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LETTER TO THE EDITOR

Molecular-dynamics simulation of the amorphization process in Ni–Zr multilayers upon annealing at medium temperatures*

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Abstract. Structural disordering upon annealing of the Ni–Zr multilayers was investigated by molecular-dynamics simulation using an n -body potential. It was found that amorphization was initiated from the interfaces through mutual diffusion and alloying between Ni and Zr layers and that the structure of the resultant Ni–Zr alloy was verified to be indeed an amorphous phase.

Amorphous alloy formation through solid-state interdiffusion of two crystalline metals was first reported by Schwarz and Johnson in the Au–La system in 1983 [1] and has since been studied experimentally by several groups in some other binary systems [2–6]. Meanwhile, to understand the mechanism of crystal-to-amorphous transition at an atomic scale in metal–metal multilayers, molecular-dynamics (MD) simulation has been employed to investigate the amorphization process upon solid-state-reaction [7, 8]. For instance, Weissmann *et al* simulated the Zr–Co superlattice upon annealing and claimed that disordering first emerged at the interface and then propagated to all the Co atomic planes at a temperature as high as 1100 K, yet did not observe any interdiffusion during the disordering process [7]. Experimentally, however, formation of an amorphous alloy phase by solid-state reaction was observed at medium temperatures, indicating an alloying process through long-range mutual diffusion of two constituent metals was necessary [1–6]. To the authors' knowledge, although extensive experimental results concerning solid-state amorphization in the Ni–Zr multilayered films have been reported in the literature [3–6], no MD simulation on the amorphization process upon isothermal annealing, especially at medium temperatures, has hitherto been reported. We therefore undertook a study to perform a molecular-dynamics simulation for a Ni–Zr multilayered model system to reveal the amorphization process at an atomic scale and to find out the role of mutual diffusion in the growth of the amorphous layer upon isothermal annealing at a temperature range of 100 to 400 °C. We report, in this letter, the major results of our MD simulation study.

A Zr–Ni–Zr sandwich model system was constructed for simulating the amorphization process taking place in the real Ni–Zr multilayered films. For simplicity, fcc crystalline layers for Zr were rationally used instead of hcp, as the two crystalline structures are very similar in their atomic configuration and the energy difference between fcc and hcp was quite small. Besides, the fcc Zr structure has already been observed in sputtered films [9].

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The Ni lattice consisted of 972 atoms arranged in the fcc structure with a stacking sequence of 6 [001] atomic planes along the z -direction. One Zr lattice consisted of 392 atoms with 4 fcc [001] atomic planes and the other consisted of 196 atoms with 2 fcc [001] atomic planes both stacking along the z -direction. The sizes of the lattices in the x - y -plane were chosen to make the misfit at the Ni-Zr interface as close as possible to an experimentally measured ratio of their lattice constants. It is known that the nearest-neighbour distances of Zr and Ni atoms are 3.18 and 2.49 Å in their single crystals, respectively, which makes an approximate ratio of 1.277. Within a manageable scale, the numbers of Ni and Zr atoms in their respective planes were selected to be $9 \times 9 \times 2 = 162$ and $7 \times 7 \times 2 = 98$, respectively, resulting in a ratio of $9/7=1.285$, which was quite close to 1.277 of the real situation. In the x - y plane, a periodic boundary condition using the Ni lattice dimension was adopted and a periodic boundary condition was also employed for the z -direction. The size of the computational block in the z -direction was obtained by varying the distance between the Ni and Zr lattices to an optimized value corresponding to a minimum enthalpy for the model system. The established model system therefore represented the Ni-Zr multilayered films.

