Dramatic Growth of Glassy $Pd_{80}Si_{20}$ during Heavy-Ion Irradiation

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Under heavy-ion irradiation of the metallic glass $Pd_{80}Si_{20}$ the sample dimensions perpendicular to the ion beam axis grow dramatically without appreciable change in volume (no swelling) or microscopic structure. The characteristics of this growth in amorphous $Pd_{80}Si_{20}$ are examined in some detail and compared with radiation growth in crystals. None of the available growth mechanisms proposed for crystalline metals is able to explain this new kind of radiation growth.

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Metallic glasses are presently under intensive investigation from many points of view, and there is already a growing number of alloys in technical applications. In particular, since the work of Kramer and Johnson[1] metallic glasses are regarded as suitable materials in radiation fields.[2,3] This opinion is based on the assumption, partly verified by experiments, that the radiation-induced disorder is easily absorbed in the heavily disordered structure of an amorphous metal. The purpose of this Letter is to demonstrate that one of the most spectacular manifestations of radiation damage occurs in glassy $Pd_{80}Si_{20}$. A new kind of radiation-induced growth, unknown in crystalline metals, appears; that is, the irradiated glass undergoes macroscopic changes in sample dimensions at constant volume and without appreciable modifications in its microscopic structure.

The irradiations were mainly performed with 285-MeV Kr ions at the VICKSI accelerator in Berlin. The range of the projectiles was about twice the thickness of the samples and thus implantation was avoided. Nevertheless, the projectile energy was below the Coulomb barrier for nuclear reactions and element transmutations were negligible. Damage inhomogeneity within the samples never exceeded 30%.

The samples were cut from a melt-spun ribbon of $Pd_{80}Si_{20}$ (1 mm wide, 30 μm thick) supplied by Vacuumschmelze Hanau. They were cold rolled to a thickness of about 9 μm. One specimen set was annealed at 520 K in high vacuum ($<10^{-6}$ mbar) for 1 h. Another set got no heat treatment. It should be noted that these pretreatments result in a more disordered state for the cold-rolled samples and in a topologically more ordered state for the other specimens in comparison with the as-quenched ribbon.[4] The sample strips were fixed to the irradiation cryostat by clamping them between two copper blocks so that definite parts (mostly 1 mm) stand out. To insure good thermal contact indium foils were laid between the specimens and the copper blocks. During irradiation the latter were held below 15 K and the temperature of the outstanding samples was adjusted by an appropriately chosen particle flux. Hence the temperatures T of the outermost ends of the samples could be varied between 50 and 500 K. Unfortunately these temperatures could not be measured directly because any fastening of a temperature sensor would considerably disturb the measurability of growth. Therefore T was calculated in a similar way as in Ref. 5 where good agreement was found between calculation and experiment. Before and after the irradiations the lengths (in the direction of the temperature gradient) and widths (perpendicular to the temperature gradient at the free end) of the samples were measured at room temperature with use of an optical microscope and a slide with a 25-μm scale for exact calibration.

The increase of the width Δb relative to the width b_0 of the unirradiated specimen versus ion fluence φt is shown in Fig. 1 for different irradiation temperatures T. In these experiments the surface normal vector $\vec{S}$ of the sample strips was orientated parallel to the beam axis $\vec{e}_x$. Each measuring point is a mean value of four to ten samples. The error bars indicate the scatter of the individual samples which we suppose is mainly due to some scatter in T as well as to measuring errors from the corrugated foils. The corrugations were caused by constraints of the copper blocks on the growing specimens. No significant differences were found between samples of different pretreatments. Within the experimental errors $\Delta b/b_0$ can be fitted by

$$\Delta b/b_0 = \gamma(T)(n - n_i), \quad (1)$$

where $\gamma(T)$ denotes the growth rate and $n = P\varphi t$ is the mean number of displacements per atom (dpa), with P the total displacement cross sec-

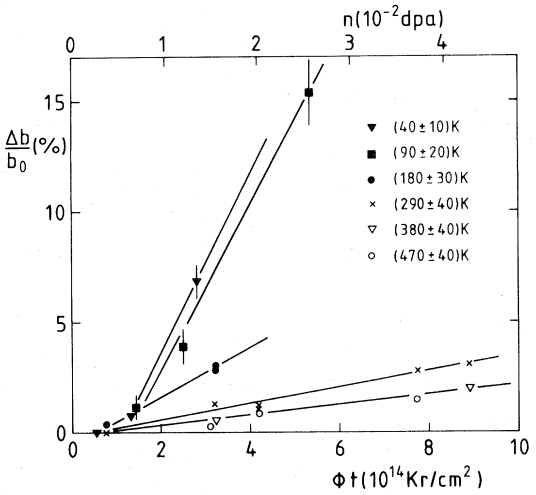

FIG. 1. Radiation-induced increase in widths Δb of $Pd_{80}Si_{20}$ samples relative to the widths b_0 before irradiation at different irradiation temperatures as a function of Kr-ion fluence φt (lower scale) and of number n of displacements per atom (dpa) (upper scale). The surface normals of the samples have been orientated parallel to the beam axis. The error bars denote the scatter of individual samples (see text). The data are well described by Eq. (1).

