Transformation into nanocrystalline or amorphous materials in Zr–X binary systems using ARB route

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Abstract

The gradual evolution of coarse grains during room temperature accumulative roll bonding into nanoscaled extra- fine grains or eventually amorphous phase in the Zr–Ti, Zr–Ni, Zr–Cu, and Zr–Al binary systems are examined. Comparisons with previous works are also presented.

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1. Introduction

Since the early discovery of amorphous metallic alloys [1], continuous efforts have been made using melt spinning, vapor quenching, particle bombardment, arc melting with drop cooling, various solid-state techniques, etc. [2–9], resulting another category of high performance materials exhibiting superior strength, toughness, wear resistance, or magnetic properties [10]. Solid-state reactions have been one of the methods receiving increasing attention in the past decade, since they permit preparation of metallic glasses in bulk form without rapid cooling rates. The accumulative roll bonding (ARB) process is a route to prepare alloys via room temperature cold rolling for alternating thin layers of various metals with a special arrangement of composition in the solid state [11].

Unlike the more mature mechanical alloying (MA) process, ARB has been much less systematically studied. The alloy prepared by ARB can be transformed into a nanograin state or eventually amorphous phase. According to the characterization of an ARB amorphous Zr–Al–Ni–Cu alloy [12], the diffusion of each element can be enhanced by several orders of magnitude via lattice defects or interfaces introduced into the sample during repeated deformed process. The applied low strain rates increase the effective reaction time during deformation. Due to the fact that lubricants or hard steel balls (as in MA) are not used during ARB, it prohibits strong contamination, and results in enhanced stability of the amorphous alloys, with less tendency in inducing a crystalline-glassy cyclic phase transformation [13] as occurred in some MA alloys (e.g. Zr50Al50, Zr67Cu33 and

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Nevertheless, the specimen cracking problem should be noted [14]. Successful vitrification of multi-element alloys by ARB has been reported [9,12,15]. However, the effects of individual elements have not been established. On the other hand, ball milling of the Zr alloys has been conducted from the 1980’s [16,17]. Recent MA studies by Inoue and co-workers [17] have shown that the starting powders tended to agglomerate and formed particles with thick multilayered structure at the early milling stage. The layer thickness decreased with increasing ball milling time and the amorphous phase formed as the layered structure disappeared. It is interesting to note that the microstructural evolution of MA powders is analogous to that occurring during ARB. The goal of the current study is to examine the evolution of various coarse-grained Zr–X binary systems, and to compare them with results obtained via other means.

2. Experimental procedures

Tables 1 and 2 list the alloy systems and related information. The stacked foils of around 80–100 µm in thickness (thicker than the foils of 7.5–50 µm used in most previous studies [18]) were all cleaned with acetone before and after rolling, and rolled at room temperature. The thickness reduction between each folding is set to be 50%. Small parts of the folded and rolled (F&R) specimen were sampled after 40, 60, 80, 100,..., F&R cycles for later analyses.

The layer (and grain size) refinement as well as the vitrification condition of the alloy structure were examined by scanning electron microscopy (SEM) using mainly back scattered images (BEI), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Before SEM characterization, the synthesized samples were ground and mechanically polished. The elemental diffusion analysis was conducted by energy-dispersive spectrometry (EDS) with a FEG-SEM. Selected microstructures were characterized by Jeol 3010 analytical TEM in rolled specimens thinned by Gatan precision ion polishing systems. Filtered Cu-Kα radiation and a graphite monochromator were employed for XRD, with a scanning rate of 1° per minute.

3. Results and discussions

3.1. Microstructural evolution

Fig. 1 compares the BEI side view of some typical ARB samples. For the Zr–Al and Zr–Cu systems, the initial hardness varied significantly (Table 2); thus the softer Al or Cu carried most of the deformation. After 40 and 80 F&R cycles (Fig. 1(a) and (b)), Al has been appreciably thinned, leaving the much thicker and harder Zr layers or broken pieces (the lighter phase). In contrast, the mixing appeared to be much more effective in the Zr–Ni and Zr–Ti systems with compatible initial hardness (Table 2) and hence more severe mutual shear strain. Table 3 compares the foil thickness reduction with increasing cycles for some representative alloys. For the Zr–Ti system, the foils can be thinned to submicrometer levels after 40 cycles.

