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Transactions of Nonferrous Metals Society of China

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Trans. Nonferrous Met. Soc. China 25(2015) 2617–2623

# Transition of plasticity and fracture mode of Zr–Al–Ni–Cu bulk metallic glasses with network structures

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Received 22 September 2014; accepted 12 May 2015

Abstract: Effect of network structure on plasticity and fracture mode of Zr–Al–Ni–Cu bulk metallic glasses (BMGs) was investigated. The microstructures of transversal and longitudinal sections were exposed by chemical etching and observed by scanning electron microscopy (SEM). The mechanical properties were examined by room-temperature uniaxial compression test. The results show that both plasticity and fracture mode are significantly affected by the network structure and the alteration occurs when the size of the network structure reaches up to a critical value. When the cell size ( $d_c$ ) of the network structure is ~3 µm, Zr-based BMGs characterize in plasticity that decreases with increasing  $d_c$ . The fracture mode gradually transforms from single 45° shear fracture to double 45° shear fracture and then cleavage fracture with increasing  $d_c$ . In addition, the mechanisms of the transition of the plasticity and the fracture mode for these Zr-based BMGs are also discussed.

Key words: bulk metallic glass; plasticity; fracture mode; network structure

## **1** Introduction

Zr-based bulk metallic glasses (BMGs) have been extensively investigated due to their unique combination of high glass forming ability, good thermal stability, and high strength [1–4]. The continued research efforts have revealed that some Zr-based BMGs also exhibit good biocompatibility, which gives rise to potential applications as biomaterials [4–6]. However, the vast majority of monolithic BMGs so far discovered are room-temperature brittle except for the appearance of exceptional room-temperature plasticity [2–4]. Thus, how to obtain and improve the plasticity in BMGs has been highly demanding to explore the practical applications of these high strength engineering materials.

There exist several investigations on the condition of ductile-brittle transition in BMG alloys [7,8]. For example, WANG [7] has showed that there was a critical Poisson ratio for brittle-ductile transition in various BMG alloys. Recently, WU et al [8] have reported that a Zr-based BMG exhibited a brittle–ductile transition while the cast-softening surface layer has been removed. In addition, it has been found that structural heterogeneity contributes greatly to the plasticity of BMGs [2,7,9,10]. For instance, WANG et al [9] found that the BMG with appropriate mechanical heterogeneity would deliver a good room-temperature plasticity. However, the exact correlation between the plasticity and the heterogeneity of BMGs is not well established. In our recent work, we have found that some monolithic Zr–Al–Ni–Cu BMGs, which show network structures after chemical etching [11], provide interesting model systems for studying the relationship between the mechanical plasticity and the structural heterogeneity.

In the present work, the plasticity and fracture mode of a series of Zr–Al–Ni–Cu BMGs associated with different network structures are investigated. It is found that the plasticity and the fracture mode are significantly related with the size of the network structure and/or the ratio of soft regions to hard regions and there is a critical value for the transition of the plasticity and fracture

Foundation item: Projects (50874045, 51301194) supported by the National Natural Science Foundation of China; Project (2144057) supported by the Natural Science Foundation of Beijing Municipality, China

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2618

mode. The obtained results would be helpful for disclosing and understanding the correlation among the network structure, the plasticity and the fracture mode for the networking BMGs.

#### 2 Experimental

Zr-Al-Ni-Cu rods with 2 mm in diameter with different compositions, as shown in Table 1, were prepared by suction casting into a water-cooled copper mould. The glassy nature of the as-cast samples was characterized by X-ray diffraction (XRD), differential scanning calorimeter (DSC) and transmission electron microscopy (TEM), respectively. The polished transversal and longitudinal sections were etched with a mixed solution of 60% HF+40% HNO3 for ~30 s. The microhardness measurement was performed on the cross sections using a BUEHLER microhardness tester under a load of 25 g and a dwell time of 10 s. Room-temperature uniaxial compression tests were performed on the samples with a gauge aspect ratio of 2:1 by using an Instron 3369 testing machine at a strain rate of  $5 \times 10^{-3} \text{ s}^{-1}$ . It should be noted that two end surfaces for the compression samples are smooth, parallel with each other, and are vertical to the symmetry axis of the rod. The microstructure was investigated using an Sirion scanning electronic microscope (SEM) operated at 25 kV.

## **3** Results

The studied Zr-based BMGs are all in amorphous states according to the XRD, TEM and DSC results [11,14]. The network structure can be clearly observed on the cross section except for the BMG I [11]. The cell and the cell wall of the network structure both characterize in the amorphous nature [14]. The average cell size ( $d_c$ ) and the average width of cell wall ( $W_c$ ) for the networking Zr-based BMGs were carefully measured by SEM and are listed in Table 1. Interestingly, the

networking Zr-based BMGs all have zebras patterns on the longitudinal section, as shown in Fig. 1. In addition, the microhardness tests were performed on the networking Zr-based BMGs [11,14]. The cell is harder than the cell wall and the hardness varies with different cells and cell walls, indicating that the amount of free volume in the cell wall is larger than that in the cell and varies with different cells and cell walls [9,11,14].