A many-body potential for the Ni-Zr system derived from the second-moment approximation of a tight-binding scheme by Massobrio *et al* [10] was adopted for simulation. Since only the contributions from the nearest-neighbour atoms were taken into account in fitting their potential parameters [10], the cut-off distances for interactions of the same atoms, i.e. Ni-Ni and Zr-Zr, were set, in our case, to be at the middle of the first- and second-nearest-neighbour distances in the respective Ni and Zr single crystals, while the cut-off distance for the interactions of different atoms, i.e. Ni-Zr, was set to be 5.3 Å, suggested by Massobrio *et al* in their simulation of phase transformation in crystalline NiZr₂ [10]. It should be mentioned that the adopted potential, though involving only nearest-neighbour atomistic interactions, has been employed to perform molecular-dynamics simulations under zero hydrostatic pressure and obtained some thermodynamic properties for pure metals, which were in good agreement with the experimental values up to a melting point temperature of around 0.65 [11]. As our simulations would be confined at temperatures as low as $T \leq 0.5T_m$ (where T_m is the melting temperature), the simulation results based on this potential are therefore relevant. The simulation was carried out with Parrinello-Rahman's constant pressure molecular-dynamics scheme [12]. The equations of motion were solved using a fourth-order predictor-corrector algorithm of Gear with a time step $t = 5 \times 10^{-15}$ s.

The simulation started by equilibrating the model system at room temperature (300 K) for 10 000 MD steps to reach an equilibrium configuration as an initial state. From the initial state, the solid-state reaction 'computer experiments' were performed by first boosting the velocities of the atoms in each time step at a rate of 4×10^{13} K s⁻¹ up to various temperatures ranging from 100 to 400 °C, and then isothermally annealing the multilayers. As the velocities of the atoms would change during annealing, a time-to-time rescaling of the velocities to the assigned temperature was executed at every 100 time steps, if an average deviation from the assigned temperature was over 1 °C. As the velocities of the atoms were not rescaled at each time step to the desired temperature, some thermal fluctuation might occur in the system. During annealing, the structural change of the model system was monitored by the pair correlation function $g(r)$, which was calculated at various times and at each specific time $g(r)$ was obtained by averaging within an interval of 200 time steps.

We now discuss the simulation results obtained by 400 °C isothermal annealing of the Ni-Zr multilayers as a typical example. Figure 1 shows the density profiles, $\rho_\alpha(n)$, of each species along the normal direction, n , perpendicular to the interface at various time steps during annealing at 400 °C. One sees that with an increase in the number of MD time steps

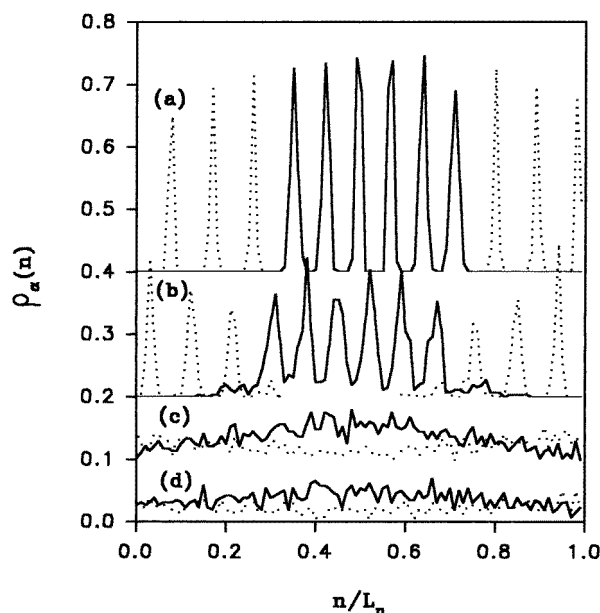


Figure 1. The calculated density profiles, $\rho_\alpha(n)$, of each species along the normal direction, n , perpendicular to the interface for the initial state and another three states obtained after 400 °C annealing at various time steps: (a) the initial state; (b) 400 °C annealing, 6000 time steps; (c) 400 °C annealing, 9000 time steps; (d) 400 °C annealing, 15 000 time steps. $\rho_{Ni}(n)$ is represented by the solid line and $\rho_{Zr}(n)$ by the dotted line. The abscissa is expressed in the scaled coordinates and the ordinate is in arbitrary units. The shift of the peaks of $\rho_\alpha(n)$ is due to the variation of volume of the computational block during annealing and the periodic boundary condition imposed in the z -direction.

