Solid-State Amorphization of Zr_3Al: Evidence of an Elastic Instability and First-Order Phase Transformation

L. E. Rehn, P. R. Okamoto, J. Pearson, R. Bhadra, and M. Grimsditch
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

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Changes in shear elastic constant, long-range order, and lattice parameter were measured during disordering and eventual amorphization of Zr_3Al by ion irradiation. Large ($\simeq 50\%$) elastic softening was observed during disordering, and anomalies occurred in all three measured parameters over a narrow range of ion doses. The results indicate that a first-order phase transformation triggered by an elastic instability occurs during solid-state amorphization. The changes reported here during disordering and amorphization are very similar to behavior observed previously in a large number of solids during heating to melting.

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Several processes are known that can transform certain crystalline materials directly into amorphous solids: irradiation with energetic particles,[1] interdiffusion,[2] annealing,[3] and mechanical alloying.[4] Considerable interest currently exists in these solid-state crystalline-to-amorphous (*c-a*) transformations because they offer ways to produce technologically useful, bulk amorphous materials. Although empirical rules have been formulated to predict which materials will undergo *c-a* transformations, very little is understood about the underlying mechanisms. Using the fact that heterogeneous nucleation is often observed, Cahn and Johnson,[5] and Johnson,[6] have recently suggested that amorphization in the solid state and melting to a liquid may be manifestations of the same first-order phase transformation. That is, amorphization may result because an elastic instability occurs at temperatures below the glass transition temperature, just as a liquid can result from an elastic instability at the melting temperature.[7]

In the following, we report the results of an investigation employing Brillouin scattering to measure a shear elastic constant, and transmission electron microscopy (TEM) to measure the long-range order parameter and the lattice dilation during irradiation-induced disordering and eventual amorphization of the intermetallic, Zr_3Al. Details of the experimental technique have been reported previously.[8] The results indicate that a first-order phase transformation driven by an elastic instability occurs during solid-state amorphization. Furthermore, these experimental findings reveal several parallels with behavior previously reported during heating to melting in a wide variety of materials,[9] and therefore strongly support the analogy between solid-state amorphization and melting postulated in Refs. 5 and 6.

A Zr-Al alloy containing nominally 25 at.% Al was furnished by R. Zee of the Chalk River Nuclear Laboratories. It was homogenized for 170 h at 950 °C, mechanically polished, then given a final electropolish. TEM examination showed that the alloy was predominantly Zr_3Al, containing $\simeq 7\%$ volume fraction of Zr_2Al grains. Shear elastic constants were measured by Brillouin scattering with a 5+2- pass Fabry-Perot interferometer and 514.5-nm radiation from a single-mode Ar^+ laser.[8] TRIM[10] calculations show that the defect production rate during irradiation varies by $\simeq 40\%$ in the first 350 nm below the specimen surface, which is the depth probed by the Brillouin technique. The absolute accuracy of the dose measurements is better than ±20%. 3-mm-diam areas of the rectangular specimens were irradiated by 1.0-MeV Kr^+ at room temperature for various times at a constant flux. After the Brillouin measurements were completed, the irradiated areas were core drilled and thinned for subsequent TEM study. Additional TEM studies of amorphization, long-range order, and lattice dilation were performed *in situ*, during irradiation, with use of the Argonne HVEM-Ion Interface.

The long-range-order parameter, S, can be defined as the square root of the ratio of intensities in the superlattice (I_s) to fundamental (I_f) reflections normalized to the ratio measured in the fully ordered starting material. That is,

$$S \equiv \left[\frac{I_s/I_f}{I_s^0/I_f^0} \right]^{1/2} . \tag{1}$$

In situ measurements of S in Zr_3Al were taken under weak-beam, $2g$ diffracting conditions (400 spot excited),[11] and are shown in Fig. 1 as a function of ion dose. Intensities were measured on film with a microdensitometer; the film was first calibrated with use of a Faraday cup to obtain the required relationship between electron dose and film density. S decreases exponentially with dose up to $\simeq 4\times10^{13}$ cm^{-2}, then drops abruptly to zero by 6×10^{13} cm^{-2}. TEM also reveals no significant volume fraction of amorphous material until doses above $\simeq 8\times10^{13}$ cm^{-2}. A very faint diffuse ring can be seen in the diffraction pattern at a dose of $\simeq 4\times10^{13}$ cm^{-2}, but loss of all diffraction spots (complete amorphization)

