Coulomb Explosions in a Metallic Glass Due to the Passage of Fast Heavy Ions?

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(Received 5 May 1986)

Bombardment of glassy $Pd_{80}Si_{20}$ below 50 K with ^{129}Xe ions of 1.34 MeV/u leads to macroscopically visible anisotropic mass transport. It is shown that this mass transport is dominated by the energy which the projectiles transfer to the electrons of the metallic glass. Such a behavior is entirely unknown for crystalline metals. As an explanation we suggest that Coulomb explosions in the wake of the projectiles lead to a mechanical polarization of the metallic glass which then undergoes plastic flow.

PACS numbers: 61.80.Jh, 61.40.+b, 62.20.Fe, 81.40.Lm

As a swift ion (kinetic energy $\simeq 1$ MeV/u) penetrates a solid it is decelerated essentially via (i) direct transfer of recoil energy to target atoms through elastic collisions and (ii) electronic excitation and ionization of target atoms (inelastic collisions). The latter process is commonly denoted as electronic energy loss S_e. It is the generally accepted view, which has entered into numerous textbooks[1] and is tacitly assumed in the evaluation of radiation damage experiments on crystalline metals, that in bulk solids with metallic conductivity atomic rearrangements (e.g., displacements, site changes) are primarily induced by elastic collisions and not by electronic excitation or ionization.

In an earlier Letter[2] the occurrence of a new kind of radiation growth was reported. This is a phenomenon where the atomic rearrangements lead to macroscopically visible mass transport. Samples of the metallic glass $Pb_{80}Si_{20}$ held at about 40 K were bombarded with a beam of ^{86}Kr ions with a target entrance energy $E_0 = 3.3$ MeV/u. Above an incubation fluence the sample dimensions perpendicular to the ion beam grew dramatically. No measurable volume changes occurred, i.e., the sample dimension parallel to the ion beam shrank. Furthermore, the samples tended to bend. The bending points to an occurrence of stresses in the samples and it is obvious that ion-beam induced growth is some kind of plastic deformation of the glassy material. From a macroscopic point of view the sample deformation has the features of homogeneous flow under a radial stress perpendicular to the beam. Up to now, 34 metallic glasses of various compositions have been investigated and in all cases large dimensional changes were found.[3,4] Therefore, ion-beam-induced growth seems to occur virtually in every metallic glass. This suggests an underlying mechanism of a very general kind.

Two features of this growth differ markedly from radiation growth in crystalline metals. First, the anisotropy is induced by the direction of the ion beam, and second, ten or a hundred atoms per displaced atom contribute to permanent growth if only elastic collisions between projectile ion and target atoms are taken into account.[2,3] Such unphysically high figures demonstrate an obvious shortcoming of standard radiation damage theory with respect to the phenomenon discussed here. It is the aim of this Letter to demonstrate that this shortcoming has its origin in the neglect of atomic rearrangements induced in metallic glasses by inelastic collisions.

The influence of elastic and inelastic collisions on ion-beam-induced growth in a glass can be separated only by their different dependence on ion energy E. In the present experiment, we used a ^{129}Xe beam with $E_0 = 1.34$ MeV/u and as target material small pieces of glassy $Pd_{80}Si_{20}$ of various thicknesses. For these ions $S_e(x)$ and the total displacement cross section $P(x)$ as a function of the target depth x were calculated by means of the computer code[5] TRIM 86 with use of a mass density of 10.3 g/cm^3 and a displacement threshold of 40 eV for $Pd_{80}Si_{20}$. $S_e(x)$ decreases and, for the most part of x, $P(x)$ increases with increasing x. In order to improve the damage homogeneity and to compensate the bending of the samples they were irradiated alternately in small fluence steps of $\simeq 10^{12}$ Xe/cm^2 from two sides. Therefore, the thickness-averaged quantity $\langle S_e \rangle$ *decreases,* whereas $\langle P \rangle$ *increases* with *increasing* target thickness d. We used samples with $d = 2.0$, 4.5, 7.0, and 8.1 μm. The various thicknesses were obtained by rolling of a melt-spun ribbon (1 mm wide, 30 μm thick, supplied by Vacuumschmelze GmbH) and were measured with a mechanical thickness monitor with an accuracy of about ± 0.5 μm. Sample mounting and measurement of the dimensional changes have been described earlier.[2] During irradiation the ^{129}Xe-particle flux was kept below 2×10^9 Xe/cm^2 s so that the irradiation temperature never exceeded 50 K and thermal gradients within the samples remained below 40 K. In all experiments the surface normal vector was oriented parallel to the beam. ^{129}Xe ions of $E_0 = 1.34$ MeV/u have a mean projected range of 7.1 μm and a range straggling of about 0.3 μm in $Pd_{80}Si_{20}$.[5] Therefore, ^{129}Xe implantation occurs for the 7.0- and 8.1-μm-thick samples. However, the ^{129}Xe concentration in

the two implantation layers in each sample is smaller than 3 ppm at the highest fluence of 1.6×10^{13} Xe/cm^2. It cannot be expected that such a low concentration affects the bulk growth appreciably.

