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Effect of thermo-mechanical histories on the microstructure and properties of $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ metallic glassy plates

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Effect of thermo-mechanical histories during hot rolling in the supercooled liquid region on the microstructure and properties of $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ metallic glassy plates was investigated by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), differential scanning calorimetry (DSC), microhardness and electrical resistivity measurements. It was found that some nano-scale clusters and a few crystalline phases were dispersed in the amorphous matrix, which may depress the crystallization onset temperature (T_x). The microhardness increased while the electrical resistivity first increased and then decreased with hot rolling times. So, it is important for the working and forming of bulk metallic glasses in the supercooled liquid region to take the thermo-mechanical histories into account. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

In recent years, Zr-based bulk amorphous alloys have attracted widespread interests because of their stronger glass forming ability and wider supercooled liquid regions [1–3]. However, being in a thermodynamically metastable state, bulk amorphous alloys tend to transform to more stable states depending on the thermal and mechanical treatments of the samples. The working and forming for bulk amorphous alloys is liable to be operated within the supercooled liquid region. A few researches have been done in this field before. Kawamura *et al.* [4] found that the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ amorphous cylindrical specimens still retained glassy phase and the original strength after being extruded with extrusion ratio of about 5 in the supercooled liquid state. The ductility and plasticity of $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{50}Cu_{30}Ni_{10}Al_{10}$ bulk amorphous alloys were improved after being cold rolled with a small reduction ratio of 0.1–0.5% per pass [5, 6]. However, the effect of thermo-mechanical histories is little known on the microstructure and properties of Zr-based bulk metallic glasses, which signifies much with potential industrial applications. So, the main purpose of this paper is to deal with such effect by changing hot rolling times in the supercooled liquid region of $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk amorphous alloy.

2. Experimental procedure

Alloy ingots were prepared by arc melting pure metals in a purified argon atmosphere. $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ (at%) bulk metallic glassy plates of 2.4 mm in thickness were produced using arc-melting apparatus where the pre-alloyed ingots were arc-melted repeatedly and then cast rapidly into a water-cooled copper mold in an argon atmosphere. The samples were machined into $60 \times 10 \times 2.4$ mm plates for hot rolling at 693 K that is about 40 K above the temperature of the glass transition T_g [3], and kept the rolling temperature for five minutes before rolling rapidly by a twin-roller apparatus with the roller radius of 90 mm. The maximum applied load and rolling velocity are 700 KN and 225 mm/s, respectively. The samples with 2.4 mm in thickness were rolled to 1.2 mm by designated rolling times (1, 2 and 3) with the same reduction. Each rolling operation was under same condition mentioned above. The structure of the as-quenched and the as-rolled samples was observed by a D/max-c X-ray diffractometry using Cu $K\alpha$ radiation. Their microstructure was identified further by the JEM-2010 high-resolution transmission electron microscope at a working voltage of 200 kv. The samples for HRTEM observation were mechanically thinned in water and ion-milled using a liquid nitrogen specimen cooling stage. The thermal stability was examined by differential scanning calorimetry (Perkin-Elmer DSC-7) at a heating rate of 0.67 k/s under 99.99% Argon atmosphere. Microhardness measurements were carried out by means of testing device HX-1000. Electrical resistivity of the sample was measured at the room temperature by four-probe method using a CPS-05 contact probe station. All samples were

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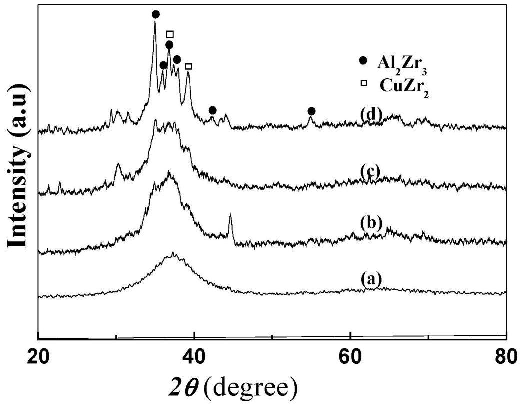


