PHYSICAL REVIEW B VOLUME 47, NUMBER 17 1 MAY 1993-I

# Kinetics of radiation-induced disordering of $A_3B$ intermetallic compounds: A molecular-dynamics-simulation study

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(Received 10 September 1992)

Intermetallic compounds are susceptible to disordering when exposed to irradiation with energetic particles. However, the atomistic mechanisms of this process are not fully understood. We present molecular-dynamics studies of the kinetics of disordering induced by 5-keV energetic displacement cascades in $Cu_3Au$ and $Ni_3Al$. Our results show that the underlying crystalline structure is lost in the local region of the cascade core. However, kinetic constraints imposed by the fast quenching rate of the cascade region prevent a complete loss of chemical short-range order from occurring. After the cascade energy dissipates, the Bragg-Williams long-range-order parameter in the central region is found to have a value near zero. The shape of the interface between the cascade-induced disordered region and the surrounding ordered lattice is shown to depend on the ordering energy of the irradiated compound.

Disordering of intermetallic compounds is known to occur during low-temperature irradiation with electrons, neutrons, or ions.[1] Electron irradiation introduces point defects in the lattice via replacement collision sequences (RCS's), which result in disorder along ⟨110⟩ directions in $L1_2$ intermetallics.[2] Irradiation with heavy ions or fast neutrons generates displacement cascades with large locally molten transient cores[3] and produces point and extended defects via RCS's and other mechanisms.[4] Such disordering and defect production processes control the microstructural evolution of a material in a high radiation environment, thereby affecting such properties as the stability of second phase precipitates[5,6] and the ability of the material to withstand the radiation field. Although the disordering of intermetallic alloys with electron irradiation at low temperature is a well-understood and characterized process, the kinetics of heavy-ion-induced disordering is more complex and not fully understood. In addition to radiation-induced disordering, both electrons and ions can induce a crystalline-to-amorphous transformation in many ordered intermetallics.[7] It is therefore of interest to understand, at an atomistic level, the kinetics of the radiation-induced order-disorder transformation and the defect production mechanisms in intermetallic compounds.

We employ molecular-dynamics (MD) computer simulation to investigate displacement cascades in two intermetallic compounds, $Cu_3Au$ and $Ni_3Al$. We relate the temporal and spatial evolution of the distribution of deposited energy in the model crystallites with the appearance of a disordered zone at the end of the cascade. Defect production mechanisms in these systems are also studied and contrasted with results for pure metals. It is observed that while vacancies agglomerate in the core of the cascade, interstitials are produced as isolated ⟨100⟩ dumbbells via RCS's. Atomic mixing takes place in the cascade region. Diffusion coefficients for both the majority and minority species are seen to be identical indicating that diffusion in the cascade core is not related to a vacancy mechanism in the solid but rather is akin to liquid diffusion.

Displacement cascades induced by 5-keV primary knock-on atoms (PKA's) have been simulated in $Cu_3Au$ and $Ni_3Al$ crystals. These two alloys were chosen because of their different ordering energies; while $Cu_3Au$ undergoes an order-disorder transition below its melting temperature ($T_m$), $Ni_3Al$ remains ordered up to $T_m$. The 5-keV recoils were chosen from atoms of the majority species in both compounds and their direction of motion was specified at random; care was nevertheless taken to insure that the PKA trajectory was not along a channeling or close-packed direction.

We use embedded atom potentials (EAM) from the Sandia group reported in Ref. 8 for Cu and Au, and in Ref. 9 for the Ni-Al system. These potentials have been modified[10] at short ranges to describe high-energy collision events according to the universal scattering potential of Ziegler, Biersack, and Littmark.[11] Of primary interest for this study is the ability of these EAM potentials to reproduce the main features of the phase diagrams. The existence of an order-disorder transformation is predicted by Monte Carlo calculations in $Cu_3Au$ at $T_{o\text{-}d}=380\pm20$ K (to be compared with the experimental value of 663 K) and the melting transition at $T_m\sim1200$ K (experimental value 1213 K). The calculated heat of melting is $\sim0.05$ eV/atom and the latent heat of disordering is found to be $\sim0.035$ eV/atom. For $Ni_3Al$, we found that the solid melts in the ordered phase at a temperature $T_m\sim1600$ K (experimental value 1668 K).

The simulations are performed at 10 K in crystallites containing 157 216 atoms, with periodic boundary conditions at constant volume. Damping of kinetic energy that arrives at the boundary is employed to minimize the effect of energy reentrance into the cascade volume as described elsewhere.[10] The results presented are representative of a total of eight events, four each in $Ni_3Al$ and $Cu_3Au$.