The increase Δb of the width relative to the width b_0 of the unirradiated sample versus ϕt is shown in Fig. 1. Generally, the dimensional change of a sample is described by the equation of continuity, $\dot{\rho}+\rho\,\mathrm{div}\mathbf{v}=0$, where ρ is the mass density and $\mathbf{v}$ is the velocity of any sample point. Since ion-beam–induced growth does not saturate,[2] it follows that the glassy structure must attain a steady state. For homogeneous irradiation conditions and small changes Δb the solution of this equation is

$$\Delta b/b_0 = A(\phi t - B) \text{ for } \phi t \geq B, \quad (1)$$

where A denotes the steady-state growth rate and B the incubation fluence at which the structure approximates the steady state. Equation (1) was fitted to our data. B is about 4.6×10^{12} Xe/cm^2 and almost independent of d within the error limits. The growth rate A, however, markedly depends on sample thickness. This behavior cannot be attributed to different original structures which might have been produced unintentionally during rolling to different thicknesses because annealed (250 °C, 1 h in high vacuum) samples showed the same thickness dependence. Clearly, the growth rate A is directly linked to $\langle S_e\rangle$.

A close inspection of the data reveals, however, that the growth rate must also be related to $\langle P\rangle$. In Fig. 2 we have tentatively plotted $\ln(A/\langle P\rangle)$ vs $\langle S_e\rangle$ for all available growth data of $Pd_{80}Si_{20}$ irradiated below 50 K with a directed beam of heavy ions[2,3,6,7] or fission fragments.[8] The data nicely follow a straight line. Hence, we find the empirical relation

$$A = \alpha\langle P\rangle \exp(\beta\langle S_e\rangle), \quad (2)$$

with $\alpha=0.077\pm0.01$ and $\beta=1.84\pm0.06$ Å/keV. α and β are material properties and may also depend on irradiation temperature, since A decreases rapidly above 100 K.[2,3] A detailed evaluation of $A(T)$ demonstrates that within the error bars the whole temperature dependence is included in $\alpha=\alpha(T)$ and β is temperature independent. It is clearly seen from Eq. (2) that $\langle S_e\rangle$ dominates the growth rate. Such a behavior is entirely unknown for crystalline metals. It should be noted that in an earlier publication Lesueur[8] stated an influence of S_e on his resistance data but ascribed this effect erroneously to surface sputtering.

The mechanism by which elastic collisions lead to

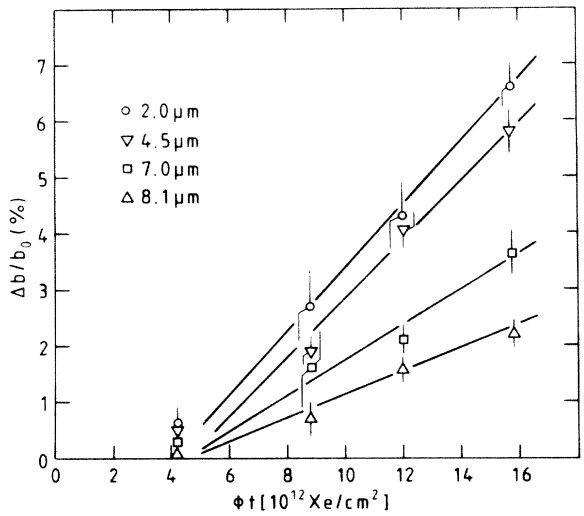

FIG. 1. Radiation-induced increase Δb in width relative to the width b_0 before irradiation of $Pd_{80}Si_{20}$ samples of various thicknesses as a function of Xe-ion fluence ϕt. During irradiation the samples were kept below 50 K. The solid lines are fits according to Eq. (1).