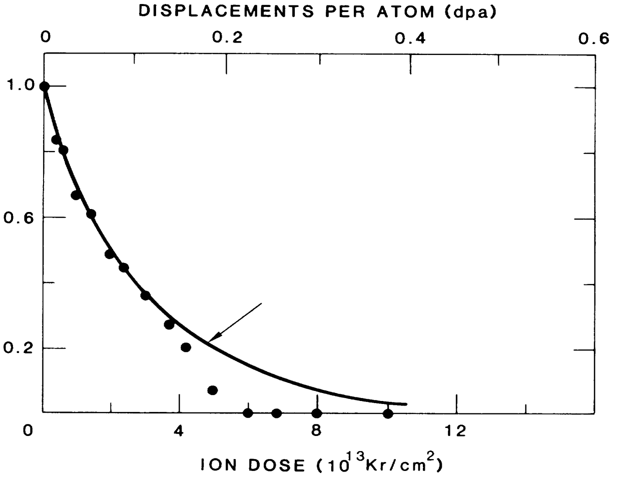

FIG. 1. *In situ* measurements of the long-range order parameter, S, in Zr_3Al as a function of irradiation fluence.

does not occur until doses $\gtrsim 2\times10^{14}$ cm^{-2}.

The Brillouin spectra from samples irradiated to doses $\lesssim 2\times10^{13}$ ions/cm^2 contained broad, and often overlapping, peaks from both the Zr_3Al and Zr_2Al phases. By our performing measurements in samples containing different concentrations of the two phases, the lower-frequency peak was shown to arise from Zr_3Al, and the higher one from Zr_2Al. The peak widths can be understood by our noting that the $\simeq 100$-μm-diam laser beam illuminates several grains in the polycrystalline specimen. For elastically anisotropic crystals, each grain orientation produces a slightly different frequency shift, which broadens the Brillouin peaks. The peaks narrowed significantly at higher doses, indicating that the elastic anisotropy decreases with irradiation dose. Measurements of the sound velocity, V_s, determined from Brillouin scattering are shown as a function of ion dose in Fig. 2; open or filled circles denote broad or narrow peaks, respectively. The shear elastic constant equals the product of the specimen density and V_s^2. As seen below, changes in density were small ($\lesssim 3\%$) during disordering and hence can be neglected in the calculation of the elastic-constant changes. The data in Fig. 2 reveal that a large (almost 50%) decrease occurs in the Zr_3Al shear constant during disordering (doses $< 6\times10^{13}$ cm^{-2}). The dependence of the Zr_2Al sound velocity (data not shown) on ion dose appears very similar, i.e., and $\simeq 50\%$ elastic softening was observed during disordering. These decreases in shear constant are substantially larger than the typical $\leq 10\%$ reported for alloys such as Cu_3Au that undergo an order-disorder transformation below the melting temperature, T_m.[12] The strong decrease in shear constant with decreasing order observed here is, however, consistent with previous measurements in Nb_3Ir,[8] another intermetallic which remains ordered up to T_m.

At a dose between (4 and 8)$\times10^{13}$ cm^{-2}, an abrupt increase is evident in the Zr_3Al sound velocity (Fig. 2). After this abrupt increase, no further change occurs in the sound velocity as a function of irradiation dose. The discontinuity seen in the sound velocity demonstrates that the c-a transformation is not a continuous function of irradiation dose as one might expect, but rather that a relatively abrupt phase transformation occurs. For Zr_3Al, the discontinuity in S indicates that the transformation is first order.[13] An abrupt phase transformation is also revealed in our *in situ* TEM measurements of lattice parameter changes, Δa, in the Zr_3Al phase during irradiation. These results, which agree well with those reported by Howe and co-workers[14-16] and Carpenter and Schulson,[17] show that a increases monotonically by 1% up to a dose of $\simeq 5\times10^{13}$ cm^{-2}, where the increase abruptly drops to $\simeq 0.8\%$, then remains unchanged up to the highest doses where diffraction spots can still be seen ($\lesssim 2\times10^{14}$ cm^{-2}).

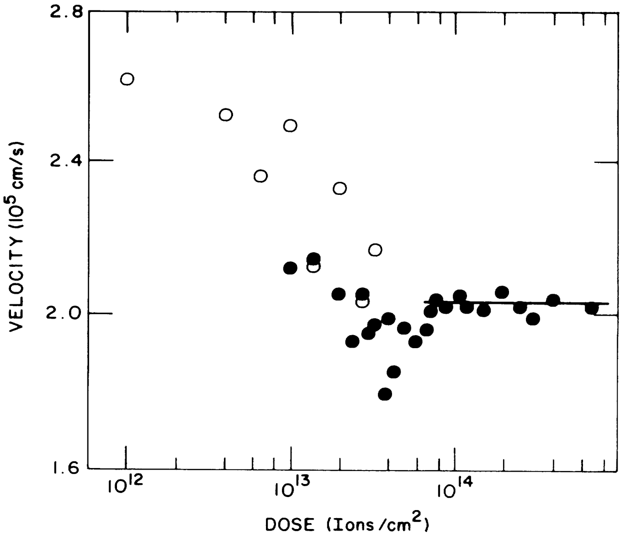

FIG. 2. Measurements of the shear sound velocity in Zr_3Al as a function of irradiation dose. Open and filled circles denote respectively broad and narrow peaks in the Brillouin spectra.

