Atomic structure evolution of Zr-Ni during severe deformation by HA pair analysis

Y. C. Lo, J. C. Huang, S. P. Ju, and X. H. Du

1Institute of Materials Science and Engineering; Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China
2Department of Mechanical and Electro-Mechanical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Republic of China

(Received 9 February 2007; revised manuscript received 9 April 2007; published 10 July 2007)

The gradual vitrification evolution of atom mixing and local atomic pairing structure of the binary Zr-Ni alloy during severe deformation at room temperature is traced numerically by molecular dynamic simulation. It is found that the icosahedra clusters will gradually develop with the increasing of disorder environment of alloys. Other compound-like transition structures were also observed in transient in the Zr-Ni couple during the solid-state amorphization process under severe plastic deformation. Since the time scale of the molecular dynamic simulation is several orders of magnitude shorter than reality, the simulated atomic evolution can be viewed as that would occur at ultrahigh strain rates.

DOI: 10.1103/PhysRevB.76.024103

PACS number(s): 61.43.Dq, 83.10.Rs

1. INTRODUCTION

Without the limitation imposed by cooling rate, the solid-state vitrification reaction can induce the crystalline-to-amorphous phase transition, of which the mechanical alloying (MA) (Refs. 1–5) and accumulative roll bonding (ARB) (Refs. 6–11) are commonly used. Compared with the MA method which has been widely and systematically studied for numerous alloys, such as Co-Ti, Zr-Cu, and Zr-Ni (Refs. 15 and 16) systems, the ARB induced amorphization has received relatively less attention in terms of atomic structure evolution.

It is known that during the course of rapid cooling, local icosahedra clusters are usually found to form during the amorphization process because the icosahedra clusters have the short range ordering which is easier to form than the long range ordering structure. The binding energy of icosahedrons (in its absolute magnitude) is also slightly higher than the close-packed arrangement. If there exist the maximum amounts of the fivefold symmetrical icosahedral clusters in the system, it is easy to form the amorphous phase during the cooling processes. But for the solid state ARB process, the amorphous phase is obtained by the strain-induced diffusion of different metallic grains and the initial bilayer is characterized by crystalline long-range order, e.g., face-centered cubic (fcc) and hexagonal closed-packed (hcp), qualitatively different from the short-range order (such as icosahedral local environment) typical for amorphous structures.

According to our previous ARB experimental studies at ambient temperature of binary Zr based alloys made by ARB, the grain size of the ARB specimen was gradually refined down to \( \sim 2 \) nm, such nanocrystals would disappear in the matrix and form the complete amorphous phase upon subsequent ARB passes. The role played by the short range ordering, such as icosahedra, or other packing forms related to the intermetallic compounds that would form in the corresponding equilibrium phase diagram, during solid-state vitrification is still not well understood.

Molecular dynamics (MD) simulations have been successfully applied to analyze the structure, thermodynamic and dynamic properties of rapidly cooled alloys and the glass forming atomic mechanism. Further, Honeycutt and Anderson has used the pair analysis technique (termed as the HA pair index) to study the local structure features in disordered systems such as liquid and glass in early years. This approach provides very clear information about the local symmetry of atomic arrangement more than the common pair correlation function, and has been used to simulate the grain boundary microstructure transition, local cluster structure, and glass forming of metallic alloys under the rapid cooling condition. However, the HA index has never been applied in the solid state vitrification such as ARB which involves atomic diffusion and amorphization driven by the imposed shear rolling stress.

In this study, the many-body tight binding potential is adopted to model the interatomic interactions of the Zr-Ni alloy during the repeated ARB strain-and-stack procedure. Since the time scale during the MD simulation is many orders of magnitude faster than the real case during solid state ARB experiment, direct comparison of the MD simulation with the experimental ARB results would be subject to questions. Thus the current MD studies can be viewed as the exploration of the atomic structure evolution during severe deformation under extra-high strain rates. The gradual evolutions of atom mixing and local atomic crystal structure of the binary Zr-Ni alloy are traced numerically by the radial distribution function (RDF) and the Honeycutt-Anderson (HA) pair analysis technique. Similar attempts focusing on the study of the amorphous phase growth in interface of bilayers have been tried by Lund and Schuh and Delogu and Cocco in terms of RDF, hence it is concentrated in this report on the function of icosahedra and other intermetallic compound clusters on the microstructural transition during the severe deformation process.