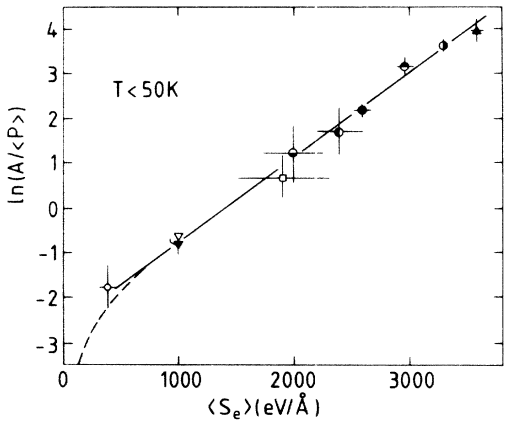

FIG. 2. Plot of the logarithm of the growth rate A normalized to the total displacement cross section $\langle P\rangle$ vs electronic energy loss $\langle S_e\rangle$ for $Pd_{80}Si_{20}$ irradiated below 50 K. Triangle, ^{129}Xe $E_0=2.8$ MeV/u, $d=6$ to 9 μm (Ref. 3); filled circle, ^{86}Kr $E_0=3.31$ MeV/u, $d=9$ μm (Ref. 2); square, fission fragments, ^{139}Xe $E_0=0.48$ MeV/u and ^{95}Sr $E_0=1.0$ MeV/u, $d=3$ μm (Ref. 8); filled inverted triangle, ^{40}Ar $E_0=4.25$ MeV/u, $d=9$ μm (Ref. 6); open inverted triangle, ^{40}Ar $E_0=4.38$ MeV/u, $d=6$ to 13 μm (Ref. 7); open circle, ^{16}O $E_0=1.56$ MeV/u, $d=4.5$ to 6 μm (Ref. 7); left-, top-, right-, and bottom-half-filled circles, this work, $d=2.0$, 4.5, 7.0, and 8.1 μm, respectively. Filled symbols refer to data derived directly from width measurements and open symbols refer to data derived from electrical resistance measurements at high fluences via the relation $A=b_0^{-1}\times d(\Delta b)/d(\phi t)=(2R_0)^{-1}d(\Delta R)/d(\phi t)$. This relation follows from the change in geometrical factor of a sample under irradiation at constant volume. The error bars include the experimental errors in the determination of A as well as the rms deviations from $\langle P\rangle$ and $\langle S_e\rangle$, respectively. Large error bars therefore indicate inhomogeneous irradiation conditions. The solid line is a fit according to Eq. (2). The dashed line corresponds to a hyperbolic sine instead of an exponential function.

atomic rearrangements is quite clear.[1] With respect to electronic excitation and ionization, however, the situation is more complicated since the excitation energy is initially in the electronic system and is located around the projectile trajectory. This excitation energy is rapidly shared with other electrons by electron-electron interaction. Hence, in a metal with a large electronic mean free path l, the free electrons carry away the excitation energy so efficiently that the sample warms up almost as a whole without considerable atomic motion.[9] One might argue that in a metallic glass l is 1 or 2 orders of magnitude smaller than in a good electrical conductor at room temperature and a sufficiently high transient temperature could be reached locally. For a glass the interesting temperatures lie between the glass temperature and the melting temperature, because in this interval the atomic jump rates become so large that appreciable atomic rearrangements may occur even in the short time of a thermal spike. However, the growth rates of 34 metallic glasses of various compositions correlate neither with l (i.e., the electrical resistivity ρ) nor with glass temperature, nor with crystallization temperature, nor with melting temperature.[4] Further doubt on the adequacy of an electronically induced thermal spike arises from the occurrence of P in Eq. (2). This is because the screened Coulomb interaction of the projectiles with the target atoms favor low-energy transfers, i.e., most of the displaced target atoms come to rest in the vicinity of the projectile trajectory. Therefore, if we should assume that a local temperature rise initiates the atomic rearrangements which ultimately cause the growth we would simultaneously have to allow for a strong annealing of defects created by the displaced atoms. Therefore, the occurrence of P in Eq. (2) is not easy to understand in this model.