Fig. 2 shows the EDS measurement across an inter-layer boundary, showing the elemental interdiffusion at room temperature enhanced by the repeated heavy deformation. For the Zr–Al (Fig. 2(a)) and Zr–Cu alloys, pronounced diffusion can

<table>
<thead>
<tr>
<th>Elements</th>
<th>Relative proportion</th>
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<tbody>
<tr>
<td>Zr and Al</td>
<td>3:1, 2:1, 1:1, 1:2, 1:3</td>
</tr>
<tr>
<td>Zr and Cu</td>
<td>3:1, 2:1, 1:1, 1:2, 1:3</td>
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<tr>
<td>Zr and Ni</td>
<td>3:1, 2:1, 1:1, 1:2, 1:3</td>
</tr>
<tr>
<td>Zr and Ti</td>
<td>3:1, 2:1, 1:1, 1:2, 1:3</td>
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</tbody>
</table>

Table 2

<table>
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<th>Elements</th>
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<tr>
<td>Zr and Al</td>
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</tr>
<tr>
<td>Zr and Ti</td>
<td>3:1, 2:1, 1:1, 1:2, 1:3</td>
</tr>
</tbody>
</table>
be seen. However, due to the thicker Zr layer remaining, complete mixing was not achieved throughout the study. For the Zr–Ni (Fig. 2(b)) and Zr–Ti systems, a homogeneous mixing state can be reached after 120 and 80 F&R cycles, respectively.

Fig. 3 shows the typical XRD patterns. All peaks in the Zr–Al and Zr–Cu alloys were contributed from the pure elements and no evidence of intermediate compound formation was found. In Fig. 3(a), the intensity of Al peaks decreased with increasing ARB cycles, but the Zr peaks did not. Apparent peak height reduction can be seen in Fig. 3(b) and (c) for the Zr–Ni and Zr–Ti systems. After 80 F&R cycles, the peaks contributed from Zr in the Zr–Ti alloy are no longer detectable in XRD patterns and the Zr–Ti alloy transformed into an amorphous state after 83 cycles (Fig. 3(c)). The center of the diffuse peak located at 2θ ~33° corresponds to a plane spacing of ~2.7 Å, slightly smaller than the closest plane spacing for HCP Zr (3.17 Å) and Ti (2.89 Å).

It appears that an efficient ARB process needs to effectively accumulate the rolling shear strain for all involved elemental foils. Since there is no external hard ball to bombard the elemental materials, as in the case of MA, the shear strain experienced by one elemental foil results from the mutual squeezing of other neighboring foils. Incompatible hardness of different elemental foils will not lead to complete mixing.

Meanwhile, the vitrification tendency did not seem to depend on the atomic size difference (Table 2) for the current four alloy systems subject to room temperature ARB. This is different from the general rule followed by cast amorphous materials.

Fig. 4 presents the TEM results of the Zr50Ti50 alloy. A partial amorphous state was observed in this sample after 80 F&R cycles and the grain sizes of the residual crystalline phase (Fig. 4(a)) are in the range of 5–20 nm, with an average of 10 nm. The residual nanocrystalline grains of Zr–Ti are mixed homogenously. In specimens after further rolling to 83 cycles, nearly complete vitrification

**Table 3**

<table>
<thead>
<tr>
<th>F&amp;R</th>
<th>Zr50Al50</th>
<th>Zr50Ni50</th>
<th>Zr50Ti50</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_f</td>
<td>T_i/T_0</td>
<td>T_f/T_0</td>
<td>T_i/T_0</td>
</tr>
<tr>
<td>40</td>
<td>34</td>
<td>44.6%</td>
<td>1.59</td>
</tr>
<tr>
<td>60</td>
<td>2.1</td>
<td>2.75%</td>
<td>0.84</td>
</tr>
<tr>
<td>80</td>
<td>1.2</td>
<td>1.57%</td>
<td>0.64</td>
</tr>
<tr>
<td>100</td>
<td>0.51</td>
<td>0.67%</td>
<td>&lt;0.1</td>
</tr>
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</table>

Fig. 1. SEM/BEI side view of the Zr-based alloys after different roll-bonding cycles: (a) 40 cycles and (b) 80 cycles for the Zr50Al50 alloy; (c) 40 cycles and (d) 80 cycles for the Zr50Ni50 alloy; (e) 40 cycles and (f) 80 cycles for the Zr50Ti50 alloy.

Fig. 2. The EDS line scan measurement in (a) Zr50Al50 after 100 F&R cycles and (b) Zr50Ni50 alloy after 120 F&R cycles.
was observed. From the diffuse intensity peak in the inserted diffraction pattern in Fig. 4(b), the high intensity extended from the beam center outward to g-vector $\sim 0.48 \text{Å}^{-1}$ (or $d \sim 2.1 \text{Å}$, which is the resolution limit of the TEM). Over $g \sim 0.22–0.38 \text{Å}^{-1}$ (or $d \sim 2.6–4.6 \text{Å}$), there seemed to be a broad peak. These may correspond to the range for the first and second nearest neighbor distances of the Zr$_{50}$Ti$_{50}$ amorphous phase.