II. SIMULATION

In the MD simulation model of the ARB process, a bilayered structure consisting of hcp Zr coupled with the fcc Ni elemental layers, measuring 20 nm in width, 20 nm in length, and 12 nm in thickness for each elemental layer, was set to be the starting alloy model in order to trace the final cyclic transformation stage between nanocrystalline and...
amorphous phases during ARB. The designed amounts of Zr and Ni atoms are 89,280 and 188,442 for the Zr-Ni system.

The simulation is performed using a parallel computing cluster consisting of six nodes. The present simulation employs the velocity Verlet algorithm\(^3\) to calculate the trajectories of the atoms and the scaling method is adopted during the simulation to control system temperature at room temperature 300 K. All atomic interactions are modeled by the many-body, tight-binding potential as follows:31–34

\[
E_i = -\sum_j \xi^2 \exp \left[ -2q \left( \frac{d_{ij}}{d_0} - 1 \right) \right]^{1/2} + \sum_j A \exp \left[ -p \left( \frac{d_{ij}}{d_0} - 1 \right) \right],
\]

where \(\xi\) is an effective hopping integral, \(d_{ij}\) is the distance between atoms \(i\) and \(j\), and \(d_0\) is the first-neighbor distance.

The first part in the potential function is the summary of the band energy, which is characterized by the second moment of the \(d\)-band density of state. Meanwhile, the second part is a Born-Mayer type repulsive form. The parameters \(\xi, A, p,\) and \(q\) are determined by the experimentally obtained values of cohesive energy, lattice parameter, bulk modulus, and shear elastic constants. The interaction force on atom \(i\) is expressed as

\[
\overline{F_i} = \sum_{j \neq i} \left( \frac{\partial E_i}{\partial d_{ij}} + \frac{\partial E_j}{\partial d_{ij}} \right) \frac{d_{ij}}{d_{ij}}.
\]

The parameters of the tight-binding potential for Zr and Ni in the MD simulation are listed in Table I.\(^3\) The transition between nanocrystalline and amorphous phase at the final stage of ARB process are characterized in terms of the variations of the cohesive energy, the radial distribution function (RDF), and the average bond length.

### III. RESULTS AND DISCUSSION

The transition between the nanocrystalline and amorphous phases at the final ARB stage is characterized in terms of the RDF and HA pair. In general, RDF is a statistical average for all configurations in the system; it is a powerful method to provide atomic pairs information but difficult to determine details of the local structural changes in the disorder system. The HA pair index can trace the local symmetry of atomic arrangement in liquid or glass. In this technique, two atoms

![Equilibrium phase diagrams for Zr-Ni](Fig. 2).
TABLE I. Parameters used in the tight-binding potential.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$\xi$ (eV)</th>
<th>$A$ (eV)</th>
<th>$p$</th>
<th>$q$</th>
<th>$d_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.070</td>
<td>0.0376</td>
<td>16.999</td>
<td>1.189</td>
<td>2.490</td>
</tr>
<tr>
<td>Zr</td>
<td>2.279</td>
<td>0.1934</td>
<td>8.250</td>
<td>2.249</td>
<td>3.179</td>
</tr>
<tr>
<td>Zr-Ni</td>
<td>2.139</td>
<td>0.2166</td>
<td>8.360</td>
<td>2.230</td>
<td>2.761</td>
</tr>
</tbody>
</table>

are viewed as forming a bond pair if they are within a given cutoff distance that equals the first minimum in the partial radial distribution function (for example, Zr-Zr, Ni-Ni, and Ni-Zr in the Zr-Ni system). There is a sequence of four integers to characterize the local structures according to the HA index. The first integer is to identify whether or not the atoms bonded in the HA pair are the near neighbors; 1 means yes, and 2 means not. The second integer is the number of the near neighbors shared by the HA pair. The third integer denotes the number of bonds among the shared neighbors. When the first three indices are identical but the bond geometries are different, the forth integer is added.

According to this method, different HA indices will represent different local structures, as shown some examples in Fig. 1. For example, the 1421 and 1422 pairs will exist predominantly in the close-packed crystalline structure such as fcc and hcp. In pure fcc crystals, the predominant pairs would be the 1421 ones; while in the pure hcp crystals, there are typically around 50% of the 1421 and 50% of the 1422 pairs. The 1441 and 1661 pairs are characteristics of the body-centered cubic (bcc) structure. The 1551, 1541, and 1431 pairs are referred to the common short-range local structures of an amorphous or liquid state. The 1551 pair is particularly characteristic of the icosahedra ordering; the 1541 and 1431 are indexes for the icosahedra defect and fcc defect local structures, respectively. Finally, the 1321 is a packing related to rhombohedra, and this pair tends to evolve when the icosahedra 1551 packing is formed and can be viewed as the side product accompanying the icosahedra atomic packing.

