Mechanisms of Radiation-Induced Viscous Flow: Role of Point Defects

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Mechanisms of radiation-induced flow in amorphous solids have been investigated using molecular dynamics computer simulations. It is shown for a model glass system, CuTi, that the radiation-induced flow is independent of recoil energy between 100 eV and 10 keV when compared on the basis of defect production and that there is a threshold energy for flow of ≈ 10 eV. Injection of interstitial- and vacancylike defects induces the same amount of flow as the recoil events, indicating that point-defect-like entities mediate the flow process, even at 10 K. Comparisons of these results with experiments and thermal spike models are made.

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Experimental investigations of stress relaxation and surface smoothing have illustrated that many amorphous solids undergo Newtonian flow during ion irradiations at temperatures far below their respective glass temperatures. This phenomenon, which occurs in materials with covalent [1], ionic [2–5], and metallic [6–8] bonding, provides new opportunities for processing materials at the nanometer length scale [9] as well as having significance for radiation waste storage through glass encapsulation. While radiation-induced viscous flow has been widely explored experimentally, a comprehensive theoretical understanding of this behavior has been more difficult to achieve. For heavy ions in the regime when electronic excitation dominates the stopping, thermal spike models provide a satisfactory description of the flow process since the energy dissipation is uniform and typically greater than ≈ 1 keV/nm. For lower energy ions, thermal spike models have also been invoked [5,10], but in this energy regime, the energy loss is much smaller and the energy distribution tends to be rather inhomogeneous along the path of the ion. Thermal spike models are therefore less attractive in this situation, since the flow occurs within a few picoseconds or less of the recoil event and large gradients in energies, densities, and stresses are present. Over the past decade, it has been recognized that molecular dynamics (MD) computer simulations provide a realistic alternative approach to treat such many-body problems, and we apply this method here to explore the mechanisms of radiation-induced viscous flow. Our results show that radiation-induced flow does not, in fact, require thermal spikes and that the creation of point defects is an equally, or, in many cases, more efficient mechanism. Within this framework, a number of experimental results from different systems are quantitatively explained.

Irradiation-induced flow was obtained by simulating the response of an amorphous (*a*-)CuTi alloy to an applied stress during a series of monoenergetic events at 10 K. The MD code PARCAS [11] was employed with the interatomic potentials for Cu-Ti developed by Sabochick and Lam [12]. Two types of boundary conditions were used. One employed periodic boundary conditions in the *x*-*y* direction and open surfaces in the *z* direction, while the other was periodic in three dimensions to avoid surfaces. The first type had fixed boundaries in the *x*-*y* direction and monitored the relaxation of the initial state of stress, σ_0, as a function of the number of recoil events. The completely periodic cell used the same applied stress, σ_0, in the *x*-*y* direction and zero applied stress in the *z* direction. After each recoil event, performed under constant volume conditions, the initial state of stress was restored and the strain in the *z* direction obtained. Many such events were then averaged. The fully periodic cell contained 2.56×10^5 atoms for all events, while the number of atoms in the cell with free surfaces increased approximately linearly with recoil energy, using a ratio of more than 25 atoms/eV. For both cells the atoms in the periodic boundaries were damped to simulate the loss of energy in infinite solids. The irradiations proceeded by alternating between Cu and Ti recoils.

The viscosity during irradiation was determined in the case of periodic boundary conditions using the expression

$$\dot{\epsilon} = \frac{\sigma}{6\eta} + \dot{\epsilon}_{\mathrm{def}}, \tag{1}$$

where ϵ is the total biaxial strain, σ is the applied biaxial stress, and η is the viscosity. The second term in Eq. (1) represents possible changes in strain due to the introduction of "defects" in the amorphous structure during an irradiation with flux, $\dot{\phi}$. Dividing by $\dot{\phi}$ yields

$$\frac{d\epsilon}{d\phi} = \frac{\sigma H}{6} + \frac{d\epsilon_{\mathrm{def}}}{d\phi}, \tag{2}$$

where $H \equiv 1/(\eta\dot{\phi})$ is the radiation-induced fluidity (RIF), and the fundamental quantity in this study. For calculations of stress relaxation, we use

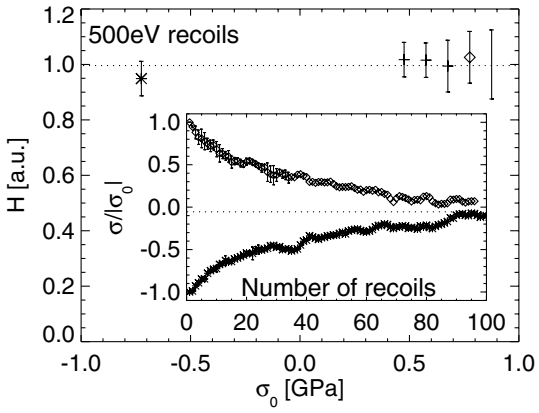

FIG. 1. The RIF H is calculated from the relaxation curves for different stresses and signs of the stresses, as show in the inset. The independence of the initial stress σ_0 indicates Newtonian flow.

