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ABSTRACT

The effects of fast neutron irradiation on a superconducting metallic glass $(\text{Mo}_{.6}\text{Ru}_{.4})_{82}\text{B}_{18}$ have been studied. Following irradiation to a total fluence of 10^{19} n/cm², T_c increases from 6.05 K to 6.19 K, and the width of the transition decreases sharply. The density of the material decreases by 1.5%, and the x-ray scattering intensity maxima are broadened. An improvement in the ductility of the samples is observed which together with the other observations suggests the production of defects having atomic scale dimensions and characterized by excess volume.

The effect of neutron irradiation on the properties of crystalline superconductors has been the subject of much recent study.^{1,2,3,4} For example, A-15 superconductors typically exhibit a rapid degradation of T_c when exposed to neutron fluences of 10^{18} - 10^{20} n/cm². Metallic glasses are an interesting class of high field superconducting materials which exhibit desirable mechanical properties, high critical fields, and transition temperatures ranging up to 10 K.⁵ It has been suggested in a recent publication that these superconducting materials should exhibit a high tolerance to radiation damage.⁶ In this letter, we report the results of neutron damage experiments on the superconducting metallic glass (Mo_{.6}Ru_{.4})₈₂B₁₈. The effects of irradiation on superconductivity, structure, and mechanical behavior are discussed.

The samples were prepared by melting the appropriate constituents on a silver boat under an argon atmosphere. Amorphous foils measuring approximately 40 microns in thickness and several square centimeters in area were obtained by a piston-and-anvil quenching process which has been fully described elsewhere.⁷ The samples were checked by an x-ray scan using copper K α radiation from a Norelco diffractometer. Samples showing any evidence of microcrystallinity in these scans were discarded.

Several foils were cut into 1 mm wide strips and sent together with whole foils to Lawrence Livermore Laboratory for irradiation with neutrons. The average energy of the neutrons was 1 MeV, with thermal neutrons filtered out by a cadmium absorber. The samples were water-cooled during exposure to prevent heating above ambient temperature. The total fluence of 10^{19} neutrons per square centimeter was accumulated over a period of 66 hours. At least one strip of each foil was kept as an unirradiated control piece. Following a 1 month "cool off" period, the foils were

found to be radioactive; the measured activity was 240 mR at 30 centimeters for the combined samples. The radiation was primarily β and γ radiation with an average half-life of about 30 days. A major source of radiation is believed to be the decay of Ru^{103} to an excited state of Rh^{103} and β^- , with the subsequent emission of γ radiation as the Rh^{103} decays to its ground state.

Critical magnetic field measurements were made resistively using a superconducting magnet system designed by Oxford Instruments. Magnetic field strengths ranged from 0 to 75 kG, and sample temperature could be reduced to approximately 2 K. The transition temperature in zero field was also measured using an ac inductance bridge with a germanium resistance thermometer and a temperature resolution of .01 K. A time lapse step scanning diffractometer, providing improved statistics, was used for the detailed x-ray scans shown in Fig. 1. Densities were determined by hydrostatic weighing with a precision balance, using toluene as the working fluid. Resistivities were measured at room temperature and at liquid nitrogen temperature only. Estimated experimental error in resistivity measurements is on the order of 10%, due to the difficulty of accurately measuring the dimensions of the sample. The temperature coefficient of resistivity was also calculated. A rough measure of ductility was provided by bending foils over the edge of a razor blade. Foils which fractured during this test were classified as brittle, while foils which could be permanently deformed in this manner were classified as ductile. Additional testing of ductile samples was carried out by collapsing the strips between parallel plates of a vice to produce a permanent 180° bend. This corresponds to a 100% deformation if the bending radius is taken to be equal to the foil thickness.

Fig. 1. Observed X-ray diffraction scan of $(\text{Mo}_{.6}\text{Ru}_{.4})_{82}\text{B}_{18}$ foils before and after irradiation with 10^{19} neutrons/cm². Corrections have been made for background counts due to radioactivity of the irradiated specimen and for electronic noise. The zeros of the two scans have been offset slightly for clarity.