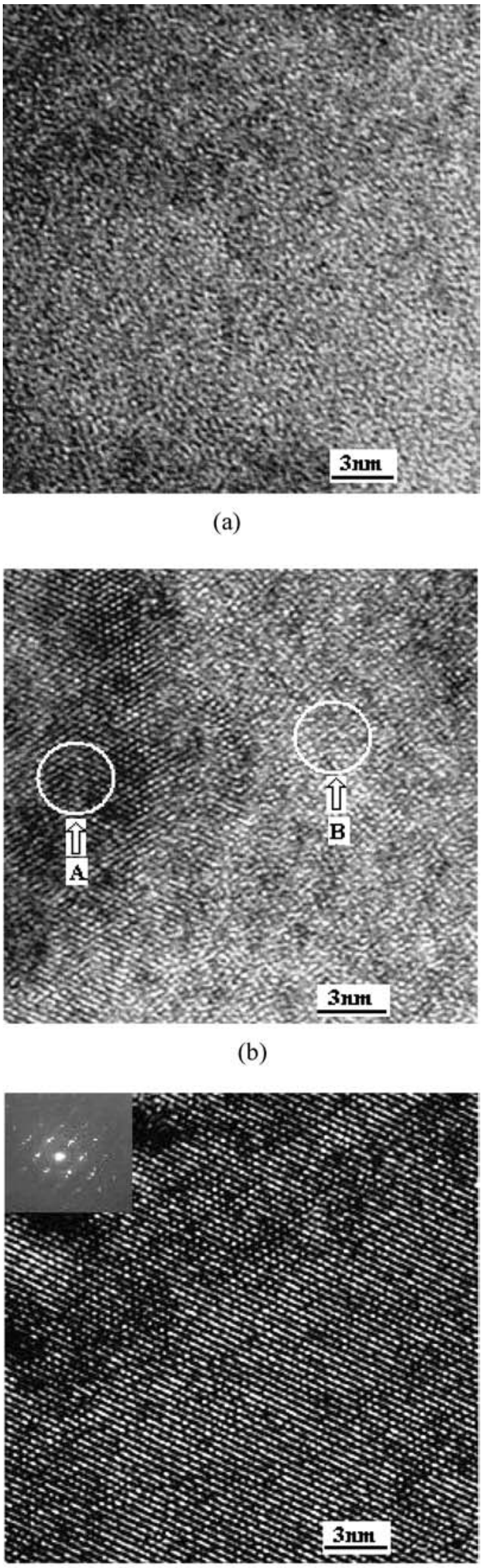
Figure 1 XRD patterns of $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk amorphous samples at various rolling times. (a) 0, (b) once, (c) twice, (d) three times.

polished for microhardness and electrical resistivity measurements.

3. Results and discussion

3.1. Microstructure and thermal stability

Fig. 1 shows the X-ray diffraction patterns of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ samples rolled in the supercooled liquid region by designated rolling times (from 0 to 3 times). It could be seen that the X-ray diffraction pattern of the as-quenched sample consists of only one broad diffuse peak, but some little and cute crystalline peaks were found superimposing on the amorphous diffuse peak with the increase of the rolling times. The high-resolution transmission electron microscopy of the samples at the different thermo-mechanical histories was shown in Fig. 2. From Fig. 2a, the as-quenched sample showed the typical amorphous microstructure with short-range order and long-range disorder. Some nano-scale clusters and a few crystalline phases were found embedding in the amorphous matrix marked A and B in Fig. 2b though the samples were rolled only once. The HRTEM image and selected-area electron diffraction pattern of the samples rolled for three times was illustrated in Fig. 2c. From Fig. 1d and Fig. 2c, we can conclude that most of the sample was crystallized whose crystalline products are mainly composed of Al_2Zr_3 and $CuZr_2$. The results of HRTEM are consistent with those of XRD. In a word, the microstructure evolution of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ rolled samples relates much to the thermo-mechanical histories.



(a)

(b)

(c)

Figure 2 HRTEM images of the rolled $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk amorphous samples at various rolling times. (a) 0, (b) once, (c) three times.

According to the rolling technology and theories [7, 8], the mean strain rate during hot rolling $(\bar{\dot{\varepsilon}})$ can be calculated as follows.

$$\bar{\dot{\varepsilon}} = \frac{2\mathrm{v} \cdot \sqrt{\Delta h/\mathrm{R}}}{H + h} \qquad (1)$$

where v is the velocity of rolling, H and h are the thickness of the sample before and after rolling, Δh is rolling reduction in thickness ($\Delta h = H - h$) and R is the radius of roller. The calculated values of $\bar{\dot{\varepsilon}}$ are 14.44 s^{-1} for once operation, 8.75 s^{-1} for twice operations, and 6.82 s^{-1} for three times operations, respectively. Inasmuch as the amorphous alloys undergo the deformation of a high strain rate during hot rolling, the rolling process in the supercooled liquid region could be considered as an adiabatic shearing one. On the basis of energy conservation law and some experimental formulas [7, 8], the increased temperature (Δt) caused by plastic deformation at high strain rate can be deduced

