

STRESS-INDUCED AMORPHIZATION AT MOVING CRACK TIPS IN NiTi*

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ABSTRACT

In situ fracture studies on thin-film NiTi intermetallic compounds have been carried out in the high-voltage electron microscope at Argonne National Laboratory. Local stress-induced amorphization of regions directly in front of moving crack tips has been observed under tensile loading conditions. The stress-induced amorphization at crack tips exhibits a temperature dependence similar to that of ion-induced amorphization of NiTi. The upper limiting temperature for stress-induced amorphization is the same as that for ion-induced amorphization of crystalline NiTi and for amorphous phase formation during ion-beam mixing of Ni and Ti multilayer specimens. This upper limiting temperature of 600K is also the lowest temperature at which stress-induced amorphous phase crystallizes during isothermal annealing. This isothermal crystallization temperature is nearly 200K less than the kinetic crystallization temperature during heating of unrelaxed NiTi glasses formed by rapid quenching or vapor phase deposition.

INTRODUCTION

Despite a long and continuing effort to understand why and how solids fracture, no generally accepted theory of the phenomenon has yet been developed. Although the local stress intensification in the immediate vicinity of the crack tip is known to be the primary driving force

for fracture, the mechanism by which the strain energy stored in crack tip is dissipated during propagation is not well understood. An intriguing question is whether the strain energy can be released via local melting of the crack tip. This possibility is suggested by recent Monte Carlo (MC) simulations which show that fcc elemental crystals under uniaxial tension can undergo stress-induced melting at temperatures $T_m(\sigma)$ well below the thermodynamic melting temperature $T_m(\sigma = 0)$ of the unstressed crystal [1]. For a given temperature, $T < T_m(\sigma = 0)$, this stress-induced melting occurs at a critical stress where the free energy of the stressed crystal becomes equal to that of the supercooled liquid. This is illustrated schematically in Fig. 1, which shows the temperature dependence of the Gibbs free energy of the unstressed crystal, of the liquid, and of two stressed crystalline states

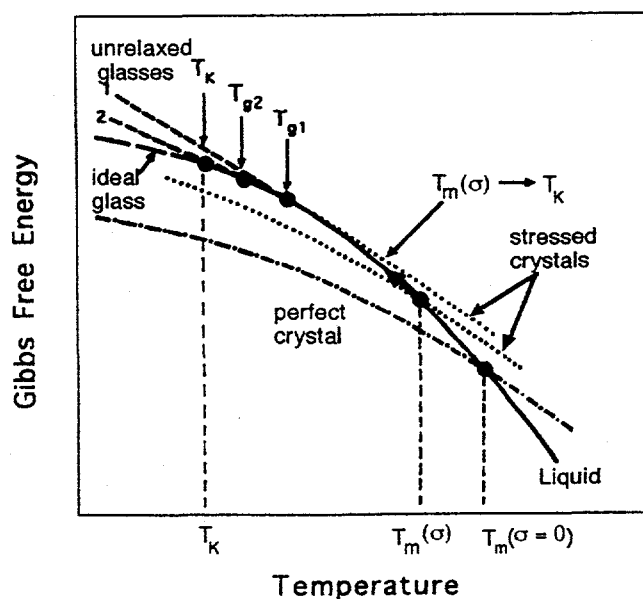


Fig. 1. Gibbs free energy versus temperature of the stressed and unstressed crystals.

indicated by the dotted curves. Also shown are: (i) the ideal glass [2], which has the same entropy as that of the perfect crystal, and (ii) two unrelaxed glassy states 1 and 2, associated with cooling rates such that $T_{g1} > T_{g2}$. T_K is the glass transition temperature of the ideal glass as defined by Kauzmann [2].

Although the MC results clearly show that stress-induced melting occurs below T_m ($\sigma = 0$) for a simple fcc metal (Pt), they also show, equally clearly, that the melting process is a transient phenomenon which will be difficult, if not impossible, to observe directly since the liquified crack tip region (which cannot sustain a load) immediately crystallizes as the crack propagates, leaving no evidence that melting has occurred. However, at very low temperatures ($T < T_K$), it may be possible to observe the phenomenon in an intermetallic compound as a stress-induced crystal-to-glass transformation (C-G) that results in the formation of the ideal glass [3]. This possibility is illustrated schematically in Fig. 1, which shows that the glassy state with the lowest Gibbs free energy, i.e., the ideal glass, will be the first glassy state to be reached from below via any disorder-driven C-G transition. Hence, the same unique ideal glassy state should be obtained whether the transformation is driven by irradiation, ion mixing, or applied stresses. Here, we report direct observations of stress-induced amorphization at moving crack tips during straining of the intermetallic compound NiTi. The temperature dependence of stress-induced amorphization and the isothermal crystallization behavior of the resulting glass are compared with those associated with irradiation-induced amorphization of NiTi [4]. As will be shown, the results confirm the hypothesis that, like other solid-state amorphizing transformations, stress-induced C-A transformations lead to the formation of the ideal glassy state [3].

EXPERIMENTAL PROCEDURES

In situ fracture observations in NiTi were carried out with a Gatan side-entry heating-straining stage in the high-voltage transmission electron microscope (HVEM) at the Argonne National Laboratory HVEM-Tandem accelerator facilities. The straining stage is capable of achieving temperatures between 300 - 825K and a maximum elongation of 2000 μm . Miniature NiTi tensile specimens were prepared from bulk alloys with Ti concentrations between 47 - 49 at. % Ti. The bulk alloys were rolled down to 100 μm thick sheets which were subsequently cut into 3.0x6.5 mm strips. Tensile specimens for the Gatan straining stage were prepared from these strips by boring 1.0-mm diameter holes in the two ends for mounting on the straining stage. A gauge length was created by electro-etching two slits along the length of the specimen. All specimens were given a high-vacuum, pre-strain anneal at 900 °C for 20 minutes to remove any mechanical damage introduced during preparation. The annealing treatment resulted in polycrystalline austenitic NiTi (B2 structure) with a typical grain size of 10 μm . Prior to mounting, the central area in the gauge length was electropolished to electron transparency, using a single-jet electropolisher with custom polishing holder.

TEMPERATURE DEPENDENCE OF STRESS-INDUCED AMORPHIZATION

In situ studies of stress-induced amorphization at crack tips on NiTi tensile specimens were carried out between 300 - 750K. Figure 2 shows a dark-field (DF) image of a typical crack formed during straining at 300K, which is well below the range of kinetic glass transition temperature 750 - 850K reported for amorphous NiTi produced by rapid quenching techniques [5]. Selected area diffraction (SAD) patterns taken from areas away from the crack tip region indicate a crystalline structure while the SAD pattern from the crack tip region exhibits diffuse intensity halos, indicating that an amorphous phase forms ahead of the crack tip. DF images taken with part of the first diffuse intensity halo show that the amorphous phase is also present



Fig. 2. Dark-field image and selected area diffraction patterns showing amorphous phase formation in the region ahead of crack tip and along the crack edges.

along the edges of the crack as well as in the region ahead of the crack tip itself. This indicates that, at 300K, the amorphous phase which forms at the crack tip remains amorphous as the crack propagates into the crystal.

The temperature dependence of stress-induced amorphization is summarized in Fig. 3, which shows the average width of the amorphous layer along the crack edges as a function of temperature measured for several NiTi specimens having either the B2 or martensitic structure prior to straining. These results show that stress-induced amorphization at crack tips only occurs for temperatures below about 600K. As shown in Fig. 4, this cutoff temperature can also be determined in a different way by plotting the percentage of specimens (12 were examined) which exhibit either complete or partial stress-induced amorphization as a function of straining temperature. Again, one sees a relatively sharp upper-limiting cutoff temperature at about 600K, which is also the upper-limiting cutoff temperature for irradiation-induced amorphization of crystalline NiTi by heavy-ions [4], and for amorphous phase formation by ion-beam mixing of Ni and Ti multilayer specimens [6]. 600K is also the lower-limiting cutoff temperature, T_{A-C} , for the reverse transformation of irradiation-induced amorphous-to-crystalline transformation.

The thermodynamic significance of the cutoff temperature is that $T_{A-C} = T_K$, the ideal glass transition temperature [3]. That T_K must be the upper-limiting cutoff temperature for all solid-state amorphization follows from the fact that a thermodynamic driving force for amorphization exists only for metastable crystalline states that have free energies higher than that of the ideal glass. As seen in Fig. 1 for the case of stress-induced amorphization, this thermodynamic criterion for amorphization will be satisfied only when $T_m(\sigma) \leq T_K$. Hence, like other C-G transformations, stress-induced amorphization cannot occur for $T > T_K$. However, stress-induced melting to a supercooled liquid can occur above T_K , provided no relaxation of the stressed state occurs.

