Nanocrystallization and Amorphization Mechanisms in Zr-X Alloys during the ARB Process

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The gradual nanocrystallization and amorphization mechanisms in various Zr-X alloys during accumulative roll bonding (ARB) are explored. The effects of strain accumulation, the relative initial hardness of the elemental foils, the enhanced diffusion, and the critical nano size for the sudden transformation from the nanocrystalline phase to the amorphous state are examined. For elemental foils with compatible initial hardness, the nanocrystallization and amorphization rates appear to be higher. The estimated diffusion rates during ARB are higher by several orders of magnitude than the lattice diffusion in bulk materials. When the nano grains are refined down to around 3 nm, sudden transformation into the amorphous phase would occur.

Keywords: Accumulative roll bonding; Phase transformation; Nanocrystalline materials; Metallic glasses

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1. Introduction

Except for the amorphization from the liquid phase using high cooling rates, numerous alloys can be vitrified by interfacial diffusion through solid state reactions. The atoms of each element in the alloy are forced to diffuse homogeneously at room or elevated temperatures, resulting in nanocrystalline (nc) or eventually amorphous (amf) phases. Mechanical alloying (MA) 1-5) and accumulative roll bonding (ARB) 6-11) belong to this category, both including extensive multiplayer interdiffusion during the process.

The samples prepared for ARB consist of alternating layers of various metals with a thin thickness of 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 mechanisms of nanocrystallization and amorphization by ARB have 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 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 the MA specimens.15) Meanwhile, the amorphization process of the MA specimens occur when the free energy of the crystalline phase becomes higher than that of
the amf phase due to the accumulated defects.\textsuperscript{16} The vitrification mechanism of the ARB and MA methods may be similar to some degrees.

But there are at least two differences between these two synthesis methods. Firstly, no lubricants or hard steel balls (as in MA) are used during the ARB process. It prohibits strong contaminations and leads to enhanced stability of the resulting amorphous alloys, with a less tendency in inducing crystalline-glassy cyclic phase transformation\textsuperscript{17} as occurred in some MA alloys (e.g. Zr\textsubscript{50}Al\textsubscript{50}, Zr\textsubscript{67}Cu\textsubscript{33} and Co\textsubscript{75}Ti\textsubscript{25}). Secondly, a severe temperature rise (to even several hundreds in Celsius degrees) occurred during MA would serious affect its nanocrystallization and amorphization processes. In contrast, if the specimen dimension is small enough so to easily release heat from the rollers, and if the rolling speed is low, the temperature rise during the ARB process could be much lower. For ARB at a rolling strain rate of 19 s\textsuperscript{-1}, the maximum temperature rise was estimated to be 167 K.\textsuperscript{18} If the rolling strain rate is controlled to be less than 1 s\textsuperscript{-1}, then the temperature rise should be less than 50 K. The possible temperature increment of 10-200 K may also assist to a certain degree in the interdiffusion of elements during ARB process.

The current study is to examine the gradual nanocrystallization and amorphization mechanisms of various Zr-X alloys during ARB, and to compare with the findings from the MA method. Besides, the influence of effective diffusion distance of atoms will also be investigated.

2. Experimental procedures

The stacked foils of Zr and other metals (Al, Ni, Ti, and Cu) around 80-100 µm in thickness (thicker than the foils of 7.5-50 µm used in most previous studies e.g.\textsuperscript{19}) were all cleaned by acetone before and after rolling, and rolled at room temperature (298 K). The elemental foils were first cut into pieces measuring 20 mm in width and 120 mm in length, and stacked in order. The stacked foils were then manually folded three times, resulting in an initial specimen, measuring 20 mm in width, 30 mm in length and 1 mm in thickness (with around 10-13 layers of various elemental foils), ready for the ARB process. The step of manual folding plays an important role to keep the staked foils in order during ARB, especially for the first ten folding and rolling (F&R) cycles.