Fig. 1 Typical image of carefully etched longitudinal section

Room-temperature uniaxial compression tests were conducted on the present Zr-based BMGs in order to investigate the effect of the network structure on the plasticity and the fracture mode. Figure 2 presents typical stress-strain curves and fracture images of the present Zr-based BMGs. The serrated flow cannot be observed for the BMG I but is obvious for the networking BMGs. The strains for the serrated flow are  $\sim 1\%$  for the BMGs II and III, and ~5% for the BMG IV, respectively. However, the cracking sound was heard during the formation of large serrate for the BMGs III and IV, indicating the formation of the cracks during large serrated flow for these BMGs. Thus, the plasticity is zero for the BMGs I, III and IV, while ~1% for the BMG II. The plastic strain values ( $\varepsilon_{\rm p}$ ) for these Zr-based BMGs are listed in Table 1. As shown in the insets of Fig. 2, the BMGs I-III nearly fracture along with 45° shear plane to loading direction, while the BMG IV fractures along with loading direction. In addition, there is one

**Table 1** Activation energies of glass transition  $E_g$  and crystallization  $E_x$  [12], Poisson ratio v, critical dimension  $\Phi_c$  [13], width of cell wall  $W_c$  [14], cell size  $d_c$  [14],  $W_c/d_c$ , and plastic strain  $\varepsilon_p$  for Zr–Al–Ni–Cu BMGs

Metallic glasses	Туре	$E_{\rm g}/({\rm kJ}\cdot{\rm mol}^{-1})$	$E_{\rm x}/({\rm kJ}\cdot{\rm mol}^{-1})$	v	$arPsi_{ m c}/ m mm$	$W_{\rm c}/\mu{ m m}$	$d_{\rm c}/\mu{ m m}$	$W_{\rm c}/d_{\rm c}$	<i>ɛ</i> p/%
Zr <sub>54</sub> Al <sub>13</sub> Cu <sub>18</sub> Ni <sub>15</sub>	Ι	191.1	332.8	0.3364	6.5	0	0	-	0
Zr <sub>62.5</sub> Al <sub>12.1</sub> Cu <sub>7.95</sub> Ni <sub>17.45</sub>		175.2	212.8	0.3355	7.5	0	0	_	0
$Zr_{64}Al_{10.1}Cu_{11.7}Ni_{14.2}$		245.0	264.6	0.3363	5.0	0.1	3.1	3.2	1.0
$Zr_{63.5}Al_{10.7}Cu_{10.7}Ni_{15.1}$	II	198.6	249.2	0.3361	6.0	0.1	3.3	3.0	0.8
Zr <sub>62</sub> Al <sub>10</sub> Cu <sub>15</sub> Ni <sub>13</sub>		226.5	239.1	0.3367	5.0	0.1	2.9	3.4	1.2
$Zr_{61.5}Al_{10.7}Cu_{13.65}Ni_{14.15}$	III	214.6	267.4	0.3364	5.5	0.3	4.7	6.4	0
Zr <sub>60.5</sub> Al <sub>12.1</sub> Cu <sub>10.95</sub> Ni <sub>16.45</sub>	IV	354.5	249.2	0.3358	4.0	0.6	8.5	7.1	0
Zr <sub>65</sub> Al <sub>8.7</sub> Cu <sub>14.4</sub> Ni <sub>11.9</sub>		374.1	254.0	0.3370	4.0	1.5	18.7	8.0	0



**Fig. 2** Stress–strain curves for Zr-based BMGs (Insets are the fracture images [11])

macroscopic shear plane for the BMGs I and II, and two for the BMG III. These results indicate the transition of the plasticity and the fracture occurs when the  $W_c$  or  $d_c$  or  $W_c/d_c$  reaches up to a critical value.

Furthermore, fracture surfaces and side surfaces for the fractured BMGs were investigated by SEM. Typical fracture surfaces for these Zr-based BMGs are shown in Figs. 3(a)–(d). The fracture surfaces for the BMGs I, III, and IV include smooth regions and vein-like regions (see Figs. 3(a), (c) and (d)). The density and the size of the vein-like patterns on two shear planes for the BMG III are obviously different from each other, as shown in Fig. 3(c). It would indicate that the shear bands on the shear plane associated with the denser and finer vein-like patterns initiate earlier than those on the other shear plane. The vein-like patterns for the BMG IV characterize in directionality and propagate along with the cracks (see Fig. 3(d)). However, the fracture surfaces for the BMG II characterize in small dimples and the average dimple size is  $\sim 3 \ \mu m$ , as shown in Fig. 3(b). In addition, Figs. 3(e)–(h) present typical side surfaces of the fractured BMGs. The shear bands can be observed on the side surfaces for all Zr-based BMGs. The intersected shear bands can be observed for the BMGs II and III (see Figs. 3(f) and (g)), while not for the BMGs I and IV (see Figs. 3(e) and (h)). Interestingly, the cracks propagate along with the shear bands and parallel with the loading direction for the BMG IV, as shown in Fig. 3(h), which is coherent with the cleavage mode (see the insets of Fig. 2).

#### **4** Discussion

Why does the transition of the plasticity and the fracture mode occur when the  $W_c$  or  $d_c$  or  $W_c/d_c$  reaches up to a critical value? The plasticity of the BMG can be estimated by Poisson ratio v [7] and activation energy for crystallization  $E_x$  [15] based on the isotropