Amorphization Induced by Chemical Disorder in Crystalline $NiZr_2$: A Molecular-Dynamics Study Based on an n-Body Potential

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(Received 21 November 1988)

We present the first molecular-dynamics study of the amorphization of a crystalline alloy ($NiZr_2$) induced by chemical disorder. We used an n-body potential in conjunction with isobaric-isothermal molecular dynamics. The behavior of the pair distribution function suggests that the instability leading to the amorphous state is a first-order phase transformation.

PACS numbers: 64.70.Pf

Solid-state crystalline-to-amorphous transformations recently received considerable attention[1] due to the possibility they offer to produce bulk amorphous materials and the challenging questions that arise when trying to understand the underlying mechanisms. Various physical processes such as irradiation,[2] interdiffusion[3] annealing,[4] or mechanical alloying[5] are able to transform a crystalline material into an amorphous solid, provided the temperature does not exceed the crystallization temperature of the amorphous system at the same composition. A common feature of these processes is the intimate intermixing of the constituents and the resulting chemical disorder. For systems where important size effects exist the chemical disorder leads to amorphization[6] possibly related to an elastic instability as suggested by recent theoretical work.[7,8] In the following we present the results of a molecular-dynamics (MD) study of the effects of the chemical disorder on the stability of crystalline $NiZr_2$. This alloy is chosen as a model system since it is known to amorphize either by electron beam irradiation[9] or by ball milling.[5]

The structure of the crystal is of the $CuAl_2$ ($C16$) type, a body-centered tetragonal lattice with lattice cell dimensions $a = 0.6483$ nm and $c = 0.5267$ nm at room temperature.[10] Our system consisted of N point particles enclosed in a parallelepipedic box. We studied systems of two different sizes: $3 \times 3 \times 3$ (Ni 108 atoms and Zr 216 atoms) and $4 \times 4 \times 4$ (Ni 256 atoms and Zr 512 atoms) lattice cells. The particles interact via an n-body potential constructed in the framework of the second-moment approximation of the tight-binding scheme, well adapted to transition metals.[11] Accordingly the total energy of the system is given by

$$E = \sum_{\alpha} \sum_{i_\alpha = 1}^{N_\alpha} \left(\sum_{\beta} \sum_{\substack{j_\beta = 1 \\ i_\alpha \neq j_\beta}}^{N_\beta} A_{\alpha\beta} \exp\left[-p_{\alpha\beta} \left(\frac{r_{ij}^{\alpha\beta}}{d_{\alpha\beta}} - 1 \right) \right] \left\{ \sum_{\beta} \sum_{\substack{j_\beta = 1 \\ i_\alpha \neq j_\beta}}^{N_\beta} \xi_{\alpha\beta}^2 \exp\left[-2q_{\alpha\beta} \left(\frac{r_{ij}^{\alpha\beta}}{d_{\alpha\beta}} - 1 \right) \right] \right\}^{1/2} \right),$$

where $r_{ij}^{\alpha\beta} = |\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}|$ and the indices i_α (j_β) run over all the particles. The parameters $p_{\alpha\beta}$, $q_{\alpha\beta}$, $A_{\alpha\beta}$, and $\xi_{\alpha\beta}$ are determined as follows[12]: (i) For $\alpha = \beta$ a fit is performed on the cohesive energy, equilibrium condition, and bulk modulus at zero temperature of the pure elements Ni and Zr. Only nearest-neighbor (NN) contributions at distances $d_{\alpha\alpha}$ are taken into account. (ii) Similarly for $\alpha \neq \beta$ the corresponding parameters are fitted on the elastic constants[13] and the cohesive energy of the alloy and $d_{\alpha\beta}$ is taken equal to the Ni-Zr NN distance in $NiZr_2$. The value of the cohesive energy is obtained from that of the ideal mixture, using the experimental cohesive energies of the pure metals Ni and Zr, modified by including the experimental formation enthalpy of the $NiZr_2$ crystal.[14] To avoid disturbing artifacts of MD related to short-cutoff distances,[15] we empirically extended the range of the potential by including in the fitting procedure interactions up to $r_c = 0.53$ nm. Values of the potential parameters, physical quantities we used for the fit, and a comparison between the experimental and calculated elastic constants of $NiZr_2$ are reported in Table I. A good agreement is obtained between predicted and experimental elastic constants. As expected, our potential reproduces the violation of the Cauchy conditions exhibited by the experimental data. Constant temperature and pressure were obtained by the Nosé-Andersen MD technique.[20,21] The equations of motion were integrated using periodic boundary conditions and a fifth-order predictor-corrector algorithm with a time step $\delta t = 10^{-15}$ s.

