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MOLECULAR-DYNAMICS STUDY OF THE AMORPHIZATION OF CuTi*

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ABSTRACT

Radiation-induced amorphization of the crystalline compound CuTi was investigated by molecular-dynamics simulations using new interatomic potentials derived from the embedded-atom method. Two different approaches to amorphization were tried: one in which Cu and Ti atoms were randomly exchanged, and another in which Frenkel pairs were introduced at random. The potential energy, volume expansion and pair-correlation function were calculated as functions of chemical disorder and atomic displacements. The results indicate that, although both chemical disordering and point-defect introduction increase the system energy and volume, the presence of Frenkel pairs is essential to trigger the crystalline-to-amorphous transition.

INTRODUCTION

Radiation-induced amorphization of intermetallic compounds has been investigated extensively in recent years (see, e.g., [1-3] and references therein). The interest in this research subject was motivated by the technological importance of amorphous materials as well as by the simple, controllable application of ion or electron beams to amorphize these substances. The latter is particularly true when the crystalline-to-amorphous (c-a) phase transition can be induced and observed *in situ* inside a high-voltage electron microscope. Amorphization by electron irradiation is also of special experimental and theoretical interest, because it represents the simplest case in which only the production of Frenkel pairs is involved.

Several models have been proposed to explain radiation-induced amorphization; they are based on various concepts, including chemical disordering [3-6], buildup of lattice defects [2,7-9], and volume expansion [10-11]. Nevertheless, which mechanism is critical in triggering the c-a transition remains to be one of the fundamental questions concerning solid-state amorphizing processes. In a study of electron irradiation-induced amorphization of intermetallic compounds of the Cu-Ti system, Luzzi and Meshii [3,5] suggested that chemical disordering played a key role in amorphization. However, since the properties of point defects produced by irradiation in these compounds are unknown, it was not possible to separate the effect of lattice defects from that of chemical disordering. On the other hand, both chemical disorder and point defects lead to an increase in the volume of the irradiated alloy, and lattice instability could result from a certain volume expansion [10-13].

In the present work, the amorphization of the crystalline CuTi compound was simulated using the molecular-dynamics technique, in conjunction with new interatomic potentials derived from the embedded-atom method. The

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relative importance of chemical disordering and point-defect generation in inducing the c-a transformation was examined.

SIMULATIONAL PROCEDURE

The primary simulation technique employed in the present work was an isothermal, isobaric molecular-dynamics scheme based on a modified version of the computer code DYNAMO [14]. The model system represents the gamma-phase CuTi compound, having the B11 structure and containing 576 atoms, equally divided between Cu and Ti. It was maintained at 160K and at zero pressure. The interactions between atoms in the lattice were governed by appropriate potentials developed for Cu, Ti and CuTi, using the approach of Oh and Johnson [15] which is based on the embedded-atom method [16]. The heat of solution of 0.0975 eV/atom [3] and the equilibrium atomic volume of 14.22 Å^3 of the compound were fitted to within ~10%, and the calculated lattice constants were within 0.3% of the experimental values [17], a = 3.108 Å and c = 5.887 Å. More details for the derivation of interatomic potentials for Cu, Ti and the compound CuTi are given elsewhere [18].

The effect of chemical disordering on the structural stability of the system was investigated by switching atoms in the lattice. A perfect lattice was equilibrated for 500 time steps ($\Delta t = 2\times10^{-15}$ s) and then every 20 time steps, a random pair of Cu and Ti atoms was exchanged. The system configuration, defined by the system edge lengths and the atom positions and velocities, was periodically saved during the switching process. The configurations were subsequently allowed to evolve for 6000 time steps, long enough for the volume and energy to achieve equilibrium. To simulate the effect of Frenkel-pair generation, on the other hand, a randomly selected atom was removed (creating a vacancy) and then reinserted at a random position (forming an interstitial). To prevent high potential-energy configurations from excessively heating the system or causing numerical instabilities, the interstitial atom was inserted at least 1.5 Å from any other atom (slightly more than half the nearest-neighbor distance) and the system was partially relaxed using an energy minimization scheme. As with the atom switching, the system configuration was also saved periodically and subsequently equilibrated for 6000 time steps in separate runs. The equilibrated systems were analyzed by comparing their volumes, total energies, and pair-correlation functions g(r) with those of the perfect lattice.