The compositions of the Zr-X alloys are all assigned to be 3:1, 1:1 and 1:3. Limited tests were conducted on the ternary Zr\textsubscript{34}Ti\textsubscript{33}Ni\textsubscript{33} and Zr\textsubscript{34}Ti\textsubscript{33}Cu\textsubscript{33} alloys and the pentanary Zr\textsubscript{20}Ti\textsubscript{20}Ni\textsubscript{30}Cu\textsubscript{20}Al\textsubscript{20} and Zr\textsubscript{52}Ti\textsubscript{15}Ni\textsubscript{15}Cu\textsubscript{18}Al\textsubscript{10} systems for confirmation. The stacked specimen was rolled by a 350-ton cold and hot rolling machine. The roller diameter is 140 mm and the roller length is 220 mm. Four different rolling speeds (30, 25, 22.5 and 20 mm/s) were adopted for each F&R cycle and the processing time for each pass is around 1-2 seconds, corresponding to a mean strain rate in the range of 10\textsuperscript{-1} s\textsuperscript{-1}. A lower rolling strain rate was applied in order to lower the possible temperature rise during ARB. The thickness reduction for each F&R cycle was set to be 50%. Small parts of the specimen were sampled after 40, 60, 80, 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), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The edge-on cross-sectional plane was viewed by SEM, and the flat rolling plane was characterized using TEM and XRD. Before SEM characterization, the cross-sectional plane of rolled specimens was ground and mechanically polished. The elemental diffusion analysis was conducted using an energy-dispersive X-ray spectrometry (EDS) equipped on a Jeol 6335 field emission gun SEM. Selected specimens, after thinned by the Gatan precision ion polishing system, were characterized by the Jeol 3010 analytical TEM with
EDS. Filtered Cu-Kα radiation and a graphite monochrometer were employed for XRD, with a scanning rate of 1° per minute. Table 1 lists the related information of the alloy systems, including the hardness and diffusion data\(^{20}\) prepared for the ARB route.

3. Results and Discussion

3.1 Strain Accumulation

The specimen thickness reduction is set to be 50% per F&R cycle and the residual strain could be accumulated continuously. Therefore the thickness and true strain (considering the von Mises yielding criterion and plain strain condition\(^{13}\)) after \(n\) cycles can be predicted as

\[
t_n = \frac{t_0}{2^n},
\]

and

\[
\varepsilon_n = \frac{2}{\sqrt{3}} \ln(t_n/t_0) = \frac{2n}{\sqrt{3}} \ln 2 \approx 0.8n,
\]

where \(t_0\) is the initial thickness of foil. Theoretically, the thickness of Zr or other foils after 40 F&R cycles will be around \(1 \times 10^{10} \mu\text{m}\), and the accumulative true strain will be 32. But according to the SEM observation (on the cross-sectional plane) in our previous report,\(^{21}\) the foil thickness instead reaches around 0.5-40 \(\mu\text{m}\) (Fig. 1) depending on the hardness of the foil. This is because of the large difference in foil hardness readings among the adopted elemental foils, rendering non-uniform deformation of the thin foils. A misaligned factor, \(k\),\(^{22}\) has been suggested to insert into the thickness estimation expression as

\[
t_n = t_0 \left[\frac{1+k}{2}\right]^n. \quad (2a)
\]

The factor \(k\) is called the misaligned factor, and is a result from the fact that the softer foils would be preferentially thinned, leaving the harder foils retained as thicker layers or forced to be fractured into pieces.

Thus the actual accumulated true strain will be

\[
\varepsilon_n = \frac{2}{\sqrt{3}} \ln(t_n/t_0) = \frac{2n}{\sqrt{3}} \ln \left(\frac{1+k}{2}\right)^n. \quad (2b)
\]

The \(k\) value can be extracted by fitting the experimentally measured data in Table 2. Table 3 reveals the estimated \(k\) values and the accumulated true strain \(\varepsilon_n\). For most cases, the \(k\) and \(\varepsilon_n\) values would gradually reach around 0.85 and 7.5 after 80 F&R cycles, instead of the theoretical \(\varepsilon_n\) value of 64 given by eq. (1b). The significant discrepancy between the theoretically predicted and experimentally measured strain values is due to the low efficiency of strain accumulation, particular at the later ARB stage. The stacked foils would sometimes slide with each other or fracture into pieces instead of being deformed or sheared. The former processes (sliding or fracture) would not cause effective foil thinning and strain accumulation.