The model is further tested by comparing an estimate of its melting temperature with the experimental one $T_m^{\exp} = 1440$ K. This is obtained by computing the atomic mean-square displacement and the potential energy per atom as functions of temperature. For the largest system

TABLE I. Values of the tight-binding potential parameters for NiZr$_2$. The experimental values of cohesive energy E_c, bulk modulus B, and NN distances δ, extrapolated at $T=0$ K, are used for the fit of the potential parameters $p_{\alpha\beta}$, $q_{\alpha\beta}$, $A_{\alpha\beta}$, and $\xi_{\alpha\beta}$. The calculated elastic constants are compared with the corresponding experimental values (in parentheses). E_c, $A_{\alpha\beta}$, and $\xi_{\alpha\beta}$ are expressed in eV/atom, elastic constants in units of 10^{12} dyn cm^{-2}, and distances in nm.

	Ni	Zr	NiZr$_2$
E_c	4.44^a	6.17^b	6.0^c
B	1.88^d	0.97^d	1.19^e
δ	0.249^a	0.3179^f	0.2761^g
C_{11}	2.57 (2.61^d)	1.53 (1.55)^d	1.61 (1.59^e)
C_{12}	1.65 (1.51^d)	0.74 (0.67^d)	1.05 (1.34^e)
C_{13}	⋯	0.55 (0.65^d)	0.95 (0.85^e)
C_{33}	⋯	1.68 (1.73^d)	1.58 (1.47^e)
C_{44}	0.93 (1.32^d)	0.45 (0.36^d)	0.54 (0.24^e)
C_{66}	⋯	⋯	0.61 (0.06^e)
p	10.0	9.3	8.36
q	2.7	2.1	2.23
A	0.1368	0.1615	0.2166
ξ	1.756	2.34	2.139

[a] Reference 16.
[b] Reference 17.
[c] See text.
[d] Reference 18.
[e] Reference 13.
[f] Reference 19.
[g] Reference 10.

we studied, the former (Fig. 1) reaches the value $\langle u^2\rangle = 6.26\times10^{-4}$ nm^2 at $T=T_m^{\rm exp}$, which corresponds to a Lindemann ratio $\delta = 8\%$.[12,22] It is therefore likely that the actual melting temperature of the model is not very different from the experimental one. This assumption is strengthened by the potential energy per atom profile, U, displayed in the same figure. An abrupt change of U is observed at $T\approx1600$ K followed by high diffusion values, $D\approx10^{-5}$ cm^2 s^{-1}, for both constituents thus indicating that melting occurred. Indeed, solid-state diffusion cannot take place in our system since sinks and sources of point defects, such as free surfaces, are absent and the barrier of formation of Frenkel pairs is too high to produce diffusion on the space and time scales of the simulation. Thus the model should melt at $T_m^{\rm model}\leq1600$ K, some overheating being unavoidable for an infinite-extension perfect crystal. The reasonable $\langle u^2\rangle$ value obtained at $T=T_m^{\rm exp}$ and the fact that melting is observed only ≈160 K above $T_m^{\rm exp}$ suggest that the dynamical properties of our model at $T\neq0$ K are not dramatically different from those of NiZr$_2$.