CRYSTALLIZATION BEHAVIOR OF STRESS-INDUCED AMORPHOUS PHASES

The ideal glass transition temperature can also be determined by plotting the kinetic glass transition and crystallization temperatures as a function of heating rate. As shown by Busch et al. [7] for amorphous $Zr_{41.2}Ti_{33.5}Cu_{12.5}Ni_{10.0}Be_{22.5}$ and by Okamoto et al. [3] for amorphous CuTi, the two curves, T_g and T_x , intersect at $T_K = 562$ and 565K, respectively, for critical heating rates of 1.67×10^{-5} K/min and 6.6×10^{-2} K/min. These heating rates correspond to 1K every 41 days for

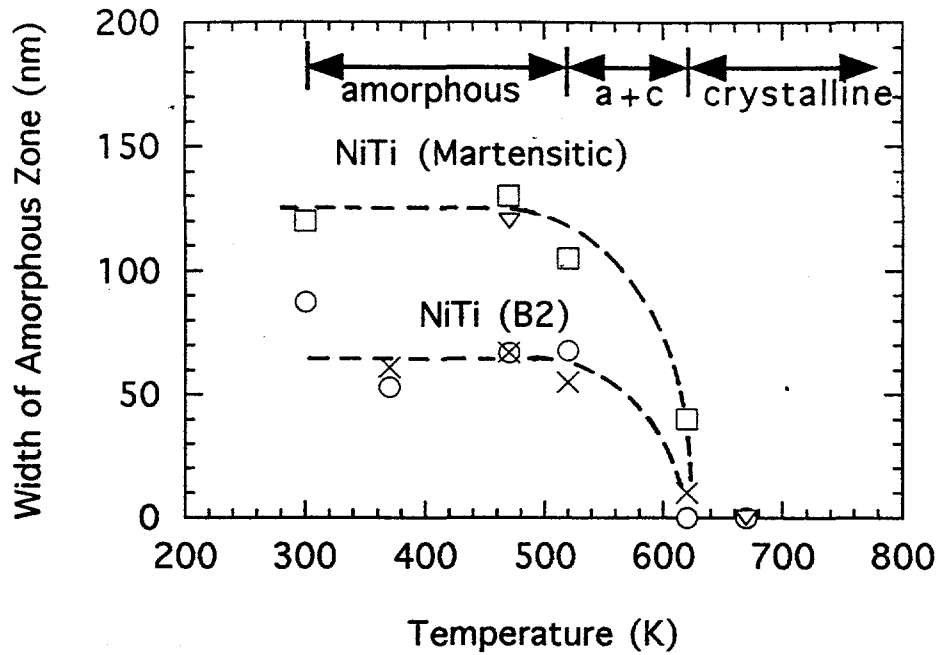


Fig. 3. Average width of amorphous zone along crack edge as a function of temperature for B2 and martensitic NiTi.

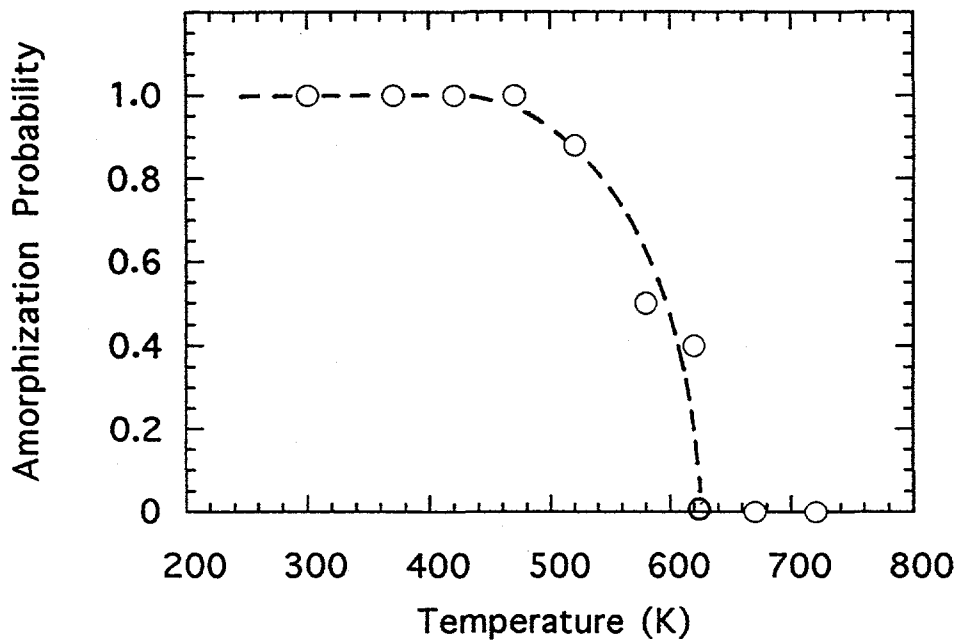


Fig. 4. Percentage of NiTi specimens exhibiting either complete or partial amorphization during fracture.