more and more Ni (Zr) atoms diffuse into Zr (Ni) lattices and that after 15 000 MD steps run the density profiles $\rho_\alpha(n)$ for Ni and Zr are almost uniformly distributed along the n direction. This clearly indicated that isothermal annealing did result in mutual diffusion. To be precise, mutual diffusion was defined as the crossing-interface movement of either a Ni or Zr atom towards its partner lattice. Figure 2 shows the total and partial pair-correlation functions taken at the same time steps as those in figure 1. One observes that with an increase of annealing time the strength of the Zr–Ni $g(r)$ initial peak increases and the peaks of total Ni–Ni and Zr–Zr $g(r)$ corresponding to the crystalline structure at long distances gradually disappear and that after a 9000 steps run, the pair correlation function curves show the exact shape known for the amorphous states. The pair correlation function curves obtained at 15 000 steps show almost the same shape as those obtained at 9000 steps. These results suggested that the crystal-to-amorphous transition is completed after approximately a 9000 steps run and the resultant amorphous phase is unchanged in the later relaxation of about 6000 steps.

Fig1

To trace the details of the amorphization process upon annealing, the change of coordination numbers was calculated at various time steps by taking the integral of $4\pi\rho_0r^2g(r)$ up to the first minimum, where ρ_0 was the number density of the model system. Figure 3 shows the variation of the coordination numbers versus annealing time. Interestingly, one observes from figure 3 that the Ni–Ni and/or Zr–Zr coordination numbers

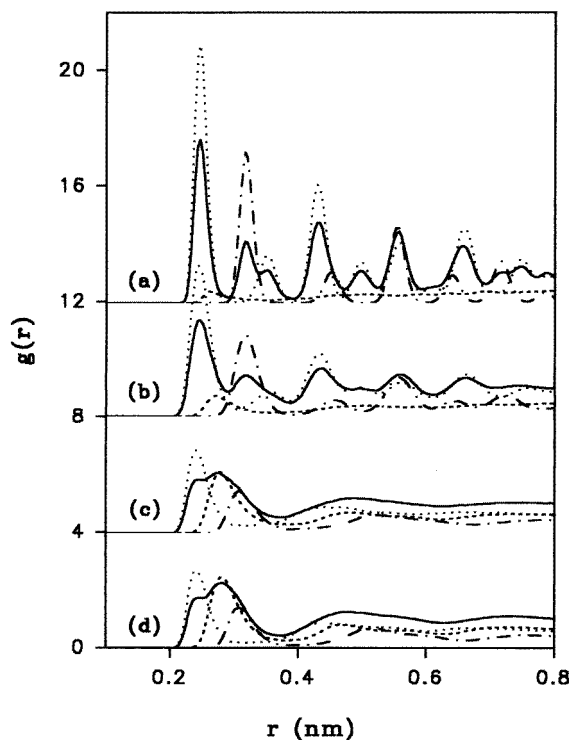


Figure 2. Partial and total pair-correlation functions for the initial state and another three states after 400 °C annealing at the same time steps as those in figure 1. The notations for (a), (b), (c) and (d) are the same as those in figure 1. The solid line is for total $g(r)$; the short dashed line is for Zr–Ni $g(r)$; the dotted line is for Ni–Ni $g(r)$; and the dot-dashed line is for Zr–Zr $g(r)$.

first decrease with increasing time and then remain unchanged after about 9000 MD steps, and that the Ni–Zr and/or Zr–Ni coordination numbers increase with time and reach respective plateaus at approximately 9000 MD steps. These results indicate clearly that alloying activity between Ni and Zr layers has been increased through mutual diffusion with increasing annealing time and that after a 9000 steps run the alloying process has been almost completed, which results in the formation of a uniform amorphous phase in the model system. As the alloying process took place first in the interfacial region, it was of interest to see the effect of alloying on the structural change of the interfacial region in a semi-quantitative way. A local region with one Ni and one Zr single atomic layer next to each other containing one interface was therefore monitored by pair-correlation functions sampling only those atoms within this region. It turned out that the change of the pair-correlation functions of the region as a function of time was similar to that depicted in figure 2, and that amorphization process in this region initiated and completed earlier than those occurring in the whole model system. In other words, our simulation demonstrated that amorphization was initiated from the interfaces through diffusion and alloying and then the formed amorphous interlayer grew to form a uniform amorphous alloy phase in the model system.