The x-ray scans of the foils before and after irradiation are shown in Fig. 1. From these scans, it is evident that amorphous samples remain amorphous after irradiation with neutrons; the intensity maxima occur at the same wavevector, k_0 , before and after irradiation. The full width at half maximum intensity, Δk , for the first diffraction maximum of the irradiated foil increased by 7% from its previous value. The results are summarized in Table 1. Each entry represents an average over several samples. The superconducting transition temperature has increased by about 2% on irradiation, from 6.05 K to 6.19 K. The width in K of the superconducting transition has decreased by a factor of 3, from .20 K to .06 K. Previous work has shown that the upper critical magnetic field of amorphous superconductors is linear in T over an extended range and therefore can be characterized by a single parameter, the critical field gradient, $\frac{dH_c(T)}{dT}$.⁵ This parameter is not noticeably affected by the irradiation, as shown in Table 1. The density decreased from 10.37 gm/cm³ to 10.22 gm/cm³ or by 1.5%. The unirradiated foils were all found to be brittle using the criteria mentioned above. Most of the irradiated foils sustained a 100% permanent deformation without fracture so a significant improvement in ductility is observed after irradiation. The measured absolute resistivity at room temperature does not change to within the accuracy of $\pm 10\%$. However, since the error in the measurement is 10%, any conclusions about the effect of irradiation on resistivity must be regarded as tentative. The temperature coefficient of resistivity has also remained unchanged to within experimental error following irradiation.

In the energy range of interest, the cross sections for neutron absorption for molybdenum, ruthenium, and boron are all relatively constant and in the range of $4-10 \times 10^{-24}$ cm².⁸ The incident neutron flux is

TABLE 1. Results.

	(Mo. ^{.6} Ru. ^{.4}) ₈₂ B ₁₈ Before Irradiation	(Mo. ^{.6} Ru. ^{.4}) ₈₂ B ₁₈ After Irradiation with 10 ¹⁹ neutrons/cm ³	Percent Change
<u>X-ray Data</u>			
Δk -width of main peak at 1/2 maximum intensity	.45 Å ⁻¹	.48 Å ⁻¹	~ 7% increase
k ₀ -maximum peak position	2.83 Å ⁻¹	2.83 Å ⁻¹	0
<u>Superconducting Transition</u>			
T _c	6.05 K ± .02 K	6.19 K ± .02 K	~ 2% increase
width of transition in 0 field from 25% to 75% points	.20 K ± .02 K	.06 K ± .02 K	~ 70% increase
$\left. \frac{dH_c(T)}{dT} \right _{T=T_c}$	-23.6 K0e/K ± 1.2 K0e/K	-24.4 K0e/K ± 1.2 K0e/K	not significant
<u>Density</u>	10.37 gm/cm ³ ± .05 gm/cm ³	10.22 gm/cm ³ ± .05 gm/cm ³	~ 1.5% decrease
<u>Ductility</u>	brittle - (see text)	ductile - (see text)	significant
<u>Resistivity</u>			
ρ(300 K)	131 ± 13 μΩ	136 ± 14 μΩcm	not significant
ρ(77.4 K)	139 ± 14 μΩ	140 ± 14 μΩcm	not significant
$\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)$	.0003/K ± .0001 K	.0002/K ± .0001/K	not significant

10^{19} neutrons/cm², so that the probability that any individual atom is involved in a nuclear collision is 10^{-4} . The small neutron cross sections ensure that only a small fraction of the incident neutrons undergo a collision ($\sim 10^{-3}$) and thus the damage produced should be uniform throughout the sample. Neutrons can interact with atoms either elastically or inelastically. That the irradiated foils were radioactive is direct evidence for the occurrence of inelastic events. For incident neutrons having energies ranging from 1 to 10 MeV, the resultant ionic kinetic energy will be on the order of 10-100 keV. This kinetic energy must be dissipated in the amorphous matrix following the nuclear collision. The typical displacement energy for a transition metal ion is about 30-50 eV.⁹ Thus, the energy released to the material by a nuclear event corresponds to roughly 10^3 displacements. Since we have 10^{-4} events per atom, this equates to roughly 0.1 displacements per atom. A second important quantity relating to the amount and type of damage produced by irradiation is the total dimension of the cascade produced by a single primary nuclear collision. A rough idea of this dimension is given by the projected range of the ion produced by the primary event. For example, a 10 keV Mo ion has a projected range of ~ 40 Å with a standard deviation of ~ 20 Å in a matrix of crystalline Mo.¹⁰ Defect clusters produced by fast reactor neutrons in crystalline Mo have typical dimensions of 25-30 Å.¹¹ A similar cascade dimension is expected for the present case. We should therefore expect damage produced by a primary event to be localized roughly to within this distance of the atomic site where the primary event occurs. Such cascade dimensions will involve 10^3 - 10^4 atoms so that each atom of the amorphous solid is on the average involved in roughly 1 cascade. The damage should be rather uniformly distributed throughout the material. This conclusion