The properties of the elementary point defects predicted by these potentials are similar.[12,13] The pair of antisites in $Cu_3Au$ has a formation enthalpy of 0.27 eV, while in $Ni_3Al$ it is of 1.11 eV, reflecting the higher-ordering energy in the latter. Interstitial properties in $Cu_3Au$ are analogous to those reported for $Ni_3Al$.[12] The Cu-Cu dumbbell contained in a Cu-plane has the lowest formation enthalpy, 1.25 eV, while that for the Au-Au dumbbell is 3.22 eV. The mixed Cu-Au dumbbell, with Au the extra atom (2.37 eV), is higher in energy than a Cu antisite plus a Cu-Cu dumbbell.

Radial temperature profiles at several times in the evolution of 5-keV PKA displacement cascades in $Cu_3Au$ and $Ni_3Al$ are shown in Figs. 1(a) and 1(b), respectively. Temperature is defined from the kinetic-energy distributions in the cascade region as $E_k = 3/2 N k_B T$, where $N$ is the number of atoms in the shell under consideration and $k_B$ is Boltzmann's constant. The results show that while in $Cu_3Au$ a region corresponding to a volume of 3400 atoms is at an effective temperature above $T_m$ at $t = 1$ psec, a volume of only 1500 atoms is at $T > T_m$ at $t = 1$ psec for the $Ni_3Al$ case. The temporal and spatial evolution of these profiles indicate that while a region of $R \approx 20$ Å remains above the melting point for approximately 4 psec in $Cu_3Au$, such a region quenches to a temperature below $T_m$ at $t \approx 2$ psec for 5-keV PKA cascades in $Ni_3Al$. This is a consequence of the fact that, as discussed above, the melting point of $Cu_3Au$ is 400 K lower than that of $Ni_3Al$. Additionally, the cooling rate in the core of the cascade (defined as $R = 4a_0$ for both types of events, where $a_0$ is the value of the lattice parameter) is about a factor of 2 larger in the case of $Ni_3Al$ than $Cu_3Au$ at times between 2 and 3 psec.

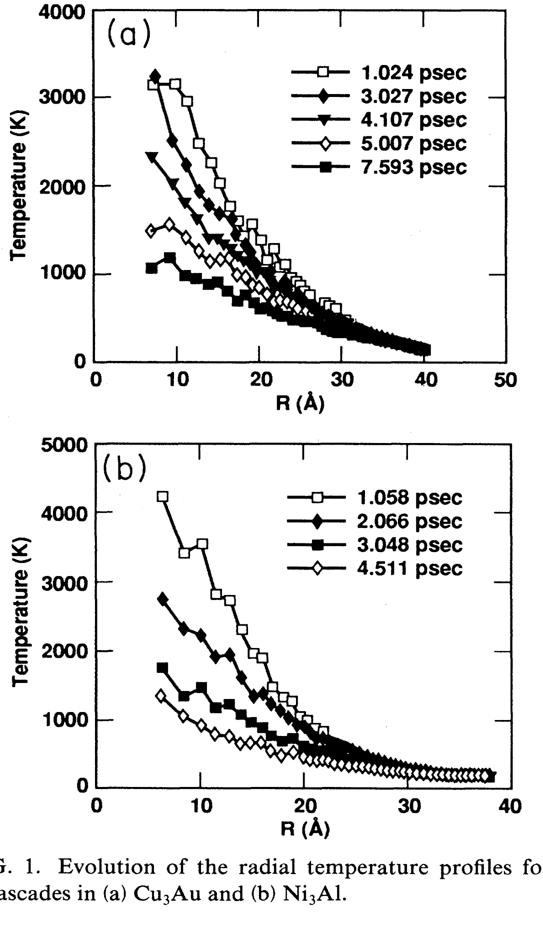

FIG. 1. Evolution of the radial temperature profiles for 5-keV cascades in (a) $Cu_3Au$ and (b) $Ni_3Al$.

