Characterization on nanocrystallization and amorphization evolution in Zr–X alloys during ARB process

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Abstract

The gradual evolution of the nanocrystallization and amorphization processes in various Zr–X-based binary, ternary, and pentanary alloys during accumulative roll bonding (ARB) are characterized by Scanning and transmission electron microscopy (SEM and TEM), in correlation with X-ray diffraction (XRD) results. It appears that compatible initial foil hardness would be most beneficial to the nanocrystallization and amorphization processes; the influence would overwhelm the atomic size effect. Based on SEM and XRD results, after 40 and 80 cycles, the foil can mostly be thinned to around 0.1–1/9262 μm, the grain size can be refined to 30 ± 20 and 10 ± 5 nm, and the amorphous volume fraction reaches 40 ± 10 and 70 ± 20%, respectively, depending on the relative hardness. The local spatial distributions of the nanocrystalline (nc) and amorphous (amf) phases are seen under TEM to be non-uniform, varying significantly in size and quantity in different regions. The diffraction spots and rings in the TEM diffraction patterns are still originated from the pure elements, meaning that the nanocrystalline phases are those unmixed hard particles left from the previous severe deformation and diffusion processes. A critical size of the nanocrystalline phases around 3 nm is consistently observed in all binary, ternary, and pentanary Zr–X-based alloys, below the critical size a sudden transformation from the nanocrystalline to amorphous state would occur.

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1. Introduction

There have been numerous fabrication means to produce bulk or thin film nanocrystalline (nc) or amorphous (amf) materials, including the rapid solidification and solid-state reaction methods. Mechanical alloying (MA) [1–5] and accumulative roll bonding (ARB) [6–11] belong to the solid state-processing route, both including extensive multiplayer interdiffusion during the process at room or elevated temperatures. The atoms of each element in the alloy are forced to diffuse homogeneously, gradually resulting in nc or eventually amf phases.

The samples prepared for ARB consist of alternating layers of various metals with thin thickness 20–100 μm. Through the accumulative passes of cold rolling for around 40–100 cycles, significant microstructure refinement will be achieved. In contrast to the MA method, ARB with its internal generation of large interfacial areas prohibits strong contamination of the foils, and leads to enhanced stability of the resulting amorphous alloys.

Most previous research on the nc or amf alloys made by the ARB route has been focused on their unique physical or mechanical properties [12–14]. The detailed characterization, especially using transmission electron microscopy (TEM), on the gradual evolution of nanocrystallization and amorphization processes by ARB has not been systematically studied. According to the characterization of an amf Zr–Al–Ni–Cu alloy processed by ARB [9], the diffusion rate of each element

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Fig. 1. SEM/BEI side views of the Zr-based alloys: 40 and 80 cycles for (a) and (b) Zr50Ti50, (c) and (d) Zr50Cu50, (e) and (f) Zr34Ti33Cu33, (g) and (h) Zr20Ti20Ni20Cu20Al20, and (i) and (j) Zr52Ti5Ni15Cu18Al10, respectively. The rolling direction is along the horizontal axis.
can be fastened by several orders of magnitude via lattice defects or interfaces introduced into the sample during heavy deformation, similar to the observation of MA specimens [15]. Meanwhile, the amorphization process of the MA specimens occurred as the accumulated defects make the free energy of the crystalline phase higher than that of the amorphous phase [16]. The nanocrystallization and vitrification mechanisms of ARB and MA methods may be similar to some degrees.

But there are at least two differences between these two synthesis methods. First, no lubricants or hard steel balls (as in MA) are used during ARB, it prohibits strong contamination and results in enhanced stability of the resulting amorphous alloys, with less tendency in inducing crystalline-glassy cyclic phase transformation [17]. Second, the severe temperature rise (to even several hundreds in Celsius degrees) occurred during MA would seriously affect its nanocrystallization and amorphization processes. The nanocrystallization and vitrification mechanisms of ARB and MA methods may be similar to some degrees.

The current study is to examine the gradual microstructural evolution of nanocrystallization and amorphization processes of various Zr–X-based binary, ternary, and pentanary alloys during ARB by means of TEM characterization. The local variation of the nc and amf phases can be identified, and the results can be compared with the X-ray findings for the overall and averaging structures.