Before characterizing the local cluster structures in this system, it is helpful to examine their equilibrium phase diagram first, as depicted in Fig. 2. The heat of mixing between hcp Zr and fcc Ni is $-49 \text{ kJ/mol}$, which would lead to a strong driving force for the pure elemental Zr and Ni atoms to mix together and to form local ordering. Coupled with the large difference in the atomic radius $r$ being 23% judging from $r_{Zr}=0.160 \text{ nm}$ and $r_{Ni}=0.124 \text{ nm}$, the Zr-Ni system has been considered to be a binary alloy with high glass forming ability upon rapid cooling. The strong tendency for local ordering results in the formation of many equilibrium intermetallic compounds, including Zr$_2$Ni, ZrNi, and Zr$_2$Ni$_2$.

Figure 3 presents the partial radial distribution function (PRDF) after the ARB cycles indicated for the Zr-Ni system. From the first three PRDF profiles of each pair, it is evident that the microstructure have gradually transformed from the crystalline to amorphous phase. In the Zr-Ni alloys, the Ni atoms have not fully transferred to amorphous until sixth cycles but Zr atoms just need three cycles. The Zr side appears to vitrify faster is not surprising, since the Ni atoms are the more dominant moving species. It appears that the fcc Ni crystals are relatively more reluctant to lose their fcc packing nature. This trend has been observed experimentally by x-ray diffraction and transmission electron diffraction that the fcc Ni crystal structure appears to the most stable phase and needs more ARB cycles to force it to transform into fully amorphous state.

Figure 4 presents the variation of average coordination number (CN) for every cycle. For example, the profile of the CN for the Zr-Ni pair is referred to the case that Ni is the referenced atom and Zr is the first neighbor atom surrounding Ni. The coordination numbers of all pairs in Fig. 4 show a continuously decreasing or increasing trend until around the sixth cycle. When the mixed microstructure becomes finer and finer, the mixing and thus the interaction between Zr and Ni atoms become stronger, leading to the more ap-
parent drop of potential energy from the fourth (−4.8 eV) to sixth ARB cycle (−4.9 eV).

The more detailed local pairing variations with increasing ARB cycles for the Zr-Ni alloy are depicted in Fig. 5, respectively. Figure 5(a) shows the evolution of the close-packed pairs of 1421 fcc-like and 1422 fcc/hcp-combined bond pairs in the Zr-Ni system. The 1421 pairs continue to decrease from the initial 54 to 25% until the fourth cycle and 1422 pairs does not reduce their population as fast as 1421 over this stage but also drop from 25 to 20%. Above the fifth cycle, both the 1421 and 1422 pairs appear to drop and then scatter at a low value of ~5%. It appears that the close-pack structures cannot be sustained in the Zr-Ni alloys after the 5th cycle.

In Fig. 5(b), the 1541 icosahedra-defect and 1431 fcc-defect pairs in the Zr-Ni system have a finite amount existing in the first stage (~10 and 5%, respectively) and continue to rise or scatter to 15 and 20%, respectively. The 1541 icosahedra-defect pairs show a particularly wide scattering during the intermediate stage, from the lowest of 8% to the highest of 25% and with an overall average of ~15%. In contrast, the 1551 icosahedra pairs continue in their evolution from the initial less than 1 to 8 % at the fourth cycle, and to 30% at the later stage. It seems that the icosahedra-defect and fcc-defect local structures are easier to form during the initial stage of the crystalline-to-amorphous transition processes. From the above evolutions, it appears that the 1541 icosahedra-defect pairs are the intermediate transition atomic arrangement, and would transform gradually into the 1551 icosahedra pairs. The fluctuation between 1541 and 1551 pairs does not tend to approach to a more steady state until the ninth cycle, thus 1551 icosahedra pair structure is the more stable atomic local arrange in the current amorphous phase of the Zr-Ni system.

