MOLECULAR DYNAMICS SIMULATION OF RADIATION-INDUCED
AMORPHIZATION OF THE ORDERED COMPOUND NiZr₂

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MOLECULAR DYNAMICS SIMULATION OF RADIATION-INDUCED AMORPHIZATION OF THE ORDERED COMPOUND NiZr₂

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ABSTRACT

We have studied the electron irradiation-induced amorphization of the ordered intermetallic compound NiZr₂ by molecular dynamics simulations in conjunction with embedded-atom potentials. Randomly chosen Frenkel pairs and chemical disorder were introduced into the system in separate processes. In both cases, the energy and volume of the system rose above the corresponding levels of a quenched liquid and the calculated diffraction patterns indicated the occurrence of a crystalline-to-amorphous transition. In addition, the average shear elastic constant fell to about 50% of its value in the perfect crystal and the system became elastically isotropic. These results indicate that NiZr₂ can be amorphized by chemical disorder as well as Frenkel pairs and are in good agreement with experimental observations.

INTRODUCTION

Electron irradiation-induced amorphization of intermetallic compounds has been extensively studied over the last decade, because it produces damage that is simple and representative of solid-state amorphization [1-7]. Irradiation by MeV electrons, usually inside a high voltage electron microscope, merely produces Frenkel pairs and chemical disorder. Despite this simplicity, the relative importance of these two forms of damage has been a subject of considerable debate. Mori and Fujita [2] irradiated the B₂ compound NiTi with 2 MeV electrons at 190 K and observed the formation of small amorphous islands along dislocation lines. Based on this, they concluded that the crystalline-to-amorphous (c-a) transition in NiTi is governed by the buildup of a critical concentration of vacancies. By contrast, Limoge and Barbu [3] suggested that the c-a transition is induced by high densities of interstitials, and attributed the amorphization mode around the critical temperature to the onset of interstitial migration. On the other hand, Luzzi et al. [4] have obtained evidence in favor of chemical disorder as a driving force for amorphization. The authors found a remarkable coincidence of the critical temperatures for amorphization and chemical disorder in Cu₄Ti₃ irradiated with 2 MeV electrons.

The controversy surrounding the mechanism of amorphization is rooted in the inability to experimentally isolate the effects of Frenkel pairs from those of chemical disorder. This drawback can be overcome by performing computer simulations of the effects of chemical disorder and randomly-introduced Frenkel pairs on the structure and properties of intermetallic compounds. However, due to the lack of realistic potentials for intermetallic compounds, most simulations performed to date have dealt only with pure metals. Sabochick and Lam [5] and Lam et al. [6] have used embedded atom potentials to study the amorphization of Cu-Ti compounds. They have concluded that, although chemical disorder leads to a large energy increase, point defects are necessary to amorphize these compounds. In contrast, Massobrio et al. [7] found, using tight-binding potentials, that chemical disorder is sufficient to amorphize NiZr₂. The role of Frenkel pairs was not examined in this study. In an effort to improve our understanding of the driving force for amorphization, we have performed a systematic molecular dynamics study of the effects of chemical disorder and Frenkel pairs in NiZr₂ using embedded-atom potentials developed for Ni-Zr compounds. In this report, we present our results from a detailed examination of the changes in the structural, chemical, thermodynamic and mechanical properties of NiZr₂ following Frenkel pair introduction and chemical disorder.
The molecular dynamics simulation was performed at constant temperature and pressure using a vectorised version of the DYNAMO computer code [8]. The simulation cell was rectangular and contained 256 atoms of Ni and 512 atoms of Zr. The model lattice of the C16 compound NiZr$_2$ is shown in Fig. 1. The interactions between the atoms were modeled by embedded-atom potentials developed using the method of Oh and Johnson [9]. The potentials for Ni and Zr were fitted to the lattice constants, elastic constants and vacancy formation energies of the pure metals. The potential for Ni-Zr interactions was then obtained by fitting to the lattice constants, elastic constants and heats of formation of three intermetallic compounds, namely, NiZr, NiZr$_2$ and Ni$_3$Zr in such a way that the correct equilibrium structures were stabilized. The details of the fit are given elsewhere [10]. The potential was tested by calculating the melting point of a crystal with a void at the center produced by the removal of 6 Ni and 12 Zr atoms. Melting occurred between 1300 and 1350 K in good agreement with the experimentally determined value of 1393 K [11].

The perfect crystal configuration was equilibrated for 5000 time steps. Electron irradiation was simulated in two separate runs: by randomly exchanging Ni and Zr atoms and by introducing Frenkel pairs every 10 time steps. During both these processes, the configurations were periodically saved and subsequently equilibrated for 10000 steps. The mechanical, thermodynamic and structural properties corresponding to various damage doses were obtained as averages over the next 20000 steps. The dose is defined as the number of Frenkel pairs per atom - also referred to as displacement per atom (dpa) - for the case of Frenkel pairs, and as the number of exchanges per atom (epa) for the case of exchanges. In addition, the properties of a system quenched to 30 K from the liquid state at 4000 K were also calculated. Throughout the simulation, a time step of $2 \times 10^{-15}$ s was used.