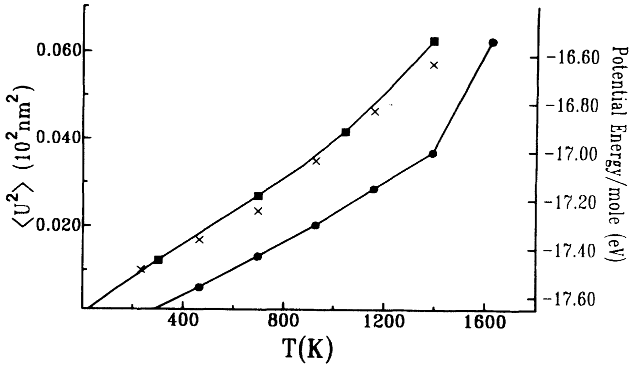

FIG. 1. Variation of the potential energy per molecule (dots) and of the atomic mean-square displacements (squares, $N=768$; crosses, $N=324$) in crystalline NiZr$_2$ as functions of temperature for the two different size systems we studied. The lines are guides for the eye.

To simulate the chemical disorder induced by the aforementioned physical processes leading to the solid-state amorphization, a given number of Ni and Zr atoms, randomly chosen, are instantaneously exchanged in an equilibrated configuration of the system at $T=300$ K. The disorder is conveniently quantified by the long-range-order parameter, $S=(p-r)/(1-r)$, where p and r are, respectively, the probability of presence of an A-type atom ($A=$ Ni or Zr) on an ordered lattice site and the molar ratio of A atoms in the system. Values $S=0$ and 1 correspond, respectively, to the full chemical disorder or to the perfectly ordered crystal. Five values of $S=0.0$, 0.2, 0.4, 0.6, and 0.9 were investigated and the partial and total pair distribution functions of the system, $g(r)$, are computed for each. The immediate effect of this perturbation is a volume increase illustrated in Fig. 2 for different S values. Before the system volume reaches a stationary value, a short relaxation occurs which lasts up to 10^4 time steps for the largest possible perturbation $S=0$. The atomic structures of the perfect and the disordered system differ drastically. The total and partial pair distribution functions, $g(r)$, displayed in Fig. 3 for $S=0.0$, provide a convenient tool to reveal those differences. Many of the peaks characterizing the crystalline structure disappear whereas others are

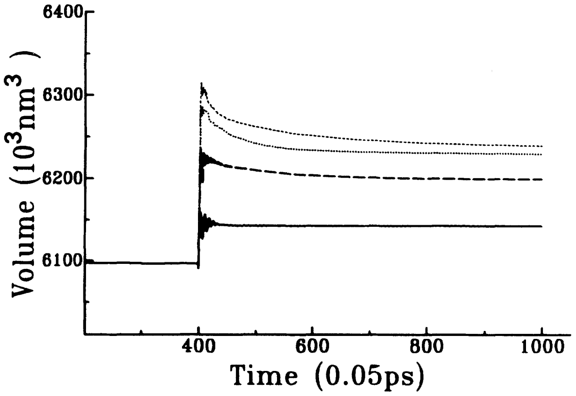

FIG. 2. Average volume of the system at $T=300$ K before and after the chemical disorder is introduced for different values of the long-range-order parameter S. Solid line, $S=0.9$; dashed line; $S=0.6$; dotted line, $S=0.2$; and short-dashed line, $S=0.0$ (bottom to top).

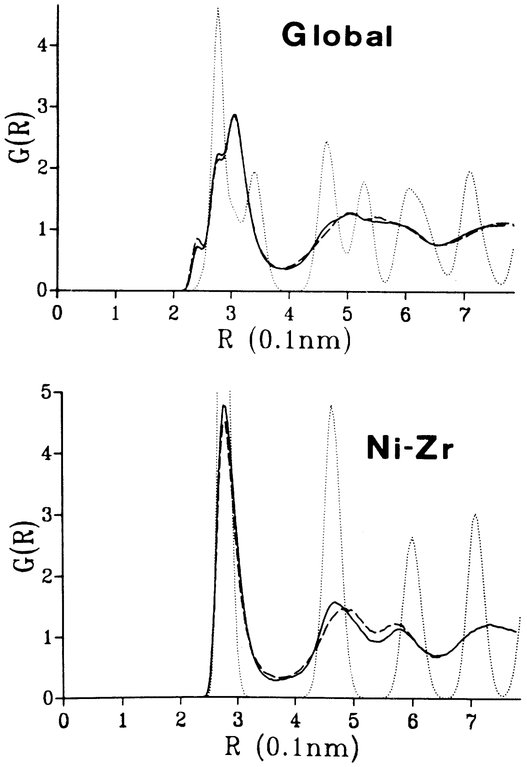

FIG. 3. Partial and global radial pair distribution functions at $T=300$ K averaged over 40 ps. Solid line, after the chemical disorder is introduced into the system, $S=0$; dotted line, crystalline $NiZr_2$; dashed line, quenched liquid.