$$\sigma = \frac{-6\alpha}{H} + \left(\sigma_0 + \frac{6\alpha}{H}\right)\exp\left(-\frac{Y_b H}{6}\phi\right), \qquad (3)$$

where $\alpha \equiv d\epsilon_{\mathrm{def}}/d\phi = \text{const.}$ and Y_b is the biaxial modulus. Here H is obtained by fitting the simulation data to Eq. (3). Typical results from the stress relaxation simulations are shown in Fig. 1 for compressive and tensile stresses. They illustrate that the stress decays exponentially with dose, that the radiation-induced viscosity is independent of stress, and from the symmetry of the response to tensile and compressive stresses, that α is small. Similar behavior was observed for the other recoil energies.

The principal results of the simulations are shown in Fig. 2 where the dependence of RIF is plotted as a function of recoil energy. At the lowest energies, a well-defined threshold is observed at $E_T \approx 10$ eV, below which H is extremely small [$\leq 1 \times 10^{-11}$ (Pa dpa)$^{-1}$, dpa: displacements per atom]. Just above this threshold, between 10 and 100 eV, the flow increases rapidly with energy. Ignoring for the moment the data above 1 keV for the simulation cells with free surfaces (open symbols), we see that above the transition regime, the flow is independent of energy up to the highest energy examined, 10 keV. When free surfaces are available, the pressure produced within cascades induces flow of mass onto the surface, thereby creating tensile stress. For films initially under compressive stress, this effect enhances the reduction in stress in the film, as seen in Fig. 2. The influence of the surface increases as the size and energy density in cascades increase. An interesting point here is that such "surface" effects can strongly influence the state of stress in thin films, and they act on crystalline as well as amorphous films [8].

The behavior at the lowest energies clearly indicates that radiation-induced flow commences only when the recoil energy is sufficiently high to displace an atom from its local equilibrium site and thus create a Frenkel

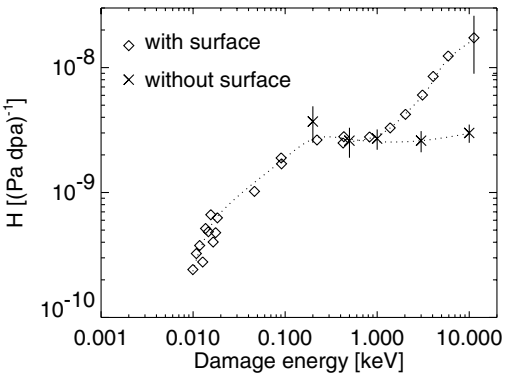

FIG. 2. The dependence of the RIF, H, on recoil energy for simulation cells with open surface or periodic boundaries.

pairlike defect. This process, therefore, very much resembles the concept of "flow defects," which was developed to explain thermally induced flow in amorphous alloys [13]. Within the picture that point-defect-like entities mediate the radiation-induced flow, the dependence of flow on energy follows directly from the Kinchin-Pease model of defect production, viz., no defect production below E_T, followed by a rapid increase in the number of defects just above E_T, and finally a linear dependence of defects on energy above ≈ 2.5–$10E_T$ [14,15].

We have further examined this defect model of radiation-induced flow by simply injecting or removing atoms in the stressed a-CuTi matrix at randomly chosen sites and following the stress relaxation. The results of these simulations for defect creation at temperatures of 10 and 400 K are illustrated in Fig. 3, where the residual stress is plotted versus the number of added or removed atoms. The radiation-induced flow is a factor of 3 larger at the higher temperature, which is 0.7 times the glass temperature of our alloy. At 100 K (not shown) the flow is twice as large as at 10 K. Similarly, small changes in the RIF with temperature have been observed experimentally [5,8]. A surprising result observed in Fig. 3 is that the induced flow per defect is the same for injecting or removing atoms, i.e., each operates as a flow defect and