Furthermore, an interesting phenomenon is evident in Fig. 5(c) that the bcc related 1441 pairs will increase and then decrease during the amorphization transition processes. The other bcc type 1661 pairs and the rhombohedra-related 1321 pairs are also found, but the fractions of 1661 and 1321 pairs are consistently present with a low value ~5%. It is well known that one of the easier forming compounds in the Zr-Ni alloys is Zr2Ni, which has a body centered tetragonal (bct) crystalline structure with lattice constants of $a = 0.65$ nm and $c = 0.53$ nm. Other intermetallic compounds include ZrNi$_5$ (cubic), Zr$_2$Ni$_7$ (monoclinic), ZrNi$_3$ (hexagonal), Zr$_2$Ni$_{10}$ (tetragonal), ZrNi (orthorhombic), etc., based on the equilibrium thermodynamic phase diagram in Fig. 2. There is no information on the relative ease of forming these intermediate phases during the rapid and metastable process-

FIG. 4. The variation of average coordination number of the Zr-Ni alloy subjected to different ARB cycles.

FIG. 5. Variations of the HA indices of the Zr-Ni alloys during different ARB cycles: (a) 1421 and 1422; (b) 1431, 1541, and 1551; and (c) 1441, 1661, and 1321.
ing of severe deformation at high rates. During the course of ARB under severe shear stress, the induced transient atomic local structures might be any one of these candidates. But the transient atomic structures might be deformed and deviated from the equilibrium phase structures. The observed 1441, 1661, and 1321 should be associated with such intermediate phases.

By closer examinations of the simulated structures, most atoms classified as the 1441 pairs are the Ni atoms, implying that the local geometric structures of the 1441 pairs is one of bcc-like short range ordering (or deformed bcc). These bcc-like pairs seem to be the transient atomic arrangement for the fcc structure to transform into the final amorphous phase. It is not clear whether this local atomic pairing is originated from the local formation of the bct Zr$_2$Ni or the cubic ZrNi$_3$. But it is evident that the transition of the fcc Ni crystals in the current Zr-Ni system will pass a transition stage forming local atomic pairs other than face centered cubic. The evolution of the local pairing structures appears to be rather complicated.

A similar observation of the above transient pairing has also been reported in the MD simulation for the rapid cooling process of Cu,\textsuperscript{36,39} where the 1441 and 1661 pairs would be observed in the MD simulation for the rapid cooling processes. In addition, the fcc Ni seems to be more difficult to change into the amorphous phase than the hcp Zr, judging from the PRDF curves. And the fcc local pairing appears to change to the bcc-type pairing before transforming into the fully amorphous phase. The structure transition mechanism of the fcc seems to be more complex and more persistent than that for the hcp structure.

IV. SUMMARY

In summary, the local atomic pairing arrangement of the Zr-Ni binary system during room temperature severe deformation under high strain rates is simulated. For the Zr-Ni system, the local defect structures of the fcc Ni and hcp Zr, or the icosahedra clusters are seen to form first in the early stage of the amorphous transition, and the fcc 1421 or fcc/hcp 1422 close-packed pairs would decay rapidly at the same time. The icosahedra defect local structures, or the 1541 pairs, will first evolve and then transform into the more stable icosahedra clusters, or the 1551 pairs. When the amorphous transition has been completed, the major local short-range-ordered atomic pairs are the icosahedra or characteristic pairs commonly existing in amorphous or liquid phase, namely, the 1551, 1431, and 1541 pairs. The latter three types of pairs occupy totally \textasciitilde70\% of the total pair population. The rest are the remaining fcc or hcp (1421 or 1422, accounting for \textasciitilde15\%) and the intermediate local structures (1441, 1661, or 1321, accounting for another \textasciitilde15\%). During the transient stage, the bcc-related cubic-typed 1321 pairs are formed up to 20\%, which may be related to the intermetallic compounds that will form according to their equilibrium phase diagram. But this transient atomic pairs would disappear at the later stage.

The current simulation results reveal that the short-range icosahedra structures always play an important role during the course of crystalline-to-amorphous transition, both during the solid state strain-induced severe deformation and rapid cooling processes. In addition, the fcc Ni seems to be more difficult to change into the amorphous phase than the hcp Zr, judging from the PRDF curves. And the fcc local pairing appears to change to the bcc-type pairing before transforming into the fully amorphous state. The structure transition mechanism of the fcc seems to be more complex and more persistent than that for the hcp structure.

ACKNOWLEDGMENT

The authors would like to thank National Science Council of Republic of China for supporting this study, under Grant No. NSC95-2218-E-110-006.

\textsuperscript{8}jacobic@mail.nsysu.edu.tw
33, 2145 (2002).