Fig. 1. The ordered structure of NiZr$_2$
RESULTS AND DISCUSSION

Figure 2 is a composite showing the changes in the [001] atom projections, calculated [001] diffraction patterns, energy increase per atom, volume expansion and shear elastic constants of NiZr$_2$ following random atom exchanges. The diffraction patterns were obtained by using the configurations from our molecular dynamics simulations as input in a multislice calculation [12].
The calculated diffraction patterns were used in place of the conventional pair-correlation function because the latter is not sensitive to structural changes preceding amorphization. The doses are indicated on the diffraction patterns and are also shown by arrows on the dose axis of the energy plot. Both the atom projections and diffraction patterns indicate that NiZr$_2$ can be amorphized by chemical disorder. At a dose of 0.16 epa, a continuous halo appears in the diffraction pattern and the atom projections exhibit considerable topological disorder. The long-range order parameter $S$ was also determined for doses up to 0.12 epa. $S$ is defined as

$$ S = \frac{f - r}{1 - r} $$

where $f$ is the fraction of Ni atoms on Ni sites and $r$ is the fraction of Ni atoms in the system. $S$ decreased to about 0.6 at 0.12 epa. This is in good agreement with the experimental value prior to amorphization of about 0.5 reported by Xu et al. [13].

Further evidence in favor of amorphization by chemical disorder is provided by the thermodynamic properties calculations. The energy increases monotonically with exchange dose, reaches the level of the quenched liquid (indicated by the dotted line) at about 0.13 epa, and saturates at that value. The volume expansion shows a behavior that is remarkably similar to that of the energy change. The lattice dilation upon amorphization agrees with experimental observations [13]. The behavior of the thermodynamic properties suggests that the volume expansion is a reliable measure of energy change in this process. In addition to these properties, the shear elastic constants of NiZr$_2$ were calculated using the method of Ray et al. [14]. In Fig. 2, $C_{44}$ denotes the average of $C_{44}$, $C_{55}$ and $C_{66}$, while the elastic constant $C'$ was determined using the expression

$$ C' = \frac{(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{13})}{6} $$

$C_{44}$, $C'$ and their average $C_{\text{avg}}$ decrease rapidly with dose and drop by 50% at a dose corresponding to the appearance of a continuous halo in the diffraction pattern. In addition, $C_{44}$ and $C'$ become equal to each other indicating that the system is elastically isotropic. This evidence is consistent with the changes in the structure, energy and volume, and shows conclusively that chemical disorder can bring about amorphization in NiZr$_2$.

Figure 3 is a composite illustrating the effect of Frenkel pair introduction on NiZr$_2$. The [001] atom projections, calculated [001] diffraction patterns, energy increase per atom, volume expansion, and shear elastic constants are shown for various displacement doses. As the dose increases from zero to 0.2 dpa, the atom projections exhibit considerable disorder, and a complete halo appears in the calculated diffraction patterns. Correspondingly, the energy and the volume increase monotonically and reach the level of the quenched liquid. The average shear elastic constant drops to about 50% of its value in the perfect crystal and the system becomes elastically isotropic. This indicates that NiZr$_2$ can also be amorphized by the introduction of Frenkel pairs.

The effect of chemical disorder on NiZr$_2$ is consistent with the results of Massobrio et al. [7] for NiZr$_2$. However, it is different from that observed in CuTi by Sabochick and Lam [5] who concluded that chemical disorder is insufficient to amorphize CuTi. In order to understand this apparent discrepancy, we have determined the energies of formation of a Frenkel pair and a pair of anti-site defects in a perfect crystal of NiZr$_2$ using the approach of Shoemaker et al. [15]. These values were found to be 2.75 eV and 2.17 eV respectively. In CuTi, which can be amorphized by Frenkel pairs but not by chemical disorder, the corresponding values are 2.79 eV and 0.38 eV. Since the anti-site defect energy is much larger in NiZr$_2$ than in CuTi, chemical disorder leads to amorphization in NiZr$_2$ but not in CuTi.

The results of our simulation can be compared with the experimental work of Xu et al. [13]. These authors irradiated NiZr$_2$ with 1 MeV electrons in the temperature range 20 K - 100 K. They observed complete amorphization at a dose of about 0.2 dpa. The values of the volume expansion following amorphization and the long-range order parameter prior to amorphization reported (5.4% and 0.5, respectively) are in agreement with our observations. In experimental irradiation studies, the volume change can be easily determined in contrast to the energy change.
The remarkable similarity in the behavior of the energy and volume seen in our simulations indicates that the volume change can be taken as a reliable measure of the energy change.

Fig. 3. The effect of Frenkel pair introduction on NiZr$_2$
CONCLUSIONS

We have used molecular dynamics simulations to examine electron irradiation-induced amorphization of the ordered C16 intermetallic compound NiZr2. Our results indicate that NiZr2 can be amorphized by chemical disorder as well as introduction of Frenkel pairs. In both cases, the energy and volume of the system rise above the corresponding quantities of the quenched NiZr2 liquid and saturate at these values. The calculated diffraction patterns and atom projections indicate the occurrence of a crystalline-to-amorphous transition. The long-range order parameter S decreases to about 0.6 prior to amorphization. The critical dose for amorphization was found to be about 0.2 dpa. At this dose, the average shear elastic constant drops to about 50% of its original value, and the system attains elastic isotropy, indicating complete amorphization. An examination of the energetics of defect formation provides an explanation for the difference in the effects of chemical disorder in Ni2x2 and CuTi. Our results are in general agreement with the experimental observations of electron irradiation-induced amorphization of NiZr2.

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REFERENCES