### Table 1

<table>
<thead>
<tr>
<th>Zr</th>
<th>Ti</th>
<th>Cu</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_0$ (µm)</td>
<td>76</td>
<td>102</td>
<td>102</td>
<td>91</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>99.8</td>
<td>99.6</td>
<td>99.9</td>
<td>99</td>
</tr>
<tr>
<td>$H_N$</td>
<td>174</td>
<td>183</td>
<td>131</td>
<td>163</td>
</tr>
<tr>
<td>$r$ (Å)</td>
<td>1.62</td>
<td>1.48</td>
<td>1.28</td>
<td>1.25</td>
</tr>
<tr>
<td>$\delta r$ (%)</td>
<td>–</td>
<td>–9</td>
<td>–21</td>
<td>–23</td>
</tr>
</tbody>
</table>

The initial thickness ($t_0$), purity, hardness ($H_N$), atomic radius, and atomic radius difference with respect to Zr for the elemental foils applied.

### Table 2

<table>
<thead>
<tr>
<th>F&amp;R cycle</th>
<th>Zr50Ti50</th>
<th>Zr50Cu50</th>
<th>Zr50Ti33Cu33</th>
<th>Zr50Ti33Cu33Ni33Al10</th>
<th>Zr52Ti5Cu18Ni15Al10</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.57</td>
<td>1.59</td>
<td>0.51</td>
<td>21.93</td>
<td>0.31</td>
</tr>
<tr>
<td>60</td>
<td>0.41</td>
<td>0.84</td>
<td>0.43</td>
<td>19.91</td>
<td>0.30</td>
</tr>
<tr>
<td>80</td>
<td>&lt;0.1</td>
<td>0.64</td>
<td>0.23</td>
<td>15.41</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Representative data on the final thickness (in µm) of the Zr foils after different F&R cycles.

2. Experimental procedures

The stacked foils of Zr and other metals (Ti, Cu, Ni, and Al) around 80–100 µm in thickness (thicker than the foils of 7.5–50 µm used in most previous studies [19]) were all cleaned by acetone before and after rolling, and rolled at room temperature. The initial specimen dimensions provided for the ARB process were 20 mm in width, 30 mm in length, and 1 mm in thickness (with around 10–13 layers of various elemental foils). The compositions of the binary and ternary Zr–X alloys in this study are all assigned to be 1:1, including the Zr50Ti50, Zr50Cu50, and Zr50Ti33Cu33 alloys. Two pentanary Zr50Ti50Cu50Ni33Al10 and Zr50Ti33Ni33Cu33Al10 systems were also characterized for comparison. The staking sequence is fixed, namely, with the sequence of Zr→Ti→Cu→Ni→Al. Alternating the sequence has been tried, but the outcome was similar. The softer Al and Cu would always encounter some harder Zr or Ti no matter what the sequence would be. The stacked specimen was rolled by a HF 200 × 200 cold- and hot-rolling machine (diameter of the roller is 140 mm and length of the roller is 220 mm). Four different rolling speeds (30,
25, 22.5, and 20 mm s\(^{-1}\)) were adopted for each folding and rolling (F&R) cycle and the processing time for each pass is around 1–2 s, corresponding to a mean strain rate in the range of 10\(^{-1}\) s\(^{-1}\). The lower rolling strain rate applied was to lower the possible temperature rise during ARB. In situ temperature measurements using attached thermocouples of the rolled specimens were conducted for selected cases. The maximum temperature rise from room temperature, \(\Delta T\), was only 25 \(^{\circ}\)C, reaching a working temperature during the current ARB experiments of \(T \sim 50 \^{\circ}\)C. The thickness reduction for each F&R cycle was set to be 50%. Small parts of the specimen were sampled after 40, 60, 80, 90, and 100 cycles for off line analyses.

The layer and grain size refinement as well as the vitrification degree of the resulting alloy structure were examined by scanning electron microscopy (SEM) using mainly back-scattered images (BEI), TEM, and X-ray diffraction (XRD). The edge-on cross-sectional plane is viewed by SEM, and the flat rolling plane is characterized using TEM and XRD. Before SEM characterization, the cross-sectional plane of rolled specimens is ground and mechanically polished. The elemental diffusion analysis was conducted using an energy-dispersive spectrometry (EDS) equipped on a Jeol 6335 field emission gun SEM. The TEM thin foils were thinned by the Gatan precision ion-polishing system, and were characterized by the Jeol 3010 analytical TEM with EDS. Filtered Cu K\(\alpha\) radiation and a graphite monochromator were employed for XRD, with a scanning rate of 1\(^{\circ}\) min\(^{-1}\). Table 1 lists the related information of the alloy systems prepared for the ARB route, including the hardness and atomic radius data.