### 3.2. Grain size estimation

The grain size, $d$, has been selectively evaluated based on TEM dark field image. Typically, $d$ was seen to decrease from over 100 µm down to 20 nm or less with increasing F&R cycles. These $d$ values can be compared with those estimated from the broadening of XRD peaks, $B_{hkl}$. The simple Scherrer function [19] was first adopted for all four alloy systems, namely,

$$B_{hkl} = \frac{k\lambda}{d_{hkl}\cos \theta}, \quad (1)$$

where $k$ is a constant $\sim 0.9$ [20], $\lambda$ the X-ray wavelength (1.5406 Å), $d_{hkl}$ the grain size along the $[hkl]$ direction. For example, the calculated $d$ value based on Eq. (1) for Zr$_{50}$Ti$_{50}$ after 80 F&R cycles
was within 5.5–8.6 nm, less than the direct TEM measurement of ~10 nm.

With the consideration of XRD peak broadening induced by residual strain $\eta$, another equation should be applied \[21\], i.e.

$$B \cos \theta = \frac{k \lambda}{d} + \eta \sin \theta.$$  \hspace{1cm} (2)

Fig. 5 shows an example for the grain size $d$ of Zr in the Zr$_{67}$Ni$_{33}$ alloy estimated by Eqs. (1) and (2), along with the extracted microstrain $\eta$. After 120 F&R cycles, the grain size of Zr in Zr$_{67}$Ni$_{33}$ decreased to a few nanometers. Overall, it is found the grain size estimated by the Eq. (2) is in good agreement with the TEM measurements. Eq. (1) tends to underestimate the nanograinsize. And the extracted microstrain $\eta$ was mostly around 1–2% (a reasonable range), except for a few cases when the F&R cycles are greater than 100. Similar results were also found in other Zr–X alloys. The close agreement for grain size measurement and the reasonable estimation for microstrain by using Eq. (2) suggest that this equation provides a promising tool in characterizing the microstructure.

3.3. Hardness measurements

Fig. 6(a) reveals the typical increasing hardness trend as a function of F&R cycles. For the Zr–Cu, Zr–Ni and Zr–Ti systems, the Hv hardness can be raised from the initial ~170 to ~500, an increment factor of ~3 due to mainly grain size refinement via the ARB process. Fig. 6(b) is the hardness variation of the five Zr–Ni alloys with different composition combinations after 120 F&R cycles. The composition dependence was not pronounced for this alloy system. Similar results were also found in other Zr–X alloys.

3.4. Comparison with other routes

Fig. 7 shows the Hall–Petch plot for the hardness and grain size of Zr$_{50}$Ti$_{50}$. The hardness of alloy increased with decreasing grain size at the early stage, but it decreased as the grain size fell below 20 nm. In the previous studies of metallic TiNi multilayers by cold rolling process \[22\], the similar observation was reported. The hardness decreased presumably due to the formation of amorphous bands or the activation of grain boundary mutual sliding in these extra-fine nano-scaled materials. Moreover, a similar phenomenon
was also observed in nanocrystalline nickel by Schuh et al. [23].

Preliminary DSC measurements have indicated a glass transition \( T_g \) temperature \( \sim 813 \) K and the temperature interval of a supercooled liquid region \( \Delta T_x \sim 60 \) K for the ARB amorphous Zr\textsubscript{50}Ti\textsubscript{50} alloy, which are in the similar range as those obtained in amorphous Zr alloys prepared by other routes [24]. The thermal stability properties of the ARB specimens, compared with those processed by other means, will be presented elsewhere.

4. Summary

1. The Zr–X alloys synthesized via ARB are flat pieces with high hardness and minimum contamination or intermetallic compound.
2. The initial hardness of the elemental foils affects the efficiency of grain size refinement and vitrification. Elemental foils of compatible hardness accumulate the shear strain in a more effective way.
3. The grain size refinements after different F&R cycles were accurately estimated by XRD broadening using Eq. (2).
4. The nearest neighbor distances and thermal properties of the amorphous alloys produced by ARB are similar to those obtained by other processing routes.
5. The inverse Hall–Petch behavior was observed as the grain size falls below 20 nm for a Zr–Ti alloy.

Acknowledgement

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References