A similar simulation was conducted at 100, 200, 250 and 300 °C and the results showed that vitrification in Ni–Zr multilayers was achieved at 250 and 300 °C, but did

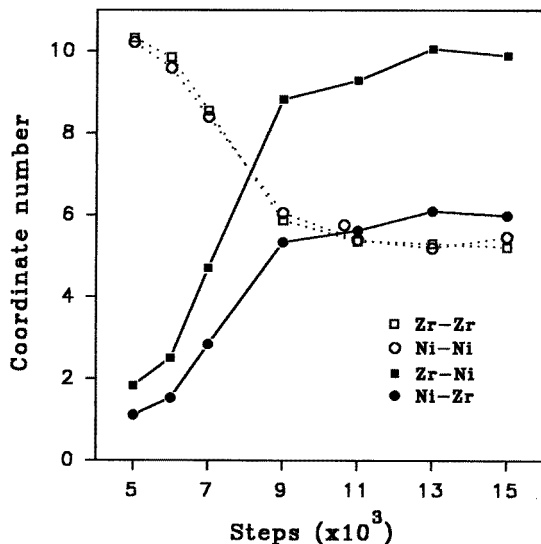


Figure 3. Variation of the coordination numbers versus time step during isothermal annealing of the Ni-Zr multilayers at 400°C.

not occur below 200°C, and that vitrification became much slower when the annealing temperature was decreased. The variations of the enthalpy and volume of the model system versus temperature are displayed in figure 4. One sees that the slopes of both enthalpy and volume are discontinuous around 250°C, which corresponds to the onset temperature for amorphization. The abrupt increase of volume at 250°C is due to the formation of amorphous alloy, which possesses more excess free volume than that in the original multilayers. To confirm this, the annealed state at 400°C was quenched and subsequently equilibrated at room temperature, and the enthalpy as well as the volume of the quenched amorphous phase are also given in figure 4 (solid symbols). One observes that the enthalpy of the amorphous phase is lower than that of the original multilayers while the volume of the amorphous phase has an increase of approximately 1% with respect to that of the original multilayers. The 1% increase of free volume of the amorphous phase is in good agreement with both the proposed model for the amorphous structure having 1.0–2.5% more free volume than that in its crystalline counterpart [13] and some experimental observations [14]. One may notice from figure 4 that with respect to the original multilayers at room temperature, there is a volume increment of about 3% in the annealed state at 400°C, which is believed to be attributed to the thermal expansion together with the formation of amorphous alloy. To illustrate the thermal expansion effect, another Zr–Ni–Zr sandwich constructed with 4 Zr/6 Ni/2 Zr all of fcc (111) atomic planes stacking along the *z*-directions was annealed at various temperatures. It was found that with respect to initial multilayers at room temperature, there were about 2% and 3% volume increases at 400 and 600°C, respectively, and that after thermal annealing at 600°C for 40 000 steps, no solid-state reaction or melting was observed, as both Ni and Zr layers retained their respective crystalline structure. These results suggested that solid-state amorphization was suppressed in such multilayers constructed by close-packed planes in each layer parallel to interfaces, which was in striking agreement with experimental reports that no solid-state amorphization was observed in a Ni/Zr diffusion couple consisting of Ni and a recrystallizing