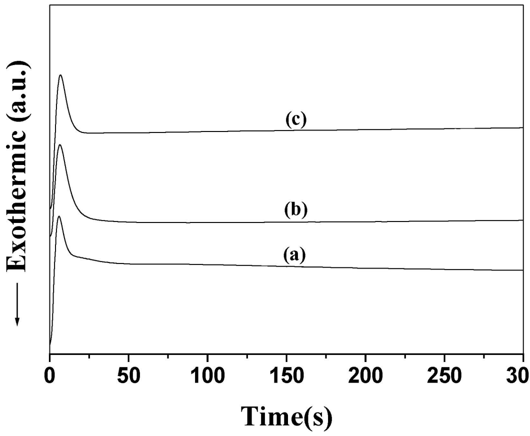


Figure 3 The isothermal DSC curves at 693 K of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ samples. (a) As-cast, (b) rolled once and (c) rolled twice.

as following:

$$\Delta t = \frac{\bar{p} \cdot s \cdot \Delta h}{c_{\mathrm{p}} \cdot m} \tag{2}$$

Where $\bar{p}$ is the average unit stress, s is the effective area of deformation ($= b \cdot \sqrt{R \cdot \Delta h}$, b is the width of sample), C_{p} is specific heat at constant pressure which is taken about 40 J· mol^{-1}· K^{-1} at rolling temperature in this paper, and m is the mass of sample. The calculated values of Δt with the increase of rolled times is 26.6 K (once), 5.6 K (twice) and 2.4 K (three times), respectively. The actual temperature ($T_a = 693$ K $+ \Delta t = 720$ K) of the rolled sample for once operation is still less than the onset crystallization temperature ($T_x = 756$ K [3]) of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk metallic glass. The isothermal DSC curves at 693 K for the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ as-cast, rolled once and twice samples were shown in Fig. 3. It could be seen that no crystallization occurred during isothermal treatments for five minutes. Therefore, the appearance of the nano-scale clusters and a little crystalline phase during rolling may be mainly ascribing to the thermal-mechanical synergetic effect. It can be deduced that for the samples rolled twice and three-times, some ordered nano-scale clusters formed in the amorphous matrix during first operation were regarded as the embryos that would be the heterogeneous nuclear sites in the process of subsequent crystallization during the next operation. As a result, many crystalline phases are formed in the glassy matrix after three-times rolling as shown in Fig. 1d and Fig. 2c.

The DSC curves of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ samples rolled in the supercooled liquid region at various thermo-mechanical histories were shown in Fig. 4. The changes of the glass transition temperature (T_g) and the crystallization onset temperature (T_x) with the rolling times were illustrated in Fig. 5. No difference in T_g was found at various thermo-mechanical histories, which suggests that T_g largely depends on the component of the amorphous alloys. An apparent decrease of T_x was observed when the rolling times was more than once. Comparing with the as-quenched sample, T_x decreased about 28 K after the samples were rolled three times. The reason of the decrease in T_x might be due to the changes of the microstructure as shown in Fig. 2a, b and c.

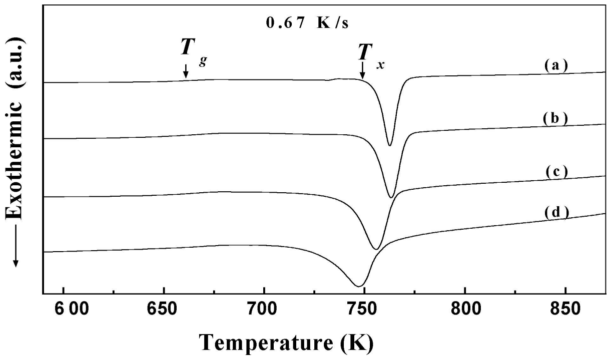


Figure 4 DSC curves of $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk amorphous samples at various rolling times. (a) 0, (b) once, (c) twice, (d) three times.

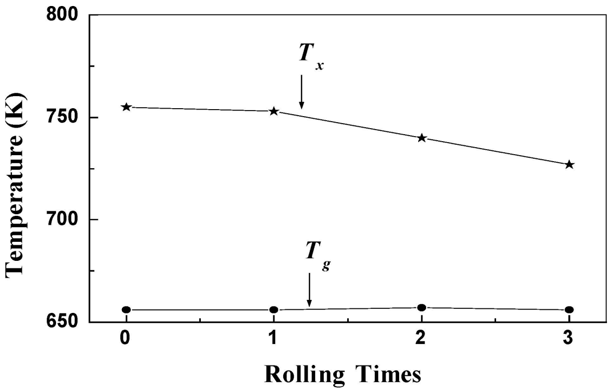


Figure 5 The changes of T_g and T_x for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk amorphous samples with rolling times.

