On the latest stage of transformation from nanocrystalline to amorphous phases during ARB: Simulation and experiment

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Abstract

By applying a simple room temperature accumulative roll bonding (ARB) process, the multilayered Zr and Ni elemental foils can be mixed and transformed into nanocrystalline and eventually amorphous bulk materials. The latest stage of the transformation from the nanocrystalline elemental phase measuring ~2 nm to the amorphous alloying phase is examined, using high resolution transmission electron microscopy and molecular dynamics simulation. The gradual evolutions of atom mixing of the binary Zr–Ni alloy, as well as the final radial distribution function and the nearest neighboring distance, are traced experimentally and numerically.

Keywords: A. Nanostructured intermetallics; B. Glasses, metallic; C. Rolling; E. Simulations, atomistic; F. Electron microscopy, transmission

1. Introduction

Solid-state vitrification methods have received increasing attention in the past decade, because these methods are the processes without the limitation of cooling rates and produce the amorphous materials in bulk form. This kind of method forces the atoms of adopted elements to diffuse in a solid state under low temperature in order to obtain the metastable amorphous phases. Both the processes of mechanical alloying (MA) [1,2] and accumulative roll bonding (ARB) [3,4] belong to the solid-state reaction routes. It has been widely studied that the amorphization of MA occurred as the introduced lattice defects make the free energy of the crystalline phase higher than that of the amorphous phase [5]. Much fewer studies were done on the amorphization process during ARB.

According to our previous reports [6–8] on the Zr base alloys made by ARB route, the grain size of ARB specimen was gradually refined to only a few nanometers while the amorphous volume fraction also increased with increasing repeated roll-bonding process. Once the nanocrystalline phases measuring a few nanometers are formed in the amorphous matrix, a fully amorphous state seems to rapidly complete after a few roll bonding cycles. The reasons and the mechanisms for such rapid transformation at the latest stage are still ambiguous. A recent molecular simulation study [9] of binary metallic systems reveals that it needs only four cycles for a layer structure with 3 nm in thickness to complete the amorphous transformation. It is conceivable that the molecular dynamics (MD) simulation could provide a powerful route to investigate the atomic mutation for a nanocrystalline phase at the critical size around a few nanometers.

In this study, the high resolution transmission electron microscopy (HREM), and the related Fourier transformation software, are used to cautiously characterize the latest stage of nanocrystalline and amorphous phases for the binary Zr–Ni alloy, and the results are compared with the MD simulation using the tight-binding potentials for the elemental Zr and Ni. No periodic boundary condition was used in the MD simulation method in order to simulate the real atomic mixing behavior and the volume change during repeating strain-and-stack procedure of ARB method.

2. Experiment and simulation details

The adopted composition is Zr_{50}Ni_{50}. The stacked pure elemental foils (with thickness ~100 μm) with equivalent amount are repeatedly roll bonded at room temperature. The ARB specimen was rolled by a 350-ton cold rolling machine, with the roller diameter and length is 140 and 220 mm, respectively. Rolling speed is 30 mm/s for each folding and
rolling cycle and the processing time for each pass is around 1–2 s, corresponding to a mean strain rate in the range of 0.4–0.8 s⁻¹. The thickness reduction for each F&R cycle was set to be 50%. Small parts of the specimen were sampled after various cycles for off line analyses. The nanocrystallization and amorphization mechanisms are examined by Jeol 3010 analytical TEM (AEM) with energy-dispersive X-ray spectrometry (EDS) analysis at a beam size of 10 nm. Fourier transformation is performed using a parallel computing cluster consisting of six nodes. The present simulation employs the velocity Verlet algorithm [10] to calculate the trajectories of the atoms and the scaling method is adopted during the simulation to control system temperature (at temperature). All atomic interactions are modeled by the many-body, tight-binding potential as follows [11,12]

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

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:

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

The parameters of the tight-binding potential for Ni and Zr in the MD simulation are listed in Table 1 [13]. 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.

3. Results and discussions

3.1. Transformation between nanocrystalline and amorphous phase

The grain size of the Zr–Ni system is refined from the original \( \sim 100 \mu m \) down to \( \sim 500 \text{ nm} \) and finally to \( \sim 2 \text{ nm} \) with increasing ARB cycles, as partly presented in our previous papers [6–8]. It is considered that the grain size refinement arose from the strain-induced dislocation activity and shear band propagation during the initial and intermediate stages of ARB. At the final stage, as the nanocrystalline phase approaches the critical size near 2 nm dispersed in the amorphous matrix, the residual nanocrystalline phase seems to suddenly transform into a fully amorphous state by only a few ARB cycles. The transition region between the nanocrystalline and amorphous phases is shown in Fig. 1(a). The nanocrystalline phase near the interface is around 2 nm with nearly sphere in shape and it seems to become unstable when the size is further refined to below 2 nm. Previous studies [6,8] have concluded that the pronounced increase in interfacial energy of the nanocrystalline phase lead to the transformation into the amorphous state, and interdiffusion across the phase boundary is the controlling atomic mechanism [14], as depicted in Fig. 1(b). The residual nanocrystalline phases after various ARB cycles are consistently composed of the unmixed pure elemental particles (based on the indexing of diffraction patterns). The analyses of diffraction patterns are also coincided with the TEM/EDS measurement (with spot size near 10 nm) in Fig. 2. No intermetallic compound was found during the room temperature ARB process.