Note that \(\varepsilon_n\) for Zr\(_{50}\)Al\(_{50}\) is lower than the other cases (such as Zr\(_{50}\)Ti\(_{50}\) and Zr\(_{50}\)Ni\(_{50}\)), reflecting that the accumulation of true strain was impeded by the large hardness difference between Zr and Al (Table 1). The actual \(\varepsilon_n\) level of \(~7.5\) experienced during ARB is compatible to those experienced during MA or equal channel angular pressing (ECAP), but the working temperatures of the latter two are usually higher due to an appreciable temperature rise. It can be regarded that the current high level of accumulated strain during ARB near room temperature would assist effectively in grain size refinement and alloy
vitrification, similar to the recent work of cryogenic MA.23,24)

3.2 Diffusion during ARB

Due to the special configuration of ARB, the elemental foils would undergo diffusion under the compression and shear stresses, resulting in physical bonding. Interdiffusion of various atoms becomes progressively effective with increasing cycles, particularly with the abundant lattice defects induced.

For instance, the lattice and grain boundary diffusivity, $D_L$ and $\delta D_B$, for Al at room temperature are $2.18 \times 10^{-29}$ m$^2$/s and $9.43 \times 10^{-29}$ m$^3$/s, where $\delta$ is the grain boundary width. Assuming the processing time for each rolling pass is 2 s and $\delta$ is 1 nm, the calculated diffusion distances, $X$, via lattice diffusion and grain boundary diffusion per cycles are $2.64 \times 10^{-5}$ nm and 1.74 nm, respectively, based on the relationship $X \approx 4\sqrt{Dt}$.25) Similar calculations for other elements were done, as shown in Table 4. Such diffusion distance at room temperature seems to be negligible. However, several effects would enhance the interdiffusion.

Firstly, the heavy rolling applied during ARB would cause severe plastic deformation plus pronounced friction (since no lubrication was used in prevention from contamination); both would raise the specimen temperature. A moderate temperature rise of ~25 K from the room temperature of 298 K to ~323 K, as directly measured by inserted thermocouples, was found to be induced as the specimen just passed through the rollers. The current rolling strain rate was around $10^{-1}$ s$^{-1}$. The temperature increment could be affected by the specimen dimension and rolling speed, as mentioned above. For example, the temperature increase for 1100 Al sheets, measuring 1 mm in thickness, 40 mm in width and 300 mm in length, was reported to be ~167 K at an ARB rolling strain rate of 19 s$^{-1}$.18) The lower temperature rise of the current ARB experiment is a result of smaller specimen size and lower rolling speed. Using the thermal trapping models proposed by Grady and Asay 26) or Kato, 27) the temperature increment during the current ARB should be at most 30 K, consistent with the direct temperature measurement.

It is conceivable that even a minor temperature rise would also affect the nanocrystallization and amorphization processes via the enhancement in the elemental interdiffusion. Table 4 presents the relationship between diffusion distance and temperature increment. The diffusion distance during each F&R cycle at 323 K would increase by one to two orders of magnitude, as compared with that at room temperature or 298 K.

Secondly, with the continuous reduction in foil thickness down to 1 µm or less, as well as grain size down to 30 nm or below, significant increment of interfacial and grain boundary diffusion would occur. As the grain size decreases to 10 nm, the grain boundary region will occupy more than 25% of the specimen volume. Thus the grain boundary diffusion would overwhelm the interdiffusion process. Even the lattice diffusion would also increase several orders of magnitude with the help of deformation induced lattice defects. Estimation of the diffusivity $D$ can be made using the Grube method, 28) in which $D$ can be extracted by solving the error function if the composition profile is known. The EDS line scan can provide various composition variation plots as a function spatial position across the elemental foils after 40-80 cycles. One example is shown in Fig. 2. The diffusivity for Al is thus calculated to be of the order of $10^{-15}$ m$^2$/s, significantly higher than the values of $D_L$ and $\delta D_B$ for Al at 298 K or 323 K, consistent with the increment of 7-9 orders of magnitude of Cr diffusion in nc Fe.29)

In short summary, the interdiffusion between neighboring elemental foils would be most greatly enhanced by the involvement of interfacial and grain boundary diffusions as
the microstructures are refined down to the nc regime. Diffusion enhanced by the deformation induced lattice defects would be secondly important. Finally, the minor temperature rise would also raise the diffusion rate by one to two orders of magnitude.