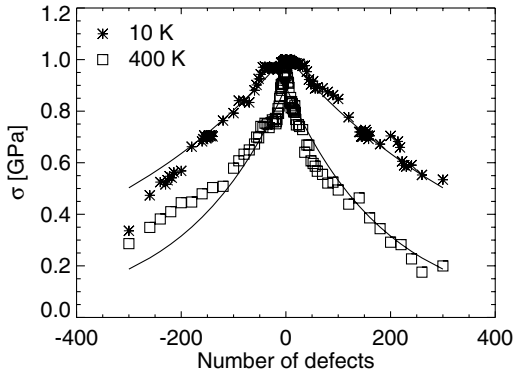

FIG. 3. The biaxial residual stress σ versus the number of injected or removed atoms.

with equal strength. It is also noteworthy that the stress relaxation for creation of either defect at 10 K occurs, more or less, in steps. After an initially slow response to adding defects, a rapid relaxation occurs, followed by another slow response. This avalanchelike behavior was also observed for the low-energy recoil events, but not for the high-energy events. Presumably, the higher density of defects produced in each of the higher-energy events, or local heating, suppresses this behavior. As seen in Fig. 3 at 400 K this behavior is also suppressed. While we have not yet examined the cause of this behavior, the fact that the width of the step is ≈ 30 injected defects in a cell containing 16 000 atoms suggests that a concentration of $\approx 0.2\%$ defects leads to an instability and subsequent relaxation.

A quantitative comparison was made between the flow caused by defect creation at 10 K with that by recoil events by calculating the flow per Frenkel pair. For the injection simulations this is straightforward since the number of defects is known. For the recoil events we assume that the threshold energy for defect production is 10 eV, as indicated in Fig. 2, and employ the Kinchin-Pease expression to calculate the number of Frenkel pairs per recoil event [16]. We find the rather remarkable result that, to within the uncertainties, simulations of both injection of defects and the recoil events yield $H = 3 \times 10^{-9}$ (Pa dpa)$^{-1}$, where dose is measured in normalized units of displacements per atom, i.e., the atomic fraction of Frenkel pairs. While this extremely close agreement must be somewhat fortuitous, owing to the uncertainties in the threshold energy and the Kinchin-Pease model, it illustrates that the creation of point defects in recoil events is sufficient in itself to induce the observed stress relaxation.

We next compare our value of $H = 3 \times 10^{-9}$ (Pa dpa)$^{-1}$ obtained by MD simulation, with published experimental measurements of RIF on the metallic glasses, $Ni_{78}B_{14}Si_8$ and $Zr_{65}Cu_{27.5}Al_{7.5}$, and glassy SiO_2: for 6.3 MeV proton irradiation of the Ni-based metallic glass $H \approx 4 \times 10^{-9}$ (Pa dpa)$^{-1}$ [6]; for 700 keV Kr irradiation of the Zr-based glass, $H \approx 2.6 \times 10^{-9}$ (Pa dpa)$^{-1}$ [7,8]; and for a series of MeV ion irradiations of different mass projectiles on SiO_2, $H = 2.8 \times 10^{-9}$ (Pa dpa)$^{-1}$ [5]. For the normalization to dpa in these irradiations, we have used the displacement energy of 10 eV in the Kinchin-Pease model. Remarkably, H has nearly the same value for these very disparate irradiations as for the simulations. Notice, for example, that the primary recoil spectrum for 6.3 MeV proton irradiation of the Ni-based glass is strongly weighted toward low energies; half the Frenkel pairs are produced in recoils below a characteristic energy, $T_{1/2}$, of 400 eV. For the 700 keV bombardment of $Zr_{65}Cu_{27.5}Al_{7.5}$, $T_{1/2}$ exceeds 20 keV. Moreover, the glass temperature for these metallic glasses is $\approx 400\,^{\circ}$C, whereas it is over 1100 °C in SiO_2.

While a defect model appears to explain a variety of experimental results for RIF, we consider whether thermal spikes play any significant role in the RIF process. Previous theories of RIF have assumed that thermal spikes are the primary mechanism of stress relaxation, and indeed, ion beam mixing in metals is usually dominated by thermal spike diffusion. We address this question by first noting that the time (i.e., dose) constant for stress relaxation in the defect injection simulations is ≈ 0.03 dpa, which corresponds in our defect production calculations to 0.75 eV/atom. We consider, therefore, the average energy required to raise an atom above a characteristic temperature, T_c, at which the viscosity is sufficiently low for relaxation to occur during a thermal spike. For simulated CuTi, $T_c = 800$ K. Thus, for a 500 eV recoil event, for example, there need be over 700 such atoms to compete with the defect mechanism. Results for the number of liquid atoms produced in recoil events are illustrated in Table I. An atom is considered liquid if it, and its neighbors, each has a kinetic energy equal to $3/2k_BT_c$. A peak in this number is observed at short time ≈ 0.1–0.2 ps, followed by a long tail. The peak is due to a rapid outward expansion, or microexplosion, surrounding the recoil site, while the tail is due to local heating. Both numbers scale with energy above 500 eV, with the ratio of liquid atoms to energy being 1.2 eV per atom and the ratio of atoms in the microexplosion to recoil energy ≈ 0.8 eV per atom. Both ratios are close to that deduced for the inserted defects.