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![XRD patterns](image.png)

**Fig. 3**. The XRD patterns for (a) Zr\(_50\)Ti\(_50\), (b) Zr\(_{50}\)Cu\(_{50}\), (c) Zr\(_{34}\)Ti\(_{33}\)Cu\(_{33}\), (d) Zr\(_{20}\)Ti\(_{20}\)Ni\(_{20}\)Cu\(_{20}\)Al\(_{20}\), and (e) Zr\(_{52}\)Ti\(_{5}\)Ni\(_{15}\)Cu\(_{18}\)Al\(_{10}\) alloys after 40 and 80 F&R cycles.
3. Results and discussions

3.1. Foil thinning evolution

Fig. 1 compares the SEM–BEI side view of some typical ARB samples, including the binary Zr\textsubscript{50}Ti\textsubscript{50} and Zr\textsubscript{50}Cu\textsubscript{50}, ternary Zr\textsubscript{34}Ti\textsubscript{33}Cu\textsubscript{33}, and pentanary Zr\textsubscript{20}Ti\textsubscript{20}Ni\textsubscript{20}Cu\textsubscript{20}Al\textsubscript{20} and Zr\textsubscript{52}Ti\textsubscript{5}Ni\textsubscript{15}Cu\textsubscript{18}Al\textsubscript{10} systems. After 40 and 80 F&R cycles (Fig. 1(a) and (b)), the foil thinning and mutual mixing appeared to be mostly effective in the binary Zr\textsubscript{50}Ti\textsubscript{50} system with compatible initial hardness (Zr: 174 and Ti: 183); the foils can be thinned to submicrometer levels after 40 cycles. For the Zr\textsubscript{50}Cu\textsubscript{50} alloy (Fig. 1(c) and 1(d)) with larger initial hardness difference (Zr: 174 and Cu: 131), the foil thinning efficiency (as well as the amorphization efficiency, as judged from the XRD results in Section 3.2) appears to be less than the Zr\textsubscript{50}Ti\textsubscript{50} one, though the atomic radius difference between Zr and Cu is larger than that between Zr and Ti (Table 1). Another factor that should be borne in mind is the similarity of crystal structure of the elements involved. With the same hexagonal close-packed (HCP) crystal structure for Zr and Ti, the mutual mixing might also be more favorable.

Fig. 4. The variations of (a) nc grain size and (b) amf volume fraction in various Zr–X alloys as a function of F&R cycles, based on the XRD results.

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 would raise more difficulties to complete mixing. Since ARB is a solid-state low-temperature reaction, the prerequisites such as the large atomic size difference (the anti-Hume–Rothery rule) or the low-eutectic temperature in the corresponding thermodynamic diagram [20,21] imposed for the most bulk amorphous alloys are not essential. The initial mutual foil hardness becomes critical since the foils need to effectively deform each other to render thinning and mixing.

Table 2 compares the resulting Zr foil thickness reduction with increasing cycles for the alloys studied. With the third elemental foil added in the ARB process, the efficiency of foil thinning and mixing depends on the relative hardness of each foil. The resulting Zr\textsubscript{34}Ti\textsubscript{33}Cu\textsubscript{33} specimens are compared in Fig. 1(e) and (f). The softest Cu foil would always be preferentially sheared and torn by the two other harder ones, but the two harder Zr and Ti foils would deform each other strongly after one F&R cycle. It needs the Cu foils to be fractured into pieces and then the Zr and Ti foils become intact and deform each other. The nanocrystallization and amorphization processes for Zr\textsubscript{34}Ti\textsubscript{33}Cu\textsubscript{33} appear to be slower than those for Zr\textsubscript{50}Ti\textsubscript{50}, but higher than those for Zr\textsubscript{50}Cu\textsubscript{50}. The worst situation is the pentanary Zr\textsubscript{20}Ti\textsubscript{20}Ni\textsubscript{20}Cu\textsubscript{20}Al\textsubscript{20} alloys with the even softer Al, as shown in Fig. 1(g) and (h). The Zr layers remained to be 10–20 \( \mu \)m even after 80 cycles. Nevertheless, the pentanary Zr\textsubscript{52}Ti\textsubscript{5}Ni\textsubscript{15}Cu\textsubscript{18}Al\textsubscript{10} alloy behaved better, as shown in Fig. 1(i) and (j), since the abundant Zr layers themselves would shear and deform each other. Thus, the initial thinning proceeds rapidly, but the later nanocrystallization and amorphization speeds slow down, as evident from Table 2.