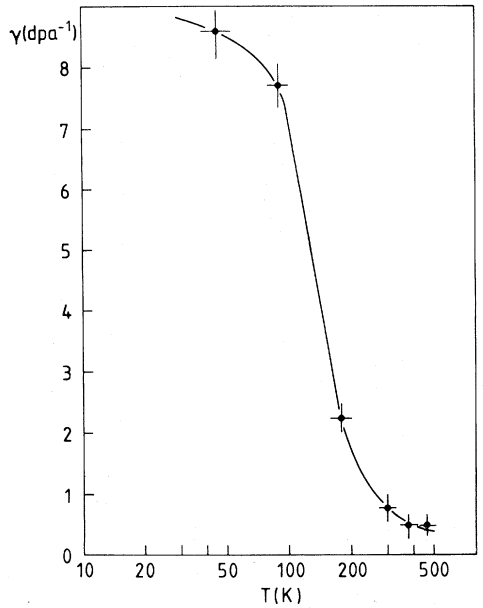

FIG. 2. Growth rate γ of glassy $Pd_{80}Si_{20}$ [see Eq. (1)] vs irradiation temperature T during bombardment with 285-MeV Kr ions.

tion. There exists an incubation dose n_i above which growth becomes appreciable. For $T_i < 100$ K, with $P = 4.8\times10^{-17}$ cm^2, and using the displacement threshold energy of Ref. 5, we obtain $n_i \approx 6\times10^{-3}$ dpa which demonstrates the significance of statistical damage agglomeration processes as is known from damage rate curves after light-ion bombardment.[5]

The growth rate $\gamma(T)$ versus irradiation temperature T is shown in Fig. 2. By irradiation of samples with different lengths at constant particle flux it was shown that $\gamma(T)$ is indeed controlled by the irradiation temperature alone and not by the damage rate. Below 100 K $\gamma(T)$ depends only weakly on T; that is, in spite of the large temperature gradients from 15 K to T length measurements are easy to interpret. For $T < 100$ K we obtain $\Delta l/l_0 = \Delta b/b_0$ within the experimental errors in the whole fluence range studied. A modified flotation technique, specifically developed to allow accurate density measurements at room temperature for very small samples, yields an unaltered mass density within the experimental resolution of 0.2%. Hence we can exclude swelling. The observed growth must be highly anisotropic and volume conserving since sputtering effects are negligible.

There are, in principle, two possible origins of anisotropy: (i) any anisotropy within the samples, e.g., orientated internal stresses or crystal nuclei with a preferential orientation; (ii) an anisotropy induced by the directed ion beam. To decide between the two possibilities a set of eight samples was irradiated where $\vec{S}$ and $\vec{e}_x$ include an angle of 45°. If the anisotropy is due to (i), one would expect growth to be independent of the orientation, that is $(\Delta b/b_0)_{45°} = (\Delta b/b_0)_0$, where the subscript denotes the angle between $\vec{S}$ and $\vec{e}_x$. If the anisotropy stems from the directed beam, the thickness axis and the width axis of the samples would be physically equivalent, that is $(\Delta b/b_0)_{45°} = (\Delta d/d_0)_{45°}$, where $(\Delta d/d_0)_{45°}$ denotes the relative changes in sample thickness. In the length direction the irradiation geometry is not changed and hence $(\Delta l/l_0)_{45°} = (\Delta l/l_0)_0 = (\Delta b/b_0)_0$. Provided the sample volume remains constant, it follows that $(\Delta b/b_0)_{45°} = -\frac{1}{2}(\Delta b/b_0)_0$ in linear approximation. The experiment clearly decides in favor of case (ii) which means that the sample dimensions perpendicular to the beam axis always grow whereas the sample dimension parallel to the beam axis shrinks.

In a further irradiation run we used 170-MeV Ar ions to check the projectile dependence of the growth. In the whole temperature range from 50 to 500 K the growth rates between the two projectiles differ by at least one order of magnitude. A single Kr ion produces many more displace-

ment cascades than an Ar ion.[5] Hence, the growth in $Pd_{80}Si_{20}$ depends not only on the number of displaced atoms but also sensitively on the local density of damage production.

Nevertheless, the stable modifications of the microscopic structure of the glassy alloy are definitely small compared with the magnitude of growth. This is concluded from the following facts: (i) No embrittlement of the samples is observed; (ii) the changes in electrical resistivity are less than 3% as can be deduced from resistance measurements[5] now taking into account the change in sample geometry; (iii) the temperature coefficient of the electrical resistivity does not change within the experimental error[5]; (iv) the density change is less than 0.2%; (v) the growth seems to continue indefinitely without saturation (see Fig. 1), which implies that even at high growth levels the amorphous structure is invariably susceptible for further growth. Unfortunately, precise x-ray structure factors of the irradiated and therefore corrugated specimens are hard to obtain because they require complex absorption corrections.[6]

In crystalline metals radiation growth is a consequence of natural crystallographic anisotropy and it is believed that the fundamental growth mechanism is the preferred condensation of point defects on certain crystallographic planes.[7] No radiation growth occurs in cubic metals,[8] which represent the best approximation to isotropic materials in the crystalline state. We have performed check irradiations on pure polycrystalline copper foils which confirmed this result for our irradiation conditions. The damage production by 285-MeV Kr ions is comparable to that by light fission fragments, and indeed growth in anisotropic crystalline metals induced by fission fragments is very similar to growth in the metallic glass $Pd_{80}Si_{20}$ after irradiation with Kr ions (see Table I). The differences in the dependence on the pretreatments should not be taken too seriously because cold rolling induces more disorder in a crystalline than in an amorphous metal.

On the other hand, there are two essential differences between growth in crystals and glasses: (i) the origin of the anisotropy and (ii) the magnitude of the growth rate γ at low temperatures. As metallic glasses are more isotropic than cubic metals and the growth anisotropy is induced by the directed ion beam, none of the growth mechanisms proposed for crystalline metals[7] is able to explain the observed growth in amorphous $Pd_{80}Si_{20}$. Furthermore, in crystalline metals the growth rates are always less than 1 dpa^{-1}. In glassy $Pd_{80}Si_{20}$ we find a growth rate of about 8.6 dpa^{-1} at 40 K (see Fig. 2) and one has to realize that, obviously, on the average, 8.6 atoms per displaced atom contribute to growth. Although the exact value of 8.6 dpa^{-1} can be called in question because of the uncertainty of the displacement threshold energy of $T_d = 40$ eV, it is improbable that T_d is below the value 5 eV which would yield $\gamma < 1$ dpa^{-1} for $Pd_{80}Si_{20}$.[5] Thus growth in $Pd_{80}Si_{20}$ seems to be explainable only in terms of a collective motion of atoms.

In crystals the relaxation of the extreme nonequilibrium state in the displacement cascade to topologically well-defined defect configurations is governed by the crystal structure and its strong symmetry which destroy any anisotropy of the damage production. In amorphous metals, lacking any long-range order, comparable anisot-

TABLE I. Comparison of radiation growth in crystalline and glassy metals.

	Crystal[a]	Glass ($Pd_{80}Si_{20}$)
Thermal recovery	No	No[b]
Saturability	No	No (see Fig. 1)
Change in mass density	No	< 0.2%
Modification in the microscopic structure	Small, alignment of dislocation loops	Not significant
Temperature dependence	Strong	Strong (see Fig. 2)
Projectile dependence	Yes	Yes
Influence of cold rolling	Yes	Not significant

[a]The characteristics were taken from Refs. 8 and 9 and refer mainly to growth induced by fission fragments.

[b]This is checked only qualitatively in the warmup period of the cryostat.

ropies may appreciably affect the damage evolution. In our experiments the anisotropy in damage production arises from the primary recoil atoms because nearly all of them start perpendicularly to the beam axis. This is a direct consequence of the screened Coulomb interaction between projectiles and target atoms. However, little is known about the nature of defects in amorphous alloys and it is currently not possible to understand this growth behavior from a microscopic point of view. Perhaps, the heavily damaged metallic glass remembers its origin from the liquid state and responds to large structural distortions with some kind of internal flow.

Since the observed growth in $Pd_{80}Si_{20}$ under anisotropic damage production seems to be inherent to its amorphous structure one may expect that all metallic glasses[6] show this kind of instability against radiation damage. Hence their applicability in radiative fields would be much more limited than presently assumed. Furthermore, this work demonstrates that relaxation processes, which are governed in crystals by crystallographic symmetry, develop in amorphous metals in a substantially different manner.

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