Cyclic transformation between nanocrystalline and amorphous phases in Zr based intermetallic alloys during ARB

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Abstract

By applying a simple room temperature accumulative roll bonding (ARB) process, the multilayered Zr/Ni and Zr/Ti 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 \( w \approx 2 \) nm to the amorphous alloying phase via gradual atomic mixing is examined, using high resolution transmission electron microscopy, Fourier transformation, and molecular dynamics simulation. Closer examination is focused on the following evolution during the subsequent ARB cycles after amorphization. Transformation from the amorphous phase back to the nanocrystalline elemental phase occurs during the next 3 ARB cycles. Upon further ARB cycles, the nanocrystalline Ni phase is again transformed into the complete amorphous state, exhibiting the cyclic transformation behavior between the nanocrystalline and amorphous phases.

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1. Introduction

Severe plastic deformation processes, such as friction stir processing [1], mechanical alloying (MA) [2,3] and accumulative roll bonding (ARB) [4,5], have received considerable attention in recent years. High plastic strains and ultrafine or even amorphous structures with outstanding properties can be induced. In this study, the ARB process is of interest since this method could directly produce the nanocrystalline or amorphous phase in a plate form without the limitation of cooling rates. The MA and ARB methods belong to the same category of solid-state reaction and both methods force the atoms of adopted elements to diffuse in a solid state at low temperatures in order to obtain the metastable amorphous phases. According to previous reports, the initial microstructural evolution of the ARB process has some similarities with the early milling stage of the MA method [6]. But unlike MA, the complete amorphization mechanisms during ARB, especially at the latest stage, have not been well developed. Hence, some of the Zr–Cu [3,6] or Zr–Ni [7] based alloys previously studied using the MA route were examined in our previous reports [8–12] using the ARB process in order to establish the graduate vitrification mechanisms during room temperature ARB. It reveals that the grain sizes of Zr based specimens are gradually refined from the micrometer scale down to a few nanometers with increasing repeated folding and rolling (F&R) steps, and the nanocrystalline phase retained is dispersed in the amorphous matrix. For the latest stage, sudden transformation of the crystalline phase into fully amorphous state was observed to proceed within a few ARB cycles. In this study, the high resolution transmission electron microscopy (HRTEM) and the related Fourier transformation software are used to cautiously characterize the cyclic transformation between the nanocrystalline and amorphous phases in the binary Zr based alloys.

Recent efforts in molecular dynamical (MD) simulation studies on binary metallic systems [13] also reveal that the rapid
nanocrystalline to amorphous transition occurred by means of only 4 cycles for a layered structure with 3 nm thickness. It is recognized that the atomistic simulation of the MD method provides a powerful tool to better investigate the atomic mutation of nanocrystalline phases measuring below 2 nm. The simulated results can be compared with the HRTEM images of the experimental ARB specimens. The many-body tight-binding potentials for the selected elements are used in the MD simulation. Meanwhile, the periodic boundary condition and volume change during repeating ARB cycles are not considered during the simulation of the atomic mixing behavior.

2. Experiment and simulation details

In the ARB experiment, stacked foils of Zr and Ni (or Zr and Ti) of equivalent amount are repeatedly roll bonded at 2. Experiment and simulation details the simulation of the atomic mixing behavior. Meanwhile, the periodic boundary condition and volume changes for the selected elements are used in the MD simulation. The parameters A, p, q and $\xi$ are determined by the experimentally obtained values of cohesive energy, lattice parameter, bulk modulus and 2 shear elastic constants ($C_{44}$ and $C' = 2(C_{11} - C_{12})$, respectively). The interaction force on atom i is expressed as:

$$ F_i = \sum_{j \neq i} \left( \frac{\partial E_p}{\partial r_{ij}} + \frac{\partial E_x}{\partial r_{ij}} \right) r_{ij}^{-\alpha}. $$

The parameters of the tight-binding potential for Ni (Ti) and Zr [16–18] in the MD simulation are listed in Table 1. For the tight-binding potential used in this study, there are 5 parameters to be determined. Considering the parameters for the same element, for example, Zr or Ni, different researchers may obtain different sets of these 5 parameters, but these different parameters in tight-binding potentials can sufficiently model the same element [19]. In addition, the parameters of Ni and Zr in Ref. [18] are newer than those in Refs. [16] and [17], and using the newer parameters in tight-binding potentials can predict the more accurate cohesive energy. In this study, we decide to adopt the newer parameters of tight-binding potentials in Ref. [18] for pure Ni and Zr, and the cross-element parameters for Ni–Zr from Refs. [16] and [17]. The variations of the cohesive energies, the radial distribution functions (RDF) and the average bond lengths are used to characterize the cyclic transition behavior between the nanocrystalline and amorphous phases.