RESULTS AND DISCUSSION

Effect of Chemical Disorder

Figure 1A shows the variations of the system volume and energy with atom switching. As the number of switches was increased, the volume smoothly increased to a value ~1.7% larger than that of the perfect lattice and then decreased slightly. Similarly, the system energy approached a value corresponding to ~0.04 eV/atom higher than the perfect-lattice energy. The long-range order parameter S, defined as $S = (p - f)/(1 - f)$ with p being the probability of finding an A-type atom (A = Cu or Ti) on an ordered lattice site and f the molar fraction of A atoms in the system, was found to be 0.13 and ~0 after 300 and 600 random switches, respectively. It is recalled that S = 1 for the perfectly ordered state and S = 0 for the complete chemical disorder. The calculated volume expansion is close to the experimental value observed at the onset of amorphization in Zr_3Al [13], and is almost twice the value obtained for $NiZr_2$ by molecular-dynamics simulation [6]. Nevertheless, amorphization was not found after switching in the present work. This is evident by comparing curve B obtained after 600 switches and curve A for the perfect lattice in Fig. 2. Although switching has reduced and even eliminated some of the peaks observed for the perfect lattice, a definite structure still remains, indicating that the system was only chemically disordered.

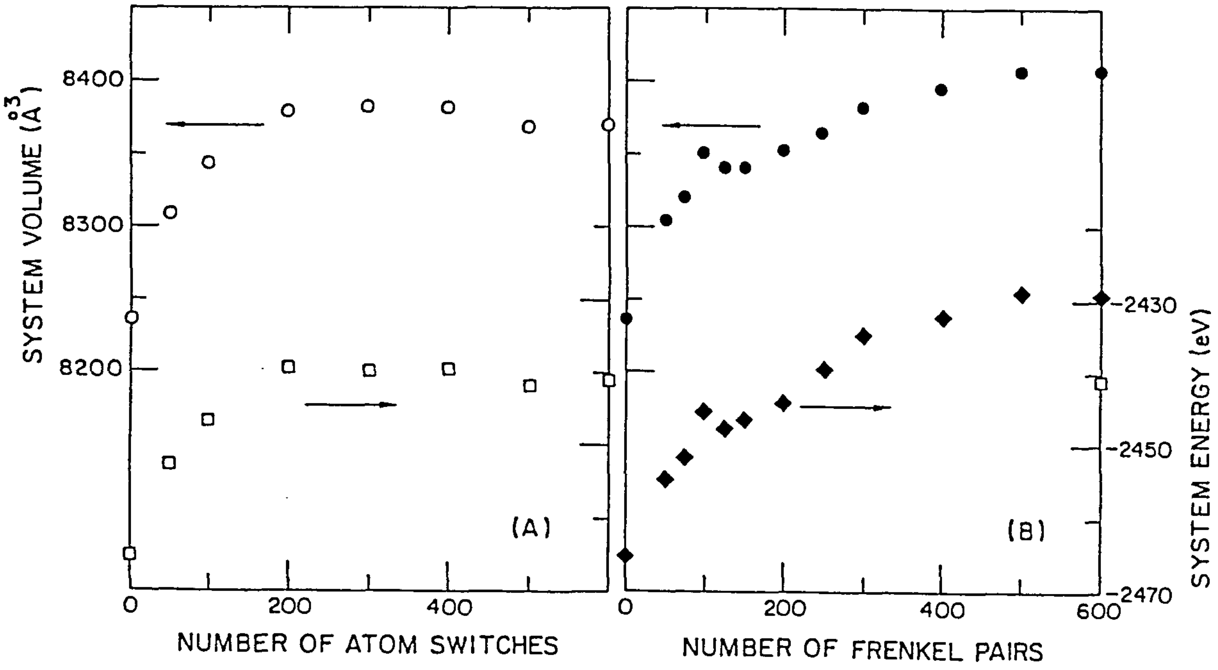

Fig. 1. System volume and energy as functions of the number of atom switches (A) and the number of Frenkel pairs (B).

Effect of Frenkel-Pair Generation

Figure 1B illustrates the dependence of the system volume and energy on Frenkel-pair introduction. These two quantities first increase rapidly and then slowly approach saturation values which are significantly larger than those obtained by simple atom switching. The maximum volume expansion achieved after 600 Frenkel pairs is ~2.0%, and the corresponding energy increase is ~0.06 eV/atom. The evolution of the structure during the introduction of point defects is shown by curves C and D in Fig. 2. After 250 Frenkel pairs (curve C), the system becomes chemically disordered; some of the peaks in the perfect-lattice g(r) can still be seen. However, after 400 or more Frenkel pairs (curve D), g(r) shows features characteristic of a quenched CuTi liquid (curve E), indicating that amorphization has occurred. The damage dose for the onset of amorphization is thus taken to be ~400/576 ≃ 0.7 displacement per atom (dpa). The volume expansion corresponding to this critical dose is ~1.9%. These results are in good agreement with recent experimental observations [13,19].