The mean-square displacement in the core of the cascades is defined as the sum of the atomic displacement of all the atoms that have moved beyond the volume of their Wigner-Seitz cell (defined for a perfect crystal). Our results show that the mobility of both the majority (Ni, Cu) and minority (Al, Au) species is identical. These results are in good agreement with recent experimental studies of ion beam mixing and radiation-enhanced diffusion in $Cu_3Au$ by Lee, Averback, and Flynn[14] who concluded that at low temperatures, the ion-beam-induced diffusivities in the Cu and Au sublattices were identical; this indicates that the diffusion mechanisms in the cascade core are not related to vacancy migration in the solid since in that case different diffusivities for Ni and Al atoms would be expected. Atomic diffusion induced by the cascades results in the formation of large numbers of antisite defects in these intermetallic compounds. In $Cu_3Au$ approximately 420 antisite defects are present in the lattice at the end of an event and typically approximately 180 antisite defects are found in cascades in $Ni_3Al$. Such large numbers of antisite defects are evidence of the efficiency of displacement cascades to induce disorder in these compounds.

In order to study the temporal evolution of the structure and the chemical order in the cascade regions, we define the short-range-order (SRO) parameter in its usual manner, i.e., in terms of the fraction of nearest neighbors to an atom of the minority species in the solid phase. This number is 12 for the ordered $L1_2$ compound and 8 for the random alloy. By using the SRO parameter we are able to follow the kinetics of disordering in the liquid phase. In addition, we define a crystallinity order (CO) parameter that follows the evolution of the underlaying fcc lattice. This parameter is defined in terms of the fraction of atoms that are inside cubes of side length $a_0/4$ centered on perfect lattice positions, regardless of their chemical nature. In the crystalline phase all atoms fall into this category, while in the liquid phase 50% belong to the complementary half-space defined by cubes centered midway between second-neighbor lattice sites. These two order parameters for both compounds are plotted in Figs. 2(a) and 2(b). Atoms inside a sphere of $8a_0$ (which fully encloses the cascades in both cases) contribute to their definition. The significant difference between the evolution of the CO and SRO parameters in both the $Cu_3Au$ [Fig. 2(a)] and $Ni_3Al$ [Fig. 2(b)] cases constitutes one of the main results of this work, namely, that although the crystalline order is lost to a large extent

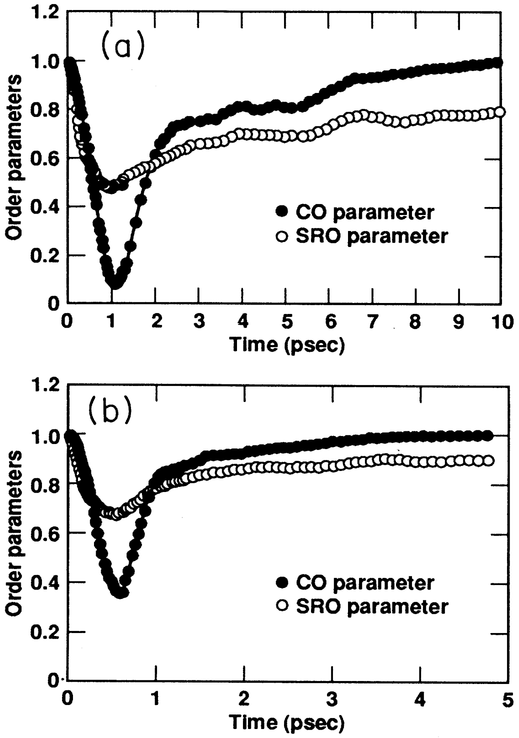

FIG. 2. Temporal evolution of the crystalline and short-range-order parameters in (a) $Cu_3Au$ and (b) $Ni_3Al$ (see text for definitions).

in the cascade region at times of $\approx 0.5$ psec (in the $Ni_3Al$ events) and 1 psec (in the $Cu_3Au$ cases) after the PKA, the chemical short-range order decreases to minimum values of only 0.68 and 0.48 in $Ni_3Al$ and $Cu_3Au$, respectively. Despite the high atom mobilities in the core of the cascades which leads to a loss of the underlying crystalline structure, the short lifetime of the cascade inhibits a complete loss of chemical short-range order.