3. Results and discussions

3.1. Transformation between nanocrystalline and amorphous phases

As presented previously [8–12], with increasing F&R cycles, the accumulated shear stress forces the harder phases to break into smaller phases and finally into a much more homogeneous and mixed structure. The foils in the Zr$_{50}$Ti$_{50}$ system with higher and more compatible hardness would undergo more efficient mutual deformation by the counterpart. Hence, the Zr$_{50}$Ti$_{50}$ alloy was found to be more efficiently vitrified, as compared to Zr$_{50}$Ni$_{50}$. After 80–100 F&R cycles, only a few nanocrystalline phases with nearly spherical shape and average size ~2 nm remain and are dispersed in the dominant

<table>
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<th>Parameters</th>
<th>$A$ (eV)</th>
<th>$\xi$ (eV)</th>
<th>$p$</th>
<th>$q$</th>
<th>$r_0$ (Å)</th>
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<td>Zr–Ti</td>
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<td>2.0318</td>
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<td>2.3184</td>
<td>3.031</td>
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</table>
amorphous matrix [11]. The residual nanocrystalline phases seem to become unstable with the further ARB passes and sudden transformation from the nanocrystalline to fully amorphous state occurred upon subjecting to a few more ARB cycles. It has been shown previously [12] using XRD and TEM diffraction that all the remaining nanocrystalline phases are unmixed elemental particles of pure Zr, Ni or Ti, i.e., no intermetallic compound was formed during the room temperature ARB process.

Fig. 1 shows the examples of the HRTEM lattice images of Zr$_{50}$Ni$_{50}$ or Zr$_{50}$Ti$_{50}$ after 80 ARB cycles. In both alloy systems, the lattice images reveal that the elemental nanocrystalline phases are surrounded by the amorphous matrix. The smallest nanocrystalline size is \( \sim 2 \) nm; the critical size of
~2 nm appears to be the lower boundary for the stability of nanocrystalline phases in the current system. The local diffraction patterns for such nanocrystalline particles measuring ~2 nm, obtained by the Fourier transformation as well as the reconstructed lattice images constructed by a second Fourier transformation after filtering the noise background, for the pure Ni, pure Zr, and pure Ti particles in such specimens are shown in Fig. 1(b)–(d).

Over the final stage of ARB from 85 to 120 cycles, it was often observed that some of the crystalline characteristic peaks reappear after full vitrification, in other words, the fully amorphous phase would transform back to nanocrystalline pure elemental phase upon subsequent ARB passes, exhibiting cyclic transformation behavior. This was particularly apparent for the Ni phase with the FCC crystal structure in the Zr$_{50}$Ni$_{50}$ system. The (111) Ni XRD peak was often the last peak to disappear (into fully amorphous state) and the first one to reappear (into nanocrystalline phase again). Parallel studies on the cyclic transformation are conducted using the nano-indentation on the fully amorphous Zr$_{50}$Ni$_{50}$ alloys. Stress induced nanocrystallization near the indented region can also be seen.

3.2. MD simulation of microstructure evolution during ARB

Figs. 2 and 3 reveal the MD simulated microstructural evolution over the final ARB stage and the associated two-dimensional Fourier transformation of the bi-layered Zr$_{50}$Ni$_{50}$ and Zr$_{50}$Ti$_{50}$ subjected to various ARB cycles. In the Zr$_{50}$Ni$_{50}$ and Zr$_{50}$Ti$_{50}$ systems, the nanocrystalline structure is fully vitrified after 6 and 4 F&R cycles, respectively. A faster amorphization process is revealed in Zr$_{50}$Ti$_{50}$, consistent with the experimental findings.
Meanwhile, the variations of the MD simulated alloy potential energy (representing the atomic interaction enthalpy energy) with increasing F&R cycles are shown in Fig. 4. In Fig. 4(a), the system potential energy for Zr$_{50}$Ni$_{50}$ starts to decline, or becomes more stable with unlike atom mixing, from the 3rd F&R cycle due to the severe structure change during the transition period and becomes saturated at the 6th cycle. This result is consistent with the strongly negative mixing enthalpy of Zr–Ni ($\Delta H_m = -49$ kJ/mol). The decreasing potential enthalpy energy leads to the lower Gibbs free energy of the mixed amorphous phase. In contrast, the potential energy variation for Zr$_{50}$Ti$_{50}$ in Fig. 4(b) does not show the similar trend. No obvious variation of potential energy is observed in Zr$_{50}$Ti$_{50}$ because of the near zero mixing enthalpy for Zr and Ti atoms and the unique characteristic of the complete dis-solubility. It appears that the faster mixing of unlike atoms in Zr$_{50}$Ti$_{50}$ is not a result of the potential or mixing enthalpy, but is due to the same HCP structure and the compatible initial hardness for Zr and Ti. The (0002) basal planes of both Zr and Ti lying on the rolling plane could be effectively sheared through with each other, accelerating the thickness reduction and mutual atomic mixing.