Typical SEM–EDS measurements across an inter-layer boundary are shown in Fig. 2 for the Zr\textsubscript{50}Cu\textsubscript{50} and Zr\textsubscript{34}Ti\textsubscript{33}Cu\textsubscript{33} alloys, indicating the elemental interdiffusion during ARB (at 25–50 °C) [22] enhanced by the repeated heavy deformation. For the Zr–Ti systems, a homogeneous mixing state can be reached after 80 F&R cycles. However, it should be noted that the SEM–EDS spatial resolution is limited, especially including the beam broadening effect [23]. The actual elemental mixing needs to be revealed by the TEM.

3.2. X-ray results for the overall bulk specimens

Fig. 3 shows the typical XRD patterns for the binary, ternary, and pentanary systems. There are three notable figures. First, the diffraction peaks in all specimens (independent of alloy systems and F&R cycles) were contributed by the pure elements with minimum or nil shifts in the corresponding diffraction angles for the pure elemental foils, even when the peaks become broadened due to the size- and
strain-broadening effects. Second, no evidence of intermediate compound formation was found. Third, with increasing F&R cycles, apparent peak height reduction can be seen, and a diffuse and broad hump located at $2\theta \sim 33^\circ$ becomes more and more evident. These three observations suggest that the refined nc phases are basically still pure elements in nature. But the amorphous matrix is a homogenous solid solution.

After 83 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, as also shown in Fig. 3(a). The broad diffuse hump starts from $2\theta$
∼ 23° and ends at 2θ ∼ 45° (corresponds to a plane spacing from 2.0–4.0 Å), with its center of the diffuse peak located at 2θ ∼ 33° (a plane spacing ∼2.7 Å). It is not referred to any of the elemental spacing and is slightly smaller than the closest plane spacing for HCP Zr (3.17 Å) and Ti (2.89 Å). It is conceivable that the closest spacing is referred to the inter-spacing between Zr and Ti in the amf alloy. In Fig. 3(b)–(e) for the Zr–Cu, and the ternary and pentanary alloys, some strong and sharp peaks are still retained after 80 F&R cycles. The peaks left after 80 cycles are basically the harder one, e.g. Zr in Fig. 3(b), and Zr and Ti in Fig. 3(c). For the pentanary Zr52Ti20Ni15Cu18Al10 alloys shown in Fig. 3(d), the nanocrystallization rate was more sluggish, due to the presence of abundant softer Al and Cu foils. For the pentanary Zr95Ti5Ni5Cu3Al2 alloys shown in Fig. 3(e), the weak peaks left after 80 cycles are all referred to Zr. The XRD results are basically in consistence with the SEM–BEI side viewed observation presented in Fig. 1.

The grain size, \( d \), was first estimated by the broadening of XRD peaks, \( B_{hkl} \), using the simple Scherrer function \([24]\),

\[
B_{hkl} = \frac{k \lambda}{d_{hkl} \cos \theta}
\]  

and the modified equation \([25]\),

\[
B \cos \theta = \frac{k \lambda}{d} + \eta \sin \theta
\]

where \( k \) is a constant ∼0.9 \([26]\), \( \lambda \) the X-ray wavelength (1.5406 Å), \( d_{hkl} \) the grain size along the \([hkl]\) direction, and \( \eta \) the residual strain.

The extracted \( d \) data by Eq. (1) tend to underestimate the nc grain size, and the values estimated by the Eq. (2) are in much better agreement with the TEM measurements. The extracted microstrain \( \eta \) was mostly around 1–2%, except for a few cases with F&R cycles greater than 100. The extracted strain level is considered to be reasonable. The volume fraction of the amf phase presents in various specimens can be estimated by the relative weighting of the XRD diffuse hump. The integrated intensity (excluding the background) of the diffuse hump divided by the overall integrated intensity (also excluding the background) of all retained peaks plus diffuse hump would represent the amf volume fraction. Fig. 4 shows the estimation of the nc phase size and amf volume fraction based on the XRD patterns. After 40 and 80 cycles, the grain size can be refined to 30 ± 20 and 10 ± 5 nm, and the amf volume fraction reaches 40 ±
10 and 70 ± 20%, respectively, depending on the relative hardness.