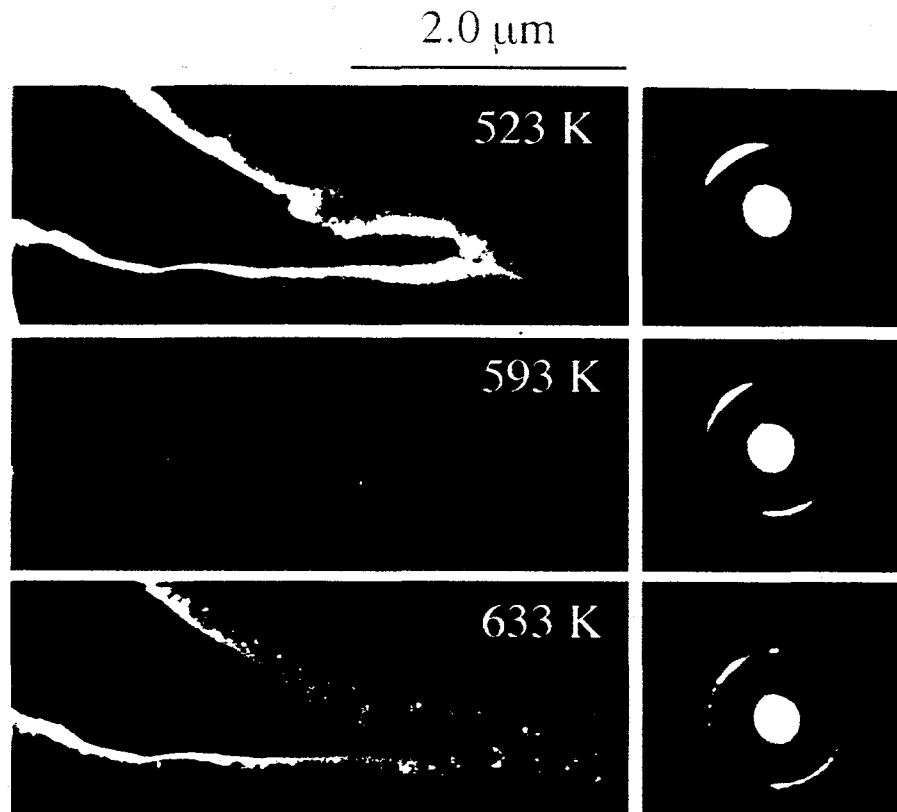


Fig. 5. Annealing of stress-induced amorphous phase at an intergranular crack in NiTi formed during straining in the HVEM at 300K. The specimen was annealed for 15 minutes at each temperature.

amorphous $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ and 1K every 25.3 hours for amorphous CuTi, which means essentially isothermal annealing conditions. Hence, since $T_K = T_X = T_{A-C}$ for these essentially zero heating rates, the ideal glass should crystallize when annealed isothermally at T_K , even though it is typically several hundreds of degrees lower than the kinetic crystallization temperatures observed during rapid heating of the unrelaxed glasses. This hypothesis was confirmed by annealing a specimen fractured at 300K for 15 minutes at various temperatures between 300 and 923K. No change in the structure of the amorphous NiTi occurs until 593K where the first hint of crystallization is observed. This is illustrated in Fig. 5, which shows DF images and the corresponding SAD patterns after annealing at 523, 593 and 633K. At 523 K, the SAD pattern shows that the crack tip is still completely amorphous. At 593K, a few small grains form at the crack tip and along its edges, although the SAD pattern indicates that these regions are still primarily amorphous after annealing for 15 minutes. At 633K, however, the SAD pattern exhibits polycrystalline rings, indicating that the crack tip is almost completely polycrystalline. The DF image shows many more fine grains at the crack tip and along its edges.

CONCLUSIONS

In situ fracture studies of crystalline NiTi strongly support recent MC simulations results which show that a transient stress-induced melting at crack tips can lead to failure by cavity formation. The stress-induced melting occurs at a critical stress where the free energy of the stressed crystal becomes equal to that of the supercooled liquid. The melting process will be difficult to observe in simple metals since immediate recrystallization of the liquified crack tip

region upon cavity formation leaves no evidence that melting has occurred. However, at low temperatures ($T \leq T_K$), the phenomenon can be directly observed in crystalline NiTi as a stress-induced amorphization of the moving crack tip. Moreover, both the temperature dependence and annealing behavior of stress-induced amorphous NiTi exhibit all the characteristic features expected of the ideal glass. As the glass with the lowest free energy, its formation at temperatures below T_K , where long-range diffusion is suppressed, can be understood as the most energetically-favored, kinetically-constrained response of crystalline alloys driven far from equilibrium by applied stresses and/or radiation damage.

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