Figure 3 shows the final value of the Bragg-Williams long-range-order (LRO) parameter as a function of distance from the center of cascades in $Cu_3Au$ and $Ni_3Al$. At the maximum extension of the molten zone ($R = 16$ Å for $Ni_3Al$ and $R = 22$ Å for $Cu_3Au$) the value of the long-range-order parameter is 0.8 in both cases. It is interesting to note that inside this volume defined by the approximate position of the liquid-solid interface ($R_{1-s}$, taken to be the interface between the volume of material at a temperature above the melting point of the alloy and that below), both curves are similar when the abscissa is normalized by $R_{1-s}$. The finite gradient of the order parameters reflects the combined influence of the large temperature gradients in the cascade core and the short lifetime of the liquid. In fact, not all of the liquid zone becomes disordered, but in a small shell of thickness $\sim 5$ Å close to the interface the LRO parameter changes smoothly from $\sim 0.8$ to $\sim 0$. In this shell, although the crystalline order is lost during the spike, some short-range order is partially preserved, as discussed in the previous paragraph. We also note that, as expected, no segregation was found in any of the events studied. Also interesting is the behavior outside the melt. In $Ni_3Al$, with high-ordering energy, the LRO parameter recovers the value 1 in a shell of about 5 Å, whereas in $Cu_3Au$ this shell is almost 15 Å thick. This latter fact appears to indicate the existence of a small disordering effect in the solid phase at the cascade periphery. In the case of $Cu_3Au$ this gives rise to a region of radius 35 Å which is perturbed by the cascade and shows an order parameter which varies smoothly between 0 and 1. The size of this disordered region is in good agreement with experimental observations of Black *et al.*[15] who employ transmission electron microscopy (TEM) to study disordered zones generated by 50-keV Cu ions in $Cu_3Au$ at 30 K and find their radius $36 \pm 1.0$ Å.

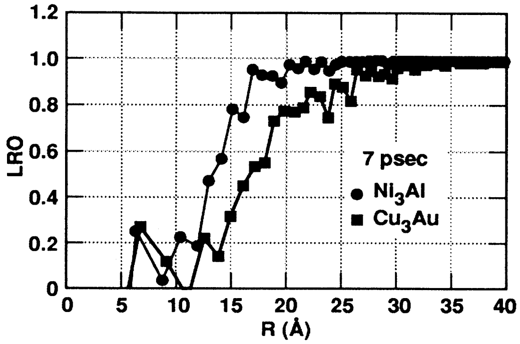

FIG. 3. Radial dependence of the Bragg-Williams long-range-order parameter at the end of 5-keV displacement cascades in $Cu_3Au$ and $Ni_3Al$.

The number and state of clustering of defects produced during irradiation with energetic particles control the microstructural evolution of a material. The results of our simulations indicate that the number of Frenkel pairs produced by 5-keV cascades in $Cu_3Au$ and $Ni_3Al$ are in good agreement with the experimentally observed defect production efficiency in metals.[16] For $Cu_3Au$, the efficiency in 5-keV cascades is $x = N_{md}/K_{\mathrm{KP}} = 0.255$, where $N_{md}$ is the number of Frenkel pairs obtained in the simulations and $N_{\mathrm{KP}} = 50$ is the number predicted by the modified Kinchin-Pease expression[17] with a value of $E_d = 30$ eV. For the case of $Ni_3Al$, $x = N_{md}/N_{\mathrm{KP}} = 0.15$, where $E_d$ has been taken as 40 eV.[18] Recent computer-simulation results of defect production in pure metals at low temperatures[4,19,20] show that, in addition to vacancy agglomeration in the center of displacement cascades, large clusters of self-interstitial atoms (SIA's) are also found in the cascade periphery. Our results in these two intermetallic compounds show vacancy clusters are produced in the core of 5-keV cascades. These vacancies are found with stoichiometric concentration. However, we have found no evidence for interstitial cluster formation. A majority of SIA's produced (95%) in $Ni_3Al$ are $\langle 100 \rangle$ dumbbells formed by Ni atoms. In $Cu_3Au \approx 80\%$ of SIA's are $\langle 100 \rangle$ Cu-Cu dumbbells. The remaining are mixed $\langle 100 \rangle$ dumbbells in both cases. These are expected to convert to pure $\langle 100 \rangle$ dumbbells at times longer than those to which these simulations have been extended to.

In summary, our results describe the kinetics of radiation-induced disordering by high-energy displacement cascades at an atomistic level. We have shown that the loss of the underlying crystalline structure and the loss of the chemical short-range order are controlled by different time scales. While the crystalline order parameter decreases to a value near zero within 1 psec, this time scale is not long enough to allow for a comparable loss of the SRO. We have also found that the ordering energy affects the structure of the interface between ordered and disordered regions leading to a sharp interface in $Ni_3Al$, and a smoother one in $Cu_3Au$.

We gratefully acknowledge Professor R. S. Averback and Dr. M. W. Guinan for fruitful discussions. This work was partially performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48 and partially supported by the Fond National Suisse de la Recherche Scientifique.

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