The large elastic softening which precedes the phase transformation suggests, in analogy with the martensitic transformation,[18] that an elastic instability triggers the transformation. A similar instability has been proposed by Egami and Waseda[19] to explain observed solute-concentration limits on amorphous-phase formation during quenching from a liquid phase. Further support for an elastic instability during solid-state amorphization is provided by our plotting (Fig. 3) the Zr_3Al shear-constant changes as a function of lattice dilation ($3\Delta a/a$). The total dilation measured during disordering is $\simeq 3\%$. Note that the data in Fig. 3 extrapolate to a zero shear constant at a volume dilation of $\simeq 6\%$. This extrapolation suggests that the disordered material is elastically unstable with respect to additional density fluctuations of

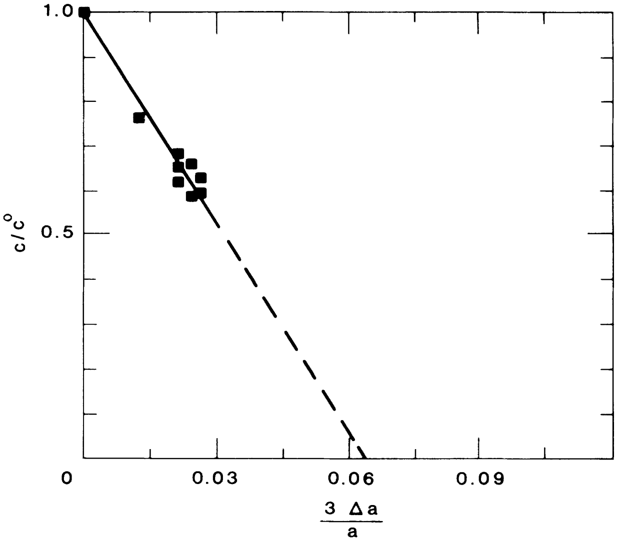

FIG. 3. Shear elastic-constant changes in Zr_3Al plotted as a function of the measured dilation ($3\Delta a/a$).

$\simeq +3\%$. Since density fluctuations of this magnitude are expected in the cores of energetic displacement cascades,[20] the irradiation itself may provide the necessary fluctuations to overcome the nucleation barrier for the first-order phase transformation.

Space limitations do not permit a thorough review of the extensive existing literature on elastic-constant behavior as a function of temperature. We note, however, three clear parallels between the shear-constant behavior measured here during solid-state amorphization and that observed previously[9] as a function of temperature up to melting at T_m: (1) A large, $\simeq$50% softening is observed (as a function of temperature up to T_m; as a function of ion dose through disordering); (2) a discontinuity occurs (as a function of temperature at T_m; as a function of ion dose at $\simeq 6\times10^{13}$ cm^{-2}); (3) the shear elastic constant (measured as a function of temperature or ion dose) extrapolates to zero at an additional dilation of $\simeq$3%. The discontinuities observed in the long-range order parameter and interatomic spacing also parallel those observed during melting. The results reported here therefore strongly support the analogy between melting and solid-state amorphization postulated in Refs. 5 and 6.

We emphasize that the apparent elastic instability and first-order phase transformation that occur during irradiation do not simultaneously drive the entire crystal amorphous. Strong fundamental spots dominate the diffraction patterns taken at doses of $\simeq 8\times10^{13}$ cm^{-2}, indicating that only a small fraction of the specimen is amorphous. The transformation to a completely amorphous material requires continued irradiation up to a dose of $\simeq 2\times10^{14}$ cm^{-2}. During this gradual transformation, however, no additional change occurs in either the lattice parameter or the shear elastic constant, indicating that the elastic properties of the material following the abrupt transformation are very similar to those of the fully amorphous phase.

In summary, large (50%) elastic softening was measured in Zr_3Al as it was progressively disordered during irradiation. When disordering was nearly complete, anomalies in the long-range order parameter, in the sound velocity, and in the lattice parameter were all observed in a narrow dose interval. These anomalies, and the Brillouin-scattering measurements at higher doses, reveal that a first-order phase transition occurs to a state characterized by the same shear elastic constant as the amorphous phase. An extrapolation of the shear-constant data as a function of lattice dilation suggests that the disordered crystal is elastically unstable with respect to the magnitude of density fluctuations that are expected in cascade cores, i.e., a few percent, and therefore that the transformation is apparently triggered by an elastic instability. The changes in the shear elastic constant and long-range order parameter observed during irradiation are remarkably similar to those reported previously in many different materials during heating to melting,[9] and therefore strongly support the analogy between solid-state amorphization and melting postulated in Refs. 5 and 6.

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