Since the introduction of Frenkel pairs was found to trigger amorphization in CuTi, one may ask whether lattice defects would also cause pure Cu and Ti to become amorphous. In order to answer this question, the calculations were repeated on pure 500-atom Cu and 512-atom Ti systems. It was found that even after 500 Frenkel pairs were introduced, the equilibrated systems remained crystalline, in accord with the experimental observations that pure metals cannot be amorphized by irradiation.

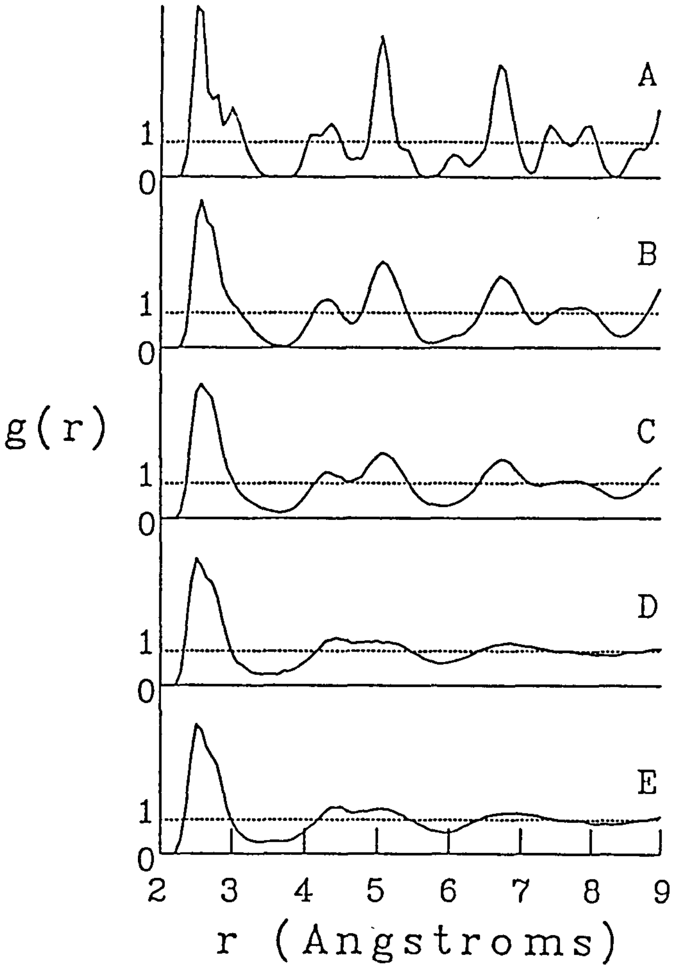

Fig. 2. Pair-correlation functions of the CuTi system at 160 K. Curve (A) is for the perfect lattice. The other curves are for configurations after the following treatments: (B) 600 random switches; (C) 250 Frenkel pairs; (D) 400 Frenkel pairs; and (E) quenched CuTi liquid from 4000K.

Discussion

To summarize the results for all calculations of g(r), we define a norm

$$G = \int_0^\alpha r^n[g(r) - 1]^2 \, dr,$$

which is a measure of the deviation of a particular g(r) from that of a perfectly random system [i.e., from g(r) = 1]. Using $n = 2$ and $\alpha = 9.0$ Å (the maximum distance at which g(r) was determined), we calculated G as a function of the number of atom switches or Frenkel pairs. Figure 3 shows the values of G, normalized such that G for the perfect lattice is unity. It is seen that G decreases rapidly initially and attains steady-state values at large numbers of atom exchanges or point defects. The onset of amorphization can be associated with $G \simeq 0.18$, achieved after ~400 Frenkel pairs.