3.3 Hardness effect

Based on our previous studies,\(^{21}\) the initial hardness of the elemental foils appeared to seriously affect the efficiency of grain size refinement and vitrification. In this study, a pre-hardening step for the softer Cu foils was applied before ARB. The initial \(H_v\) hardness of the purchased pure Cu foils was 46. After the pre-hardening step by prior rolling, the hardness increased to 131 (Table 1), much more comparable to the rest of Zr \((H_v=174)\), Ni \((163)\) and Ti \((183)\).

Figure 3 shows the SEM micrographs of the Zr\(_{50}\)Cu\(_{50}\) alloys with and without the pre-hardening step for the Cu foils. The foils thinning and atom mixing situations of the alloy with the pre-hardened Cu foils were seen to be much more efficient. Also, the XRD peak broadening was more apparent in the pre-hardened specimens, as compared in Fig. 4. The similar effect was also seen in the ternary or pentanary alloys. Throughout the study, it is consistently found that elemental foils with compatible initial hardness would be nanocrystallized or vitrified in a more effective way.

3.4 Nanocrystallization and amorphization mechanisms

With increasing F&R cycles to over 20, the grain size was seen to decrease rapidly to the nano regime, and an apparent amf phase can also be traced by the XRD and TEM diffraction patterns, as well as by the subsequent DSC curves of the ARB specimens. Rough estimation of the volume fraction of the amf phase, \(V_{amf}\), was done based on XRD patterns. With the initial XRD patterns with sharp peaks for the elemental foils as \(V_{amf}=0\%\) and the final XRD patterns with broad and diffuse hump as \(V_{amf}=100\%\), the evolution of \(V_{amf}\) as a function of F&R cycles can be assessed by the overall weighting of the XRD integral intensities for the sharp and diffuse peaks. The estimated \(V_{amf}\) values were also selectively checked by TEM micrographs taken from the specimens subjected to different ARB cycles. In fact, the DSC curves obtained from the ARB specimens to different F&B cycles also indirectly reflect the amf amount. With complete occupancy of the amf phase, the DSC curve shows no exothermal peak before the glass transition \(T_g\) temperature, but exhibits one or more recrystallization or growth peaks in specimens with abundant nc phases. It is still difficult to extract quantitative \(V_{amf}\) amount from the DSC curves, but it is adequate to act as the complementary check for the values estimated from the XRD and TEM observations. The extracted \(V_{amf}\) data for various Zr-X alloys are shown in Fig. 5(a).

In addition, the size of the nano phase, \(d\), was measured by the modified Scherrer function \(^{30}\)

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

where \(B\) and \(K\) are constants, \(\lambda\) is the X-ray wavelength, and \(\eta\) is the residual strain. Our previous results \(^{21}\) have shown that eq. (3) could provide convincing grain size information consistent with TEM observations. Figure 5(b) shows the variation of the measured grain size of various Zr-X systems as a function of F&R cycles.

After 40 cycles, the average grain size is scattered within 10-50 nm, and the amf volume fraction is varied within 30-50%. For the Zr-Ti system with compatible hardness readings for Zr and Ti, the nanocrystallization and amorphization processes seem to proceed most efficiently. In contrast, the Zr-Al system with distinct hardness values evolves in a
much slower pace. Meanwhile, the TEM dark field image reveals apparent dislocation activities in the nc grains larger than 20 nm (Fig. 6); and hardly any defect contrast can be seen in the Zr or Ti nc phase smaller than 15 nm. There is no intermetallic compound induced in any of the Zr-X systems, unlike the MA case with appreciable adiabatic heating. All peaks or reflections in the XRD and TEM diffraction patterns for the ARB specimens are referred to the pure elements.