3.3. Cyclic transformation between nanocrystalline and amorphous phases

It has been shown that it needs only 4 or 6 cycles for the current bi-layered structure, with 5–6 nm in each layer thickness, to fully transform into an amorphous state, similar to the simulated results of Lund and Schuh [13]. However, the phase stability [20] of the accumulative roll bonded amorphous alloys with further F&R passes has not been discussed and is of concern. Thus, the MD simulation continues to model the structure until 20 rolling cycles. In the Zr$_{50}$Ti$_{50}$ system, the amorphous structure, though with very slight fluctuation in the radial distribution functions, was basically maintained.
till the end of all rolling processes. In contrast, the fully amorphous structure in the Zr50Ni50 system remains over the 6th and 7th F&R cycles, and exhibits the first cyclic transformation into the nanocrystalline FCC Ni (with grain size of about 3 nm) at the 8th cycle, and is transformed back to fully amorphous from the 10th F&R cycle. Fig. 5(a) reveals the associated Fourier transform of the pure FCC Ni in the [111] zone axis. The Ni (111) plane texture tends to be stress induced and lie along the rolling plane. The re-crystallized Ni phase size is very close to the observed critical phase size of ~2 nm before vitrification. And a phase with such a small size cannot maintain its crystalline structure upon further rolling cycles. Thus, the nano-sized FCC Ni re-states to collapse from the 9th F&R cycle and returns back to amorphous structure at the end of the 10th F&R cycle. The second minor cyclic transformation occurs again at the 12th F&R cycle. Fig. 6 reveals the variations of RDF and the relative packing density of Zr50Ni50 alloy subjected to various F&R cycles. The RDF in Fig. 6(a) exhibits sharper peaks at the 8th and 9th cycles, marked by the circle, and the packing density is seen to increase as the appearance of nanocrystalline Ni phase at the 8th, 9th and 12th F&R cycles. The corresponding morphologies at the 8th and 9th cycles shown in Fig. 5(a) and (b) indicate that the crystalline structure, surrounded by circles, reappear during ARB cycles. Because the shape of the simulation system after the ARB cycle is not cubic, it is more convenient to choose 1 cube inside the simulation model after each cycle to calculate the packing density of this system. Consequently, the packing density is defined as the ratio of the total atom number inside this cube to the volume of this cube.

The MD simulation was also performed on the atomic reconstruction during nano-indentation. Similar to the experimentally observed re-crystallization of the amorphous alloys under the applied load from the indenter, the MD simulated microstructures also reveal this trend, implying the stress induced nanocrystallization. Fig. 7 shows the local
microstructures of Zr50Ni50 near the indenter. The Ni atoms under loading tend to cluster more and form the FCC nanocrystalline phase.

The cyclic phase transformation of the 2 nm nanocrystalline particles to the amorphous phase during ARB is considered to be caused by the strain or stress accumulation process, similar to the Zr67Cu33 alloy made by MA method [3]. No thermal factor can be taken into account since the ARB is processed at room temperature. The thermodynamically related glass forming ability parameters, such as higher negative mixing enthalpy $\Delta H_m$ and larger size mismatch $\Delta r$, do not seem to play the dominant roles for the vitrification during room temperature ARB. The faster vitrified Zr50Ti50 possesses lower $\Delta H_m$ and $\Delta r$ ($\sim 0$ kJ/mol and 8%) as compared with Zr50Ni50 ($\sim 49$ kJ/mol and 23%). The controlling factors for solid-state amorphization during ARB are thus the relative hardness and crystal structure.

4. Conclusions

The critical stage for the cyclic phase transformation between the nanocrystalline ($\sim 2$ nm) and amorphous phases during room temperature ARB are examined by HRTEM and MD simulation. Both results obtained from the Zr50Ni50

![Fig. 6. The variation of (a) RDF and (b) volume-based number density distribution of the Zr50Ni50 alloy subjected to various F&R cycles.](image)

![Fig. 7. MD simulated microstructures near the indenter at different stages. The Ni atoms tend to form nanocrystalline clusters under the applied load.](image)
and Zr$_{50}$Ti$_{50}$ systems reveal that the nanocrystalline structure would be quickly vitrified within a few cycles at the final ARB process. The Zr$_{50}$Ti$_{50}$ would vitrify faster than Zr$_{50}$Ni$_{50}$, due to the compatible hardness and HCP crystal structure. The thermodynamically related glass forming ability parameters, such as higher negative mixing enthalpy $\Delta H_m$ and larger size mismatch $\Delta r$, do not seem to play the dominant roles for the vitrification during room temperature ARB. Cyclic transformation in Zr$_{50}$Ni$_{50}$ is evident from the HRTEM and MD results, with the FCC Ni nanocrystalline phase disappearing and reappearing with increasing F&R cycles, as well as under the applying load during nano-indentation.

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References