is further substantiated by the observation that a fluence of $5 \times 10^{18} \text{ n/cm}^2$ produces saturation of defect clusters in crystalline Mo.¹¹

If the cascade event is modeled as a "thermal spike", then an average energy of several eV per atom is deposited within the cascade region on a time scale comparable to the thermal relaxation time of the cascade region to the surrounding medium. This can easily be shown by comparing the velocity of sound in the material to typical ionic velocities for ions which undergo displacement collisions. The "effective quench rate" of the cascade region can be estimated to be of order $\sim 10^{14}$ or 10^{15} K/sec. It is important to observe that this "effective quench rate" is far larger than the 10^6 K/sec rate which was used to produce the initial amorphous solid by liquid quenching.⁷ It is not surprising therefore that crystalline phase nucleation does not occur as a result of irradiation.

Information about the nature of the defects produced during irradiation can be obtained from the observed changes in properties. The broadening of the first diffraction maximum in the x-ray intensity (7%) indicates that atomic rearrangement has occurred during irradiation on the localized scale of atomic distances. This in turn suggests that defects having atomic scale dimensions are produced. The decrease in density (1.5%) of the amorphous alloy following irradiation suggests that these defects are characterized by excess volume. Vacancy production in crystalline materials following irradiation and resulting swelling have been extensively studied by numerous investigators.^{11,12,13} In an amorphous solid, the concept of a vacancy is not well defined. Instead, excess volume is likely to be distributed in a variety of local atomic configurations.

The dramatic decrease in width of the superconducting transition (70%) gives additional information on the nature of the damage. Broadening of the superconducting transition results from inhomogeneity in the specimen on a scale comparable to or larger than the superconducting temperature dependent coherence length $\xi(T)$. For the present alloy, the coherence length at $T = 0$, $\xi(0)$ can be estimated from the critical field data¹⁴ to be $\sim 45 \text{ \AA}$. If we use the term "local T_c " to refer to the average T_c of a local region with characteristic dimension d , then we can define a standard deviation of T_c , Δ_d , which measures the dispersion of T_c over an ensemble of these regions. Broadening of the sample transition by an amount Δ_d will occur only if

$$d \gtrsim \xi(T_c \pm \Delta_d) = \xi(0) \left(\frac{\Delta_d}{T_c} \right)^{-1/2} \quad (1)$$

If this condition is not obeyed, the broadening will be less than Δ_d or eliminated entirely if $d \ll \xi(T \pm \Delta_d)$. The dramatic decrease in broadening following irradiation suggests two things. First, the amorphous material is more uniform on a scale of ξ following irradiation. Consequently, any defects produced must be uniformly distributed throughout the sample within sampling volumes of dimension ξ . Second, the defects must necessarily have dimensions considerably smaller than ξ . This again suggest defects with atomic dimensions.

Finally, the improved ductility of the samples following irradiation is likely related to the production of rather localized defects characterized by excess volume. Spaepen¹⁵ has related flow in metallic glasses to the existence of "vacancy-like" defects. Johnson and Williams¹⁴ have noted that ductility of $(\text{Mo}_{.6}\text{Ru}_{.4})_{1-x}\text{B}_x$ alloys correlates well with excess

structural volume. Annealing of the present samples at 475 C produces a dramatic embrittlement effect although no evidence of crystallization is observed. These observations together suggest that defects characterized by excess volume control the ductility of this metallic glass, and that such defects are produced by neutron irradiation. Direct observation of these defects may be possible by high resolution transmission electron microscopy or by ion microprobe techniques.¹³ Such defects should also contribute to small angle x-ray scattering, SAS. Measurements of the SAS intensity are presently in progress and will be discussed in a future publication.

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