beam heating when the beam was off or the sample was lowered out of the beam.

*Unfortunately, the length change measurements made during some of the earlier irradiations were found to be invalid because of radiation-induced length changes of unknown magnitude which occurred in a bakelite specimen holder. These earlier measurements did, however, confirm the increase in length such as in Fig. 1

It is worthwhile to consider the change in electrical resistivity from the measured resistance and length changes. If the length changes are considered to be isotropic, and this is a reasonable assumption for an amorphous material, then the fractional change in cross sectional area of the sample is twice the value of the measured fractional length change, $\Delta A/A = 2\ \Delta L/L$. Thus the fractional change in resistivity, $\Delta\rho/\rho = \Delta R/R + \Delta A/A - \Delta L/L$ is given by $\Delta R/R + \Delta L/L = 5 \times 10^{-3} + 2 \times 10^{-3} = 7 \times 10^{-3}$ at saturation. This means that the irradiation-induced increase in sample dimensions was causing the fractional change in resistivity to be appreciably greater than the observed fractional change in resistance. For the $Fe_{40}Ni_{40}P_{14}B_6$ alloy the total resistivity increase is thus 1.7 μΩ-cm with a pre-irradiation value of 244 μΩ-cm. In future experiments it will be desirable to make these measurements simultaneously during the same irradiation instead of sequentially as in this study.

DISCUSSION

By analogy to radiation effects in crystalline metals, we now consider several different models for how particle irradiation can be expected to affect a metallic glass. Models can be conveniently classified according to whether they assume freely-moving defects which are created by the irradiation. We note that the concept of a "defect" needs to be expanded for metallic glasses as compared to crystalline metals. For example, instead of the vacancy or the interstitial atom defect in a crystal lattice, one can consider in an amorphous material that there are regions of locally high or low density which are created by the atomic displacements during the irradiation. As pointed out by Chang and Li, [10] these non-localized defects may be mobile so that they can cause atomic rearrangement. Also, they can be expected to mutually annihilate in the same way that vacancies and interstitials do.

Some models that can account for a radiation-induced increase to saturation in the electrical resistivity of an alloy are as follows: (i) steady state annealing to sinks of irradiation produced defects with saturation occurring when the rate of defect loss to sinks equals the rate of defect production by irradiation, (ii) irradiation-induced atomic ordering created by mobile defects with saturation occurring when the quasi-equilibrium state of atomic order is reached, (iii) creation of small disordered regions due to the atomic displacements of collision cascades and saturation with full overlap of all the regions.

The experimental study of Andouard, et al [4] on amorphous $Fe_{80}B_{20}$ in combination with the interpretation of their results by Ritcher and Blewitt [11] is useful in distinguishing between models. They found a portion of their irradiation-induced resistivity increase to anneal at well below room temperature. This annealing appeared to be the annihilation of simple defects, perhaps analagous to Frenkel pairs, which were created by the $^{10}B(n, \alpha)$ reaction due to the large flux of thermal neutrons [11]. The results of our experiments do not appear to fit this interpretation. For one thing, we do not have the $^{10}B(n,\alpha)$ reaction because the thermal neutron flux is estimated to be extremely low. More importantly, our result that there is no annealing away of the $\Delta\rho$ or $\Delta L/L$ indicates that these changes are not due to enhanced concentrations of mobile defects. Also, since the defects observed by Andouard, et al annealed out at relatively low temperatures (100°K and 200°K), the defect mobility would be extremely high at the ambient temperatures of our experiment so that the steady state defect concentration would be very low. Based upon these arguments, we tend to eliminate steady state defect concentration models for understanding our results.

It would appear more likely that the property changes which we observe are due to either of the two atomic ordering models, case (ii) or case (iii). The former of these, irradiation-induced atomic ordering, might appear to explain our results; however, recent quenching studies on the $Fe_{40}Ni_{40}P_{14}B_6$ alloy [12] provide findings which tend to disagree with this interpretation. It was found that when the resistance was monitored after samples were cooled over short temperature ranges (~ 20°C), there was a time dependent decrease in the electrical resistivity, $\Delta\rho$ (quench) = - 0.12 μΩ-cm. This decrease was associated with atomic rearrangements leading to a new state of atomic order. Since the temperature decrease can be expected to produce an increase in atomic order, then the resistivity increases observed with irradiation can only be explained by a decrease in the degree of atomic order. This conclusion is in agreement with the interpretation of previously mentioned irradiation experiments [1-3].

The interpretation that the irradiation produces collision cascades which result in an increase in the structural disorder of the alloy appears to fit our experimental results as well as agree with other studies. Using the estimated damage energy cross section for 800 MeV protons given by Parkin and Coulter [7] for our composition, we estimate 0.12 dpa for the saturation dose for $Fe_{80}B_{20}$. Also, at this saturation dose, the average distance between cascades is estimated at 40 atomic distances. By analogy to results in which irradiation caused disordering in crystalline alloys [13], this number of atomic displacements could be expected to be sufficient to create a concentration of disordered regions such that there is overlap between regions and thus saturation in the resistance increase. It is worth mentioning that the saturation value for $\Delta\rho$(irrad) is equivalent to that for a decrease in atomic order corresponding to an increase in temperature of 200°C [12]. This provides an indication of the extent to which these alloys are being disordered by the irradiation.

The length increases which were observed are more difficult to fit to a model for radiation damage than those for resistivity. The different saturation fluences observed for resistivity and length change may be due either to wide differences (factor of two) which have been observed in the behavior of samples of the same alloy [4] or to the different fluxes (factor of three) for the two radiations. Further studies are needed to understand this. The nature of the radiation may be related to the length increases. Calculations of damage due to 800 MeV protons [5] indicate the creation of significant amounts of nuclear transmutation products, particularly hydrogen and helium. The predicted production rates yield 50 ppm hydrogen and 3 ppm helium for the full irradiation in Figs. 1 and 2. Probably these concentrations are not large enough to result in agglomeration and the formation of gas bubbles.

The length increases observed in this study agree qualitatively with those of Chang and Li [10] on the same metallic glass but irradiated with heavy ions. However, it is difficult to make a quantitative comparison because their irradiation resulted in a narrow region of very high damage and very localized length changes. Their interpretation for the length increase was that it was due to the formation either of voids or of small regions of excess volume analagous to a vacancy. This explanation does not, however, provide a mechanism by which the saturation of the length increase occurs, while our explanation does.

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