smeared out, thus suggesting that the system becomes amorphous. This conclusion is qualitatively and to a lesser extent quantitatively confirmed when comparing the $g(r)$ of the rapidly quenched liquid (quenching rate $q=10^{13}$ K/s) at $T=300$ K (Fig. 3). The total $g(r)$ thereby obtained is identical to that of the disordered solid while small differences persist between the corresponding partial pair distribution functions. These differences may be attributed to the different structural relaxations occurring when quenching the liquid or during the amorphization process of the disordered crystal.

The amorphous system we produced is stable against recrystallization on annealing, at least on the time scale of our simulations: No noticeable structural changes are observed over a 4×10^4 time-steps equilibrium trajectory at $T=300$ K. For values of the long-range-order parameter $S<0.6$ amorphization is always observed. However, for $S=0.9$, despite the small volume increase (Fig. 3), the crystal is stable on the time scale of our simulations. The narrow range of S values, $0.6<S<0.9$, separating the stability and instability regions of the crystalline state indicates first-order-like features for the crystal-to-amorphous state transition in $NiZr_2$. Rapid diffusion of one of the components of the alloy, in our case Ni atoms in a Zr crystal, has been invoked as being a necessary condition to decide on whether or not a solid-state amorphization reaction is possible.[3] It is worth noticing that in the present case the amorphization occurs without long-range diffusion and is exclusively due to local relaxations starting when the chemical disorder is introduced into the system.

A comparison of our results with experimental data is possible due to recent work on amorphous $NiZr_2$ prepared by rapidly quenching the liquid[23-25] and to experiments in which ion irradiation induces chemical disorder and the subsequent amorphization of the alloy Zr_3Al.[6] In the former, partial pair distribution functions have been determined by neutron scattering. Although a comparison of the shapes of the experimental pair distribution functions and ours cannot be made, due to the large uncertainties of deconvoluted experimental data, the positions of first- and second-neighbor peaks compare favorably well with our results as shown in Table II. Rehn *et al.*[6] observed the amorphization of the Zr_3Al alloy to occur when the irradiation dose results in a long-range-order parameter value $S\leq0.2$. The volume expansion of their system at the value $S=0.2$ above which amorphization does not occur, $x=\delta V/V\approx2\%$, is close to what we found at the same S value, $x=1.8\%$. However, in the system we studied amorphization is observed up to $S=0.6$ and $x=\delta V/V\approx1\%$, this difference being probably related to the different stability regions of Zr_3Al and $NiZr_2$ crystals. In addition, Rehn *et al.*,[6] as well as previous work,[26] suggested that the solid-state amorphization may be a first-order phase transition monitored by an elastic instability following the chemical disorder. The results of the present study show similarly that strains resulting from the chemical disorder induce amorphization. However, more work is needed to clarify the details of the amorphization mechanism.

We are deeply indebted to G. Evangelakis who made available to us the minimization software MERLIN and

TABLE II. Partial pair distribution peak positions, expressed in nm, and number of nearest neighbors in the amorphous $NiZr_2$ alloy. Comparison of present computations with experimental data (Refs. 24 and 25). Experimental values are given in parentheses.

	First maximum	First minimum	Second maximum	No. of NN
Ni-Ni	0.24 (0.25–0.27)	0.32 (0.33–0.34)	0.45 (0.42)	2.75 (2.3–3.3)
Zr-Zr	0.31 (0.32–0.33)	0.42 (0.40–0.43)	0.52 (0.52)	10.46 (9–11)
Ni-Zr	0.28 (0.27–0.29)	0.37 (0.4)	0.47 (0.45)	3.9 (2.9–4.8)

for his help in elucidating the feature of this software. E. Gaffet, M. Guillopé, B. Legrand, Y. Limoge, and G. Ciccotti are gratefully acknowledged for fruitful discussions. We are pleased to thank Y. Adda for his constant interest in this work.

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