3.2. Mechanical and electrical properties

The mechanical properties of materials can be indicated by the microhardness. Fig. 6 shows that the microhardness slightly increased with the rolling times. In contrast to the as-quenched samples, the microhardness value was enhanced by about 20% after the samples were rolled three times. The gradual increase of the microhardness value should be attributed to the change in

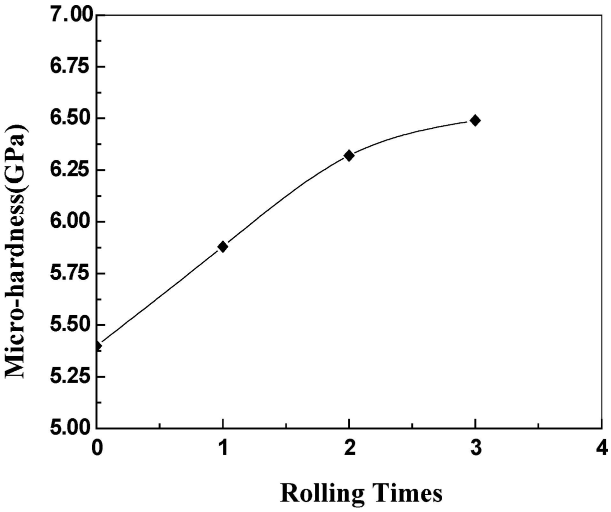


Figure 6 The changes of the microhardness for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk amorphous samples with rolling times.

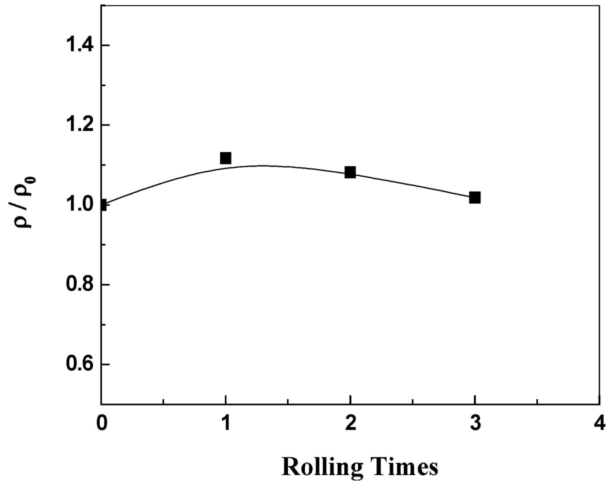


Figure 7 The changes of the ρ/ρ_0 for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk amorphous samples with rolling times.

the microstructure of the bulk amorphous alloys. The microhardness of the as-quenched sample with completely glassy structure is relatively low, and that of the rolled samples with nano-scale clusters and crystalline structure in the amorphous matrix would be enhanced slightly with the thermo-mechanical histories.

It is well known that the electrical resistivity is a sensitive parameter to the microstructure. The room temperature resistivity of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ samples rolled in the supercooled liquid region at various thermo-mechanical histories was measured to further identify the microstructure evolution. The relative electrical resistivity curve (ρ/ρ_0, ρ and ρ_0 represent the electrical resistivity of the as-rolled and the as-quenched samples, respectively) versus rolled times was plotted in Fig. 7. It was noticed that the electrical resistivity slightly increased after the samples were rolled once, and then gradually decreased with the rolling times. As we know, the electrical resistivity of the alloys at room temperature relates much with the microstructure and the composition and the defect concentration of the materials. The increase of the electrical resistivity might be due to the change of the defect (e.g., free volume) concentration caused by rolling. The subsequent decrease of the electrical resistivity should be ascribed to the ordered nano-scale clusters and crystallization structure in the bulk amorphous matrix. The remarkable decrease of the ρ/ρ_0 after being rolled three times is caused by a majority of crystallization appearing in the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk metallic glasses.

4. Conclusions

To sum up, the microstructure of the $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ bulk metallic glasses was changed from completely amorphous structure to partial crystallization induced by thermo-mechanical synergetic effect in the supercooled liquid region, which leads to the decrease of the thermal stability. The microhardness of the samples gradually increases, and the electrical resistivity increases firstly and then decreases with rolling times. So, thermo-mechanical synergetic effect is a significant aspect with the working and forming of bulk metallic glasses in the supercooled liquid region.

Acknowledgments

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