The effects of point-defect introduction observed in the present work agree with the experimental observation that CuTi can be amorphized by electron irradiation [4,19]. The findings that atom switching did not cause amorphization conflict with the model proposed by Luzzi and Meshii [5] who stressed the importance of chemical disorder, on the basis of observations in electron-irradiated alloys. However, it is not possible in experiments to induce chemical disorder without also producing lattice defects. On the other hand, the CuTi structure studied in the present work has a special symmetry which may preclude amorphization from atom exchanges. If all the Cu and Ti atoms were exchanged with each other and the system allowed to relax, the original structure, slightly translated, would be obtained. This is not true in general for other compounds whose compositions are not 50-50. This may also explain why Massobrio et al. [6], who simulated $NiZr_2$, observed amorphization by atom exchanges, in contradiction with the present study. In their work, only the effect of chemical disordering was simulated, by simultaneously exchanging a number of atoms corresponding to a chosen value of S and then relaxing the system. This way of switching atoms is quite different from the procedure adopted in the present work, because our atom switching was done rather slowly, allowing enough time between switches for the system to relax somewhat. This difference, however, was not the cause for the discrepancy between our and Massobrio et al.'s findings since, by performing 500 random switches simultaneously and then equilibrating, we obtained the same result as with the slow rate of switching. It should be pointed out that in the study of Massobrio et al. [6], amorphization was observed up to S = 0.6, with a corresponding volume expansion of ~1%. These values are approximately a factor of two larger and smaller, respectively, than those measured experimentally on Cu_4Ti_3 [3,20] and Zr_3Al [12,13].

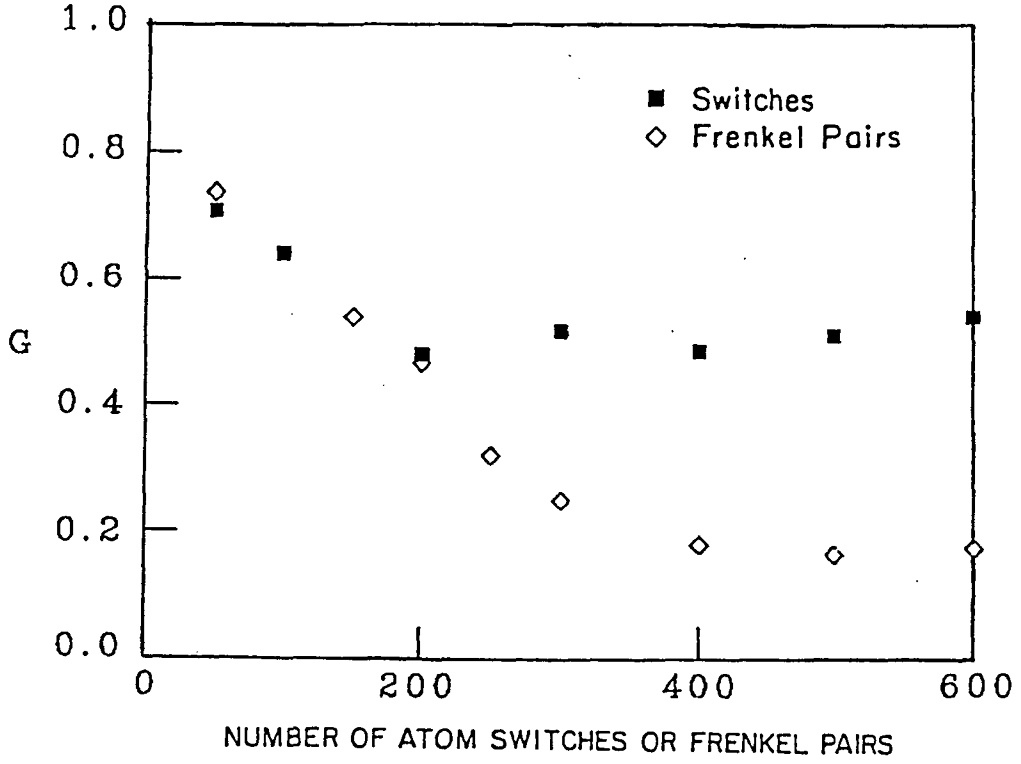

Fig. 3. Normalized G plotted versus the number of atom switches or Frenkel pairs.

CONCLUSION

Solid-state amorphization induced by chemical disordering and nonequilibrium Frenkel defects in the crystalline compound CuTi was computer-simulated, using new embedded-atom potentials in conjunction with isobaric-isothermal molecular dynamics. The potential energy, volume expansion and pair-correlation function were calculated as functions of random atom exchanges and atom displacements. It was found that chemical disordering alone cannot lead to amorphization and that the presence of Frenkel pairs is essential to induce the crystalline-to-amorphous transition. The onset of amorphization occurs when the system volume is expanded by ~1.9%, due to a damage dose of ~0.7 dpa, in general agreement with experimental observations.

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