These several results indicate that three separate mechanisms may contribute to stress relaxation, creation of point defects, atomic reorganization around a microexplosion, and local melting. In metals they appear to operate with nearly the same efficiency and above ≈ 500 eV; they all scale linearly with recoil energy. Below 500 eV, the thermal spike mechanism does not appear viable since the cooling rate is too fast, less than 0.3 ps; consequently, either defect production or the microexplosion mechanisms must dominate. Since the microexplosion, i.e., a local excitation at the site of the newly created Frenkel pair, always accompanies the addition of a Frenkel pair in a recoil event, we refer to the two simply as defect production. We find that, despite the different mechanisms of RIF, its value remains constant over the entire energy range of our simulations, 100 eV to 10 keV. This further illustrates that the local melting mechanism can be no more efficient than defect production. For this reason, RIF in the 6.4 MeV p-irradiated

TABLE I. Number of atoms during the microexplosion N_M, number of liquid atoms N_L and lifetime τ as a function of damage energy E_D.

E_D [keV]	0.1	0.5	1.0	3.0	10
N_M	80	763	1709	4549	13 865
N_L	0	320	840	2450	8050
τ [fs]	180	1100	2100	3000	6000

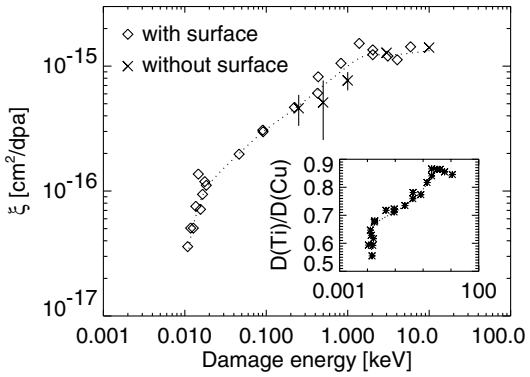

FIG. 4. The dependence of the average radiation-induced diffusivity ξ on the damage energy. The inset shows how the ratio of the diffusivities of Ti and Cu change with damage energy.

$Ni_{78}B_{14}Si_8$ glass, despite its low recoil energy spectrum, is equally efficient as 700 keV Kr irradiation of the $Zr_{65}Cu_{27.5}Al_{7.5}$ glass. Additional experiments on other metallic glasses using different ions to determine the universality of the value of $H = 3 \times 10^{-9}$ (Pa dpa)$^{-1}$ would be valuable. While the simulations have been performed only on metallic glasses, the results appear to explain why the value for RIF is the same in SiO_2, whose value of T_g greatly exceeds that for the metallic glasses, and for which thermal spikes are not expected. It is simply because the energy to create a Frenkel pairs does not vary by more than a factor of 2 in most materials and defect production is at least as efficient a flow mechanism as the thermal spike. Perhaps our result that defect production can account for RIF should not be considered surprising since a relaxation dose of 0.03 dpa (see Fig. 3) implies that a volume equal to 33 atomic volumes, or a sphere of radius 0.33 nm surrounding the Frenkel pair, undergoes relaxation, as the Frenkel pair relaxes. In crystalline materials the spontaneous relaxation volume is ≈ 100 atomic volumes or $r \approx 0.5$ nm [17].

As a final consideration of thermal spikes, we plot the mean square displacement per atom, per dpa, ξ, as a function of recoil energy; see Fig. 4. The value is seen to increase with energy up to ≈ 1 keV and then it becomes constant. Similar behavior is observed for the ratio of the Cu and Ti diffusion coefficients, $D_{\mathrm{Ti}}/D_{\mathrm{Cu}}$ (Fig. 4). We know from our simulations, moreover, that this ratio is near unity in liquid CuTi. We conclude, therefore, that the thermal spike becomes increasingly important with energy up to 1 keV, when local melting becomes significant. The behavior for RIF, in contrast, becomes independent of energy by 100 eV, suggesting that the increasing importance of the thermal spike has little influence on the RIF.

In conclusion, the MD simulations illustrate that radiation-induced viscous flow results primarily by the creation of point defects, which act as flow defects. The calculations are in excellent agreement with experimental results. Thermal spike models of RIF were carefully analyzed by determining the number of atoms in the liquid and were shown to be at most as efficient as point defects, and then in only some cases.

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