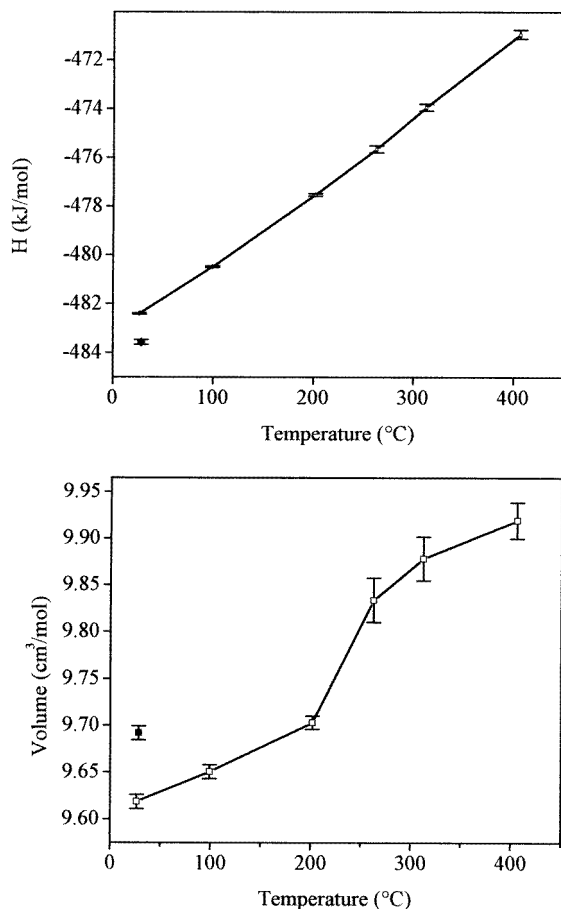


Figure 4. Variations of the enthalpy and volume of the model system versus temperature. Two datum points standing alone in the figure are for a quenched state, which was obtained by quenching and subsequently equilibrating the amorphous phase formed by 400 °C annealing.

Zr foil of close-packed planes parallel to the interface [15, 16].

To further confirm the solid-state amorphization is occurring instead of melting in the multilayers, we performed another simulation by a Zr–Ni–Zr sandwich constructed with 6 Zr/12 Ni /6 Zr all of fcc (001) atomic planes stacking along the z -direction. Two snapshots of atomic positions projected on the x – z -plane during annealing at 400 °C for 20 000 and 40 000 MD steps are plotted in figure 5 and figure 6, respectively. One sees that the mixing interlayer is formed through diffusion-induced alloying and the layers outside still remain a crystalline structure, as no alloying atom has diffused into its partner layer. Furthermore, the pair-correlation functions of the interlayer were calculated by sampling those atoms situated in the interlayer and the results showed that the interlayer was of amorphous structure. Comparing figure 5 and figure 6, one notices that the initial 20 000 steps run causes 2 Ni and 2 Zr original crystalline atomic planes next to one interface to become disordered as shown in figure 5, while further running of another 20 000 steps only results in the extension of the amorphous interlayer by one Ni and one Zr atomic plane as shown in figure 6. The fast diffusion of alloying atoms into their partner lattices at initial stages is attributed to

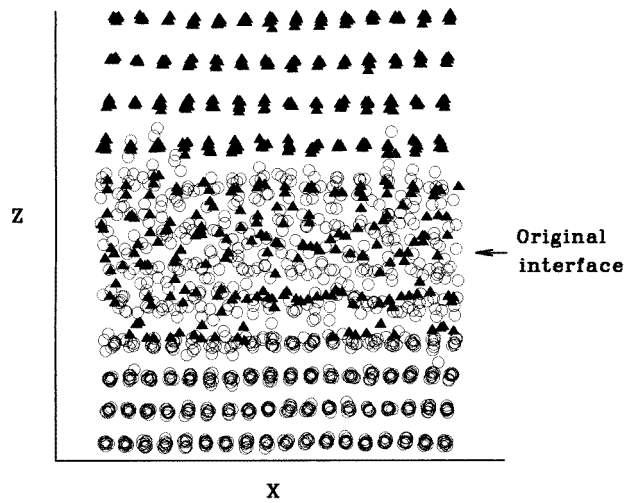


Figure 5. The snapshot of atomic positions projected on the x - z -plane after annealing at 400 °C for 20 000 steps. Only partial atoms around one interface are displayed. The open circles stand for Ni atoms and the solid triangles represent Zr atoms.

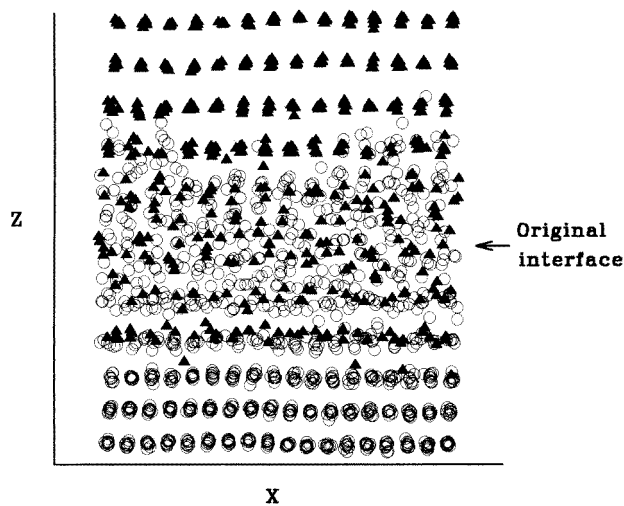


Figure 6. The snapshot of atomic positions in the same region as in figure 5 projected on the x - z -plane after annealing at 400 °C for 40 000 steps.

a great concentration gradient and the growth rate of the amorphous layer, governed by diffusion, decreases with increasing annealing time, which is also in good agreement with experimental observations [3, 4, 6].

In conclusion, the simulation revealed that alloying between Ni and Zr layers was first induced by mutual diffusion upon isothermal annealing and then solid-state amorphization was initiated in the interfacial region. The subsequent growth of an interfacial amorphous layer resulted in the formation of amorphous alloy in the Ni-Zr multilayers.

References

- [1] Schwarz R B and Johnson W L 1983 *Phys. Rev. Lett.* **51** 415
- [2] Schröder H, Samwer K and Koster U 1985 *Phys. Rev. Lett.* **54** 197
- [3] Clemens B M 1986 *Phys. Rev. B* **33** 7615
- [4] Cotts E J, Meng W J and Johnson W L 1986 *Phys. Rev. Lett.* **57** 2295
- [5] Meng W J, Fultz B, Ma E and Johnson W L 1987 *Appl. Phys. Lett.* **51** 661
- [6] Meng W J, Nieh C W and Johnson W L 1987 *Appl. Phys. Lett.* **51** 1693
- [7] Weissmann M, Ramírez R and Kiwi M 1992 *Phys. Rev. B* **46** 2577
- [8] Mura P, Demontis P, Suffritti G B, Rosato V and Vittori Antisari M 1994 *Phys. Rev. B* **50** 2850
- [9] Chopra K L, Randlett M R and Duff R H 1967 *Phil. Mag.* **16** 261
- [10] Massobrio C, Pontikis V and Martin G 1989 *Phys. Rev. Lett.* **62** 1142
- [11] Rosato V, Guillopé M and Legrand B 1989 *Phil. Mag. A* **59** 321
- [12] Parrinello M and Rahman A 1980 *Phys. Rev. Lett.* **45** 1196
- [13] van den Beukel A and Radelaar S 1983 *Acta Metall.* **31** 419
- [14] See for example
Chen Y G and Liu B X 1996 *Appl Phys. Lett.* **68** 3096
- [15] Meng W J *PhD Thesis* California Institute of Technology
- [16] Samwer K, Fecht H J and Johnson W L 1995 *Glassy Metals III: Amorphization Techniques, Catalysis, Electronic and Ionic Structure* ed H Beck and H J Güntherodt (Berlin: Springer) p 5