3.3. TEM results for the local regions

The X-ray results are all referred to the averaging measurements for the bulk volume. Local variations of the nc and amf phases in terms of the nc phase size, spatial distribution of the nc and amf regions cannot be traced. TEM observations provide the direct information on the spatial distribution.

Fig. 5 presents the TEM micrographs of the Zr50Ti50 alloy after 40 cycles. The Zr and Ti elemental grains have been effectively refined to 50–100 nm, with an average phase size of 70 nm. This average size is slightly larger than that estimated by XRD using Eq. (2). The reflection spots in the associated diffraction patterns, after one-to-one indexing, are all referred to hexagonal pure Zr or Ti. There are very limited amounts of the amf phase (less than 20% in volume fraction), as judged from the bright and dark field images as well as diffraction patterns. With the F&R cycles increased to 60 for the Zr50Ti50 alloy, the phase sizes are suddenly refined to around 10 nm, varying from 5–20 nm, as shown in Fig. 6(a). The background in Fig. 6(a) shows the presence of limited amf phases. The diffraction spots and rings in the inserted diffraction pattern are still originated from pure Zr and Ti, meaning that the nc phases are those unmixed hard particles left from the previous severe deformation and diffusion processes. Appreciable amounts of the amf regions are found (∼40% in volume fraction), as illustrated in Fig. 6(c). After F&R cycles of 80 for the Zr50Ti50 alloy, most regions are either complete vitrified or contain a few fine nc phases around 3–5 nm in size in the amf matrix, as shown in Fig. 7. The estimated amf volume fraction is around 80%. The diffuse intensity holo in the diffraction pattern of Fig. 7(d) is seen to extend from the beam center outward to g-vector ∼0.48 Å⁻¹ (or d ∼ 2.1 Å), which is the resolution limit of the TEM. In-between g ∼ 0.22–0.38 Å⁻¹ (or d ∼ 2.6–4.6 Å, similar to the XRD results), there is a continuous broad peak. These may correspond to the range for the first and second nearest neighbour distances of the Zr50Ti50 amorphous phase. The evolution trend of the nc size and amf volume fraction as a function of F&R cycle based on TEM characterizations is presented in Fig. 8. The data in Fig. 8 are slightly different from those in Fig. 4 obtained from the XRD analyses.

Parallel TEM characterizations on the Zr50Cu50 alloy reveal the similar story, but the evolution pace is somewhat slower. With the F&R cycles up to 80, the average size of the nc phase is ∼10 nm, and the amf volume fraction is estimated to be around 65%. The representative TEM micrographs are shown in Fig. 9.

As for the ternary Zr53Ti13Cu34 alloy, the spatial distribution of the nc and amf phases was seen to be more scattered. Fig. 10 shows the apparent different microstructures in this alloy after an even higher F&R cycle of 100, one with nc grains of ∼20 nm and minimum amf phases (Fig. 10(a)), and the other with finer nc grains of ∼5 nm in the amf matrix (Fig. 10(c)). In some other large region, complete amf phase is observed, as presented in Fig. 10(e). The higher degree of structure in-homogeneity in this ternary alloy is a result of initial hardness difference of Cu with respect to Zr and Ti. The microstructure evolution trend of this alloy is also compared in Fig. 8.

The pentanary alloys show even more sluggish and more inhomogeneous structure evolution at later stages. Fig. 11 is an example for the Zr52Ti5Ni15Cu18Al10 alloy after 100 F&R cycles, showing the still rather large nc phase of pure Zr measuring ∼60–100 nm in Fig. 11(a), fine nc phases ∼5 nm in size within the amf matrix in Fig. 11(c), and finally a complete vitrified region in Fig. 11(e). The occasionally large nc phases greater than 50 nm in size were not observed in the binary and ternary alloys after 100 F&R cycles. The evolution trend of the pentanary alloys is also included in Fig. 8.

Selective TEM–EDS measurements were done in the binary, ternary and pentanary alloys. Due to the strong Cu peaks induced from the Cu TEM specimen grid and holder, more meaningful results were gathered from the Zr–Ti systems.
3.4. Nanocrystallization and amorphization transformation

Over the systematic TEM characterizations on the Zr$_{50}$Ti$_{50}$, Zr$_{34}$Ti$_{33}$Cu$_{33}$, and Zr$_{52}$Ti$_{5}$Ni$_{15}$Cu$_{18}$Al$_{10}$ systems showing more effective nanocrystallization and amorphization, it is sometimes observed the transition region between the nc and amf regions. The nc size is gradually reduced as approaching the transition boundary, mostly from $\sim 10$ nm down to $3$ nm. The smallest nc size observed in the TEM bright or dark field images near the boundary is around $3$ nm. Such a transformation tendency was observed in all binary, ternary and pentanary alloys, and did not appear to be composition dependent. This size is also about the smallest grain size estimated, based on the modified Scherrer equation for XRD broadening peaks. Fig. 13 shows an example for the interface region between the nc and amf phases, taken from the Zr$_{50}$Ti$_{50}$ alloy after 80 F&R cycles. As the grain size is further refined to below $3$ nm, the nc phase seems to become unstable. It can be easily calculated that the atoms associated with the interface in a sphere of $\sim 3$ nm in size would be around 60% of the total atoms. Since there are about 500–700 atoms inside the nc phase of $\sim 3$ nm in size, there would be
Fig. 10. TEM bright field images and their associated diffraction patterns for the Zr$_{34}$Ti$_{33}$Cu$_{33}$ alloy after 100 F&R cycles: (a) and (b) showing the nc region, (c) and (d) showing the nc phases in the amf matrix, and (e) and (f) showing the amf regime.

around 300–400 atoms located near the interface. The surface energy per mole for the pure metallic elements would be raised from $\sim 10^2 \text{ J mol}^{-1}$ for coarse-grained materials to $\sim 10^3 \text{ J mol}^{-1}$, for 3 nm grains [28], or an increment of $\sim 100$ times. The increase of interfacial energy term would raise the system Gibbs free energy to a level greater than that for the metastable amf state, as depicted schematically in Fig. 14. Similar thoughts have also been proposed by Chen and Liu [29]. Simultaneous transformation from the nc phase into the amf state would occur. Previous studies of the current alloys have reached the conclusion that there is no dislocation or fault left in all nc phases smaller than 15 nm in this study [30]. It follows that the increment of Gibbs free energy of the nc phases should be solely a result of the interfacial energy term with no contribution from the defect strain energy.
The critical size of ∼3 nm appears to be a lower bound for the stability of the nc grains in these systems. The 500–700 atoms inside the nc phase of ∼3 nm would suddenly lose their stability in form of crystalline phase. The long-range-order crystalline structure is broken down into an amorphous structure with only short range ordering. This phenomenon should be aware of when the nc materials are applied for structural or functional applications. The unique characteristics of nano phases might be lost upon transformation to amf phases. Furthermore, the amf phase could also transform back to the nc state at the critical size of ∼3 nm, exhibiting cyclic transformation near this critical size regime. This has been observed in a number of systems subject to severe deformation [17,31]. This was because that the Gibbs free energies of the amf and nc phases near such a critical size are marginally close.
4. Conclusions

1. The gradual evolution of nanocrystallization and vitrification as a function of F&R cycles is established. After 40 and 80 cycles, the average grain size can be refined to 30 ± 20 and 10 ± 5 nm, and the amf volume fraction reaches 40 ± 10 and 70 ± 20%, respectively, depending on the relative hardness.

2. The local variation of the resulting grain size and amorphous regions in alloys after the ARB process increases with increasing number of compositional elements. It means that a more inhomogeneous structure would be obtained for alloys with more complicated composition, even after high-F&R cycles.

3. The evolution trends extracted from the XRD and TEM results are consistent, but slight discrepancy is observed. The TEM results reveal the local variation of the nc phase size and amf volume fraction.

4. It appears that compatible initial foil hardness would be most beneficial to the nanocrystallization and amorphization processes during the room temperature solid-state ARB process; the influence would overwhelm the atomic size effect. The prerequisites such as the large atomic size difference (the anti-Hume–Rothery rule) or the low-eutectic temperature in the corresponding thermodynamic diagram imposed for the most bulk amorphous alloys during cast and solidification are not essential.

5. The critical size of ~3 nm appears to be a lower bound for the stability of nc phases in the current binary, ternary and pentanary alloy systems, and does not seem to be a function of alloy composition. Further refinement would result in sudden transformation to the amf state. Cyclic transformation between the nc and amf phases near this critical size would occur.

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References