Meanwhile, the characterization of the nanocrystalline and amorphous phases by high resolution lattice images is also performed. The two-dimensional Fourier transform and the reconstructed lattice images are used to confirm the crystal structure, shape and size of the nanocrystalline phases at the latest stage of ARB. The lattice image in Fig. 3(a) reveals that the nanocrystalline phases are surrounded by an amorphous matrix and the nanocrystalline size was seen to decrease from \( \sim 10 \text{ nm} \) down to \( \sim 2 \text{ nm} \) (Fig. 3(c)) in regions close to the transition boundary. The spatial distribution of the nanocrystalline and amorphous phases is inhomogeneous in fine scales. Fig. 3(a) also reveals that the long-range-order

<table>
<thead>
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<th>Parameters</th>
<th>( \xi ) (eV)</th>
<th>( A ) (eV)</th>
<th>( p )</th>
<th>( q )</th>
<th>( d_0 ) (Å)</th>
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<td>Ni</td>
<td>1.070</td>
<td>0.0376</td>
<td>16.999</td>
<td>1.189</td>
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</tr>
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<td>Zr</td>
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<td>8.250</td>
<td>2.249</td>
<td>3.179</td>
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<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>
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</table>
crystalline structure is broken down into the short range ordering during ARB with an amorphous phase inserted into it. Simultaneously, the reconstructed image from the specified square region in Fig. 3(a) showed the exact size and shape of the nanocrystalline phases. The smallest size of nanocrystalline phase is around 2 nm with the shape of ellipse and still constructed by the pure element of Zr. The critical size of ~2 nm appears to be a lower bound for the stability of nanocrystalline phases in the current system. Based on our previous experience, for a nanocrystalline phase of ~5 nm in size semi-homogeneously dispersed, only a few ARB cycles (<10) would be needed to convert the system into amorphous state.

3.2. Simulated microstructure evolution during ARB

Fig. 4 reveals the microstructural evolution of bi-layered Zr50Ni50 alloy subjected to various ARB cycles, together with the associated two-dimensional Fourier transform. The bi-layered Zr and Ni structures, with domain size of the same order as the layer thickness (~5 nm), are fully vitrified after six ARB cycles via pronounced interdiffusion, consistent with our TEM observations and propositions. The simulation shows that the two elemental nanocrystalline phases transform directly to the amorphous alloying phase. There is no intermediate phase or intermetallic compound induced; the same observed experimentally. The interval from the third to the sixth ARB cycle is the transition between nanocrystalline and amorphous state. For the current binary metallic system, it needs only 6x cycles for the bi-layered structure, with 5 nm in each layer thickness, to transform into a fully amorphous state. The current result on ARB is very similar to the MA case observed by Lund and Schuh [9]. Meanwhile, with further rolling (to 14 ARB cycles), the amorphous structure was maintained until the end of simulation processing, though there are slight local reversions back to the partial nanocrystalline phases (i.e. slight local cyclic transformation between the eighth and 10th ARB cycle). This conclusion is also supported by the results of Fourier transformation.

Fig. 1. (a) TEM bright field micrograph of the interface region between the nanocrystalline and amorphous phases taken from the Zr50Ni50 alloys after 100 ARB cycles. The smallest nanocrystalline phase size near the interface is around 2 nm. (b) Schematic illustration of the transformation mechanism via interdiffusion.

Fig. 2. TEM/EDS measurements for (a) the nanocrystalline area (nearly pure Zr) and (b) the amorphous area (nearly 50%Zr–50%Ni) in the TEM micrograph shown in (a).
The variation of potential energy of Zr–Ni alloy subjected to different ARB cycles is shown in Fig. 5. The potential energy in alloy system represents the atomic interaction energy. In Fig. 5, the potential energy starts to increase at the stage subjected to the third ARB cycle and saturated at the sixth cycle. The binding energy between Zr and Ni atoms increases during the transition period (between nanocrystalline and amorphous state) due to the severe structure change. The larger binding energy between two distinct atoms increases the difficulty for atoms to locate in the precise position and maintain the stable and ordered crystalline structures.

The Gibbs free energy $\Delta G$ of a crystalline phase can be expressed in terms of their enthalpy $\Delta H$ and entropy $\Delta S$ contributions [15]:

$$\Delta G = \Delta H_c + \Delta H_e + \Delta H_s - T\Delta S,$$

(3)

including the chemical, electrostatic and structure terms for the enthalpy. The structural contribution term $\Delta H_s$ in Eq. (3) arose due to the formation of a common d-band during processing [15], which is also supported by the energy-band calculation in Fig. 5. Once the Gibbs free energy of the nanocrystalline phase is raised to the level greater than that for the metastable amorphous state, the fully amorphous phase is formed suddenly.