The transformation from the nc to amf state is of concern. The smallest grain size observed in the TEM bright or dark field image, as well as the estimated grain size based on the Scherrer equation for XRD broadening peaks, is around 3 nm. Figure 7 shows the interface region between the nc and amf phases. As the grain size is further refined to a level 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 ~3 nm in size would be around 60% of the total atoms. Since there are about 500-700 atoms inside the nc phase of ~3 nm in size, there would be around 300-400 atoms located near the interface. The surface energy per mole for the pure metallic elements would be raised from ~10^2 J/mol for coarse grained materials to ~10^3 J/mol, for 3 nm grains, or an increment of ~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. Simultaneous transformation from the nc phase into the amf state would occur. Note that no dislocation or fault was observed in all nc phases smaller than 15 nm in this study, thereby 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. 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 average ARB true strain reaches ~7.5 (instead of the theoretical value of 64) after 80 F&R cycles, and such a strain level is compatible to those experienced during MA or ECAP. A large difference in hardness among elemental foils will limit the accumulation of true strain during ARB.
2. Apparent enhancement of diffusion is evident during ARB via grain boundary and lattice diffusion with the help of high grain boundary area and induced lattice defects.
3. The pre-hardening step is useful to enhance the efficiency of strain accumulation, nanocrystallization, and amorphization.
4. The gradual evolution of nanocrystallization and vitrification as a function of F&R cycles is established. 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.
5. The critical size of ~3 nm appears to be a lower bound for the stability of nc phases in
the current systems. 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.

Acknowledgements

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REFERENCES

Table 1  Initial thickness ($t_0$), purity and hardness ($H_v$) of each elemental foil; as well as the lattice and grain boundary diffusivity ($D_L$ and $\delta D_B$) \(^{20}\)

<table>
<thead>
<tr>
<th></th>
<th>Zr</th>
<th>Al</th>
<th>Ni</th>
<th>Ti</th>
<th>Cu</th>
<th>Pre-hardened Cu</th>
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<td>91.4</td>
<td>101.6</td>
<td>101.6</td>
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<tr>
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<td>99%</td>
<td>99%</td>
<td>99.6%</td>
<td>99.9%</td>
<td>--</td>
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<tr>
<td>$H_v$</td>
<td>173.8</td>
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<td>183.4</td>
<td>46.1</td>
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<td>$D_L$ at RT, m$^2$/s</td>
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<td>$\delta D_B$ at 323 K, m$^3$/s</td>
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Table 2  Representative data on the final thickness (in $\mu$m) of the Zr foils after different F&R cycles (Z5 represents the Zr$_{52}$Ti$_{13}$Ni$_{13}$Cu$_{18}$Al$_{10}$ alloy)

<table>
<thead>
<tr>
<th>F&amp;R</th>
<th>Zr$<em>{50}$Al$</em>{50}$</th>
<th>Zr$<em>{50}$Ni$</em>{50}$</th>
<th>Zr$<em>{30}$Ti$</em>{50}$</th>
<th>Zr$<em>{34}$Ti$</em>{33}$Ni$_{33}$</th>
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<td>40</td>
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<td>1.59</td>
<td>0.57</td>
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<td>0.31</td>
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<tr>
<td>60</td>
<td>2.1</td>
<td>0.84</td>
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<tr>
<td>80</td>
<td>1.2</td>
<td>0.64</td>
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Table 3  The misaligned factor $k$ and accumulated true strain $\varepsilon_n$

<table>
<thead>
<tr>
<th>F&amp;R</th>
<th>$k$</th>
<th>$\varepsilon_n$</th>
<th>$k$</th>
<th>$\varepsilon_n$</th>
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<tr>
<td>40</td>
<td>0.96</td>
<td>0.93</td>
<td>0.81</td>
<td>4.61</td>
<td>0.77</td>
<td>5.67</td>
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<td>60</td>
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<td>5.40</td>
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<td>7.16</td>
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<td>80</td>
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<td>5.22</td>
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<td>6.64</td>
<td>0.85</td>
<td>7.50</td>
<td>0.87</td>
<td>6.45</td>
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Table 4  Diffusion distances via lattice and grain boundary diffusion ($X_L$ and $X_{GB}$, in nm) per F&R cycle at room temperature (RT, 298 K) and 323 K