Therefore, we bring forward another mechanism which can convert part of S_e into atomic motion.[10] In the wake of a fast ion, neighboring positive target ions are produced which are mutually repulsive. For ^{129}Xe ions of 1.34 MeV/u we estimate that all Pd atoms and Si atoms in the immediate surroundings of the projectile are, on the average, ionized to charge states 5^+ and 4^+, respectively. The basis for this estimate is a purely classical consideration of the ionization cross sections taking into account the various ionization energies of the target atoms and a Coulomb interaction between the screened projectile and the target electrons. The time of a ^{129}Xe ion to cover a distance of one atomic diameter $a_0 \simeq 2.8$ Å is about 2×10^{-17} s. This time is short in comparison to the response time of the conduction electrons. Hence, in the wake of the projectile a long cylinder of radius a_0 contains Pd^{5+} and Si^{4+} ions. This cylinder explodes radially under the Coulomb forces until the ions are screened by the conduction electrons. In order to give an idea of the Coulomb explosion time T_C which we take as sufficient to induce atomic rearrangements we apply the following criterion. Local shear transformations can be initiated as soon as a row of atoms moves collectively with an energy of about $\epsilon = \mu\Omega/20$ per atom. Here, $\mu/20$ is the theoretical shear strength of a solid and Ω is the atomic volume. For $Pd_{80}Si_{20}$ the shear modulus μ is about[11] 35 GPa and $\Omega = 1.1\times10^{-29}$ m^3, which yields $\epsilon = 0.13$ eV. By integration of the equation of motion, it can easily be shown that three Pd^{5+} ions, being initially in contact, are accelerated to ϵ within 7×10^{-16} s. During this time the Pd^{5+} ions cover a distance so small that the influence of the surrounding atoms can be well neglected. This time may be identified with t_C and is considerably lower than the value of 10^{-13} s assumed in Ref. 10. In that work atomic rearrangements are assumed to occur if the Coulombic stress surmounts the theoretical shear strength at least for an atomic vibration time. The latter criterion, however, does not take into account the energy which the ions gain in the charged cylinder.

After screening, the matter surrounding the projectile trajectory is mechanically polarized as a result of the movement of the ions and relaxes "gradually." In a glass there are small regions containing a relatively large amount of free volume in comparison with the average. In these regions (shear sites) some atoms will easily find new positions under the transient shear stress τ. Since each shear event reflects the anisotropy of the ion beam, the macroscopic anisotropy of the flow (= ion-beam–induced growth) is obvious. Consequently, the growth rate A should be directly linked to an effective shear strain rate $\dot{\gamma}$. If we speculate that $\dot{\gamma}$ is related to a transient shear stress in the same manner as to a static shear stress we have[12]

$$\dot{\gamma} \propto n \sinh(\tau V/k_B T). \tag{3}$$

n is the concentration of shear sites with an effective volume V, k_B is the Boltzmann constant, and T is the temperature. Steady-state growth requires n to be constant. Therefore, at low temperatures, the steady-state value of n is determined by three processes: (i) athermal creation of free volume by the projectiles; this process may be regarded as similar to the creation of vacancies in crystalline metals, i.e., $n \propto \langle P \rangle$ [7]; (ii) thermally activated annealing of irradiation-induced free volume, i.e., $n = n(T)$ [7]; and (iii) annihilation of free volume at a free sample surface as a result of shear transformations. The existence of an incubation fluence points to the creation of a necessary amount of free volume before appreciable growth can appear. Provided that the effective transient stress τ appearing from the Coulomb explosion is proportional to S_e, Eq. (2) is an immediate consequence of Eq. (3) for high stresses. The temperature appears in the denominator

of the hyperbolic sine function of Eq. (3) but does not appear in β in Eq. (2). This is plausible because the transient of the stress is probably so short that thermally activated shear processes are negligible. Therefore, the temperature dependence of $A(T)$ is essentially attributed to the temperature dependence of $n(T)$.

Finally, we should add that a computer simulation of the relaxation of a model glass which is mechanically polarized in a way as it would result from a Coulomb explosion reproduces many details of ion-beam–induced growth.[13]

The duration of the Coulomb explosion as well as the resultant mechanical polarization in a crystalline metal should be of the same order of magnitude as in a metallic glass. The fundamental difference for the occurrence of ion-beam–induced growth lies in the subsequent relaxation process. In a crystalline structure there is a unique atomic configuration with lowest internal energy. The relaxation is therefore dominated by the crystal structure itself and no radiation growth like that in glassy metals is expected. This statement is in accordance with computer simulation[13] and experiments.[4] The absence of ion-beam–induced growth in cubic metals and alloys, however, may not imply the absence of more subtle effects such as, e.g., the annihilation of vacancies and interstitials by the electronic energy loss. It would be interesting to search for such phenomena.

We thank J. P. Biersack and D. Fink for their calculations with the TRIM code and the VICKSI staff for support during the irradiation experiments.

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