The present MD simulation is done for two distinct unmixed bi-layers. Future simulation can be conducted for one pure-element nanocrystalline phase in conjunction with fully mixed amorphous matrix, as for the experimentally observed situation. It is expected that the ARB cycles needed to complete the mixing and vitrification may be further reduced to around three cycles, as observed previously in the Zr–Ti system [7,8].

### 3.3. Atomic spacing of nearest neighbors

The intensity distributions of the maxima and minima of the halo in the TEM diffraction pattern for the amorphous $Z_{50}Ni_{50}$ phase are carefully extracted from the (000) center beam outward to the high $g$ values. The representative plot is presented in Fig. 6. There are usually two clearer maxima; one locating at $g_1 \approx 0.41 \text{ Å}^{-1}$ and the other at $g_2 \approx 0.69 \text{ Å}^{-1}$. Both the $g_1$ and $g_2$ data are of concern. Nevertheless, the $g_2$ values of 0.69 Å$^{-1}$, or corresponding to $d \approx 1.45$ Å, is below the resolution limit of the current TEM. The contrast transfer function would be oscillatory near the latter $g$-vector ranges.
Thus the maxima or minima over these regions might not reflect the actual plane spacing. Thus, only the $g_1$ data are compared. The experimentally extracted $d$-spacing ($= 1/g = 2.43\ \text{Å}$) value from the diffuse ring of TEM diffraction pattern is smaller than the theoretically calculated value ($d = 0.5(r_{Zr} + r_{Ni}) = 0.5(1.60 + 1.24) = 2.84\ \text{Å}$), as compared in Table 2.

The RDF profiles extracted from the MD simulated atom configurations for Zr–Ni subjected to different ARB cycles are
shown in Fig. 7. The clear peaks in the initial RDF profiles are contributed from the long-range ordered nanocrystalline structure. Therefore, the corresponding Fourier transform is the spot pattern, as shown in Fig. 4(a) and (b). The characteristics of these obvious and sharp peaks decrease with increasing ARB cycles. After the sixth ARB cycles, a fully amorphous phase is formed and only three peaks remained in the RDF profile. The three residual peaks are related to the Fourier transformed diffuse ring pattern and revealed the distribution of the atomic spacing of nearest neighboring. Hence, the average bond length for all atoms (equal to the nearest neighboring distance) in the three-dimensional model can be statistically computed and the extracted average value is shown in Fig. 8. The value in Fig. 8 reveals the statistical atomic spacing of nearest neighboring distance in the first peak of RDF profile; it is 2.58 Å for the amorphous Zr$_{50}$Ni$_{50}$ alloy after six ARB cycles. This value is also smaller than the theoretically calculated value in Table 2.

It appears that the average atomic pairing between neighboring atoms in the amorphous phase is not as simple as one would expect from the sum of the two radii. The atoms of amorphous alloy formed a new tight packing structure. The average atom spacing within the amorphous structure is lower than the sum of the atomic radii. The structure of the amorphous alloy is characterized by short-range order, which is evident from the sharp peaks in the RDF profile. However, the long-range order is absent, which can be deduced from the absence of any sharp peaks in the RDF profile after the sixth ARB cycle. The average atomic spacing within the amorphous structure is lower than the sum of the atomic radii, indicating a new tight packing structure. The average bond length for all atoms (equal to the nearest neighboring distance) in the three-dimensional model can be statistically computed and the extracted average value is shown in Fig. 8. The value in Fig. 8 reveals the statistical atomic spacing of nearest neighboring distance in the first peak of RDF profile; it is 2.58 Å for the amorphous Zr$_{50}$Ni$_{50}$ alloy after six ARB cycles. This value is also smaller than the theoretically calculated value in Table 2.

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due to closer package and mutual attraction. The mixing enthalpy $\Delta H_m$ for Zr–Ni is $-49$ kJ/mol [16], which seems to strongly affect the tight packing structure of the resulting amorphous phase. Although the first nearest neighboring distance of the amorphous phase is shorter, the second and third neighboring distances would be larger, making the overall lower packing density and more free volumes in the amorphous alloy.

4. Conclusions

The elemental pure Zr and pure Ni phases in the Zr–Ni system seem to become unstable during ARB when refined to the scale of a few nanometers. Amorphization would quickly proceed within a few ARB cycles. The molecular dynamics simulation reveals that it needs only six cycles for a bi-layer structure, with 5 nm in each layer thickness, to fully transform into a completely amorphous state. The potential energy between two distinct atoms increases during the transition between nanocrystalline and amorphous state due to the severe structure change. It increases the difficulty for atoms to maintain the crystalline structures. The values of the nearest neighboring distance extracted from the TEM observation and the molecular dynamics simulation are both smaller than the theoretically calculated value. A new tighter packing atomic structure in the Zr$_{50}$Ni$_{50}$ amorphous alloy is formed due to the large negative mixing enthalpy.

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References