<table>
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<tr>
<th></th>
<th>Zr</th>
<th>Al</th>
<th>Ni</th>
<th>Ti</th>
<th>Cu</th>
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<td>$X_L$, at RT</td>
<td>6.89x10^{-10}</td>
<td>2.64x10^{-5}</td>
<td>1.00x10^{-17}</td>
<td>1.18x10^{-8}</td>
<td>1.37x10^{-10}</td>
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<tr>
<td>$X_{GB}$, at RT</td>
<td>6.86x10^{-4}</td>
<td>1.74x10^{0}</td>
<td>8.82x10^{-4}</td>
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<td>9.70x10^{-3}</td>
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<tr>
<td>$X_L$, at 323 K</td>
<td>1.34x10^{-8}</td>
<td>2.43x10^{-4}</td>
<td>8.46x10^{-16}</td>
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<td>$X_{GB}$, at 323 K</td>
<td>4.75x10^{-3}</td>
<td>6.45x10^{0}</td>
<td>5.32x10^{-3}</td>
<td>4.87x10^{-2}</td>
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Figure captions

Fig. 1  SEM/BEI side view of the Zr-based alloys: (a) 40 cycles and (b) 80 cycles for the Zr50Al50 alloy; (c) 40 cycles and (d) 80 cycles for the Zr50Ti50 alloy. The rolling direction is along the horizontal axis.

Fig. 2  The EDS curves in Zr50Al50 after 40 F&R cycles.

Fig. 3  SEM/BEI side view of the Zr50Cu50 alloys after 40 F&R cycles: (a) without and (b) with the pre-hardening step of the Cu foils. The rolling direction is along the vertical axis.

Fig. 4  XRD patterns of the Zr50Cu50 alloys after 80 F&R cycles: (a) with and (b) without the pre-hardening step of Cu foils.

Fig. 5  The variations of (a) amf volume fraction and (b) the measured grain size of various Zr-X systems as a function of F&R cycles.

Fig. 6  TEM dark field images Zr50Ti50 alloys after 40 F&R cycles showing (a) the intense dislocation strain contrast in larger grains, and (b) much less defect activities with decreasing nc size.

Fig. 7  TEM bright field images of the interface region between the NC and AMF phases taken from the Zr50Ti50 alloys after 80 F&R cycles. The smallest nc phase size near the interface is around 3 nm.
Fig. 1  SEM/BEI side view of the Zr-based alloys: (a) 40 cycles and (b) 80 cycles for the Zr$_{50}$Al$_{50}$ alloy; (c) 40 cycles and (d) 80 cycles for the Zr$_{50}$Ti$_{50}$ alloy. The rolling direction is along the horizontal axis.

Fig. 2  The EDS curves in Zr$_{50}$Al$_{50}$ after 40 F&R cycles.
Fig. 3 SEM/BEI side view of the Zr50Cu50 alloys after 40 F&R cycles: (a) without and (b) with the pre-hardening step of the Cu foils. The rolling direction is along the vertical axis.

Fig. 4 XRD patterns of the Zr50Cu50 alloys after 80 F&R cycles: (a) with and (b) without the pre-hardening step of Cu foils.
Fig. 5  The variations of (a) amf volume fraction and (b) the measured grain size of various Zr-X systems as a function of F&R cycles.

Fig. 6  TEM dark field images Zr_{50}Ti_{50} alloys after 40 F&R cycles showing (a) the intense dislocation strain contrast in larger grains, and (b) much less defect activities with decreasing nc size.
Fig. 7 TEM bright field images of the interface region between the NC and AMF phases taken from the Zr$_{50}$Ti$_{50}$ alloys after 80 F&R cycles. The smallest nc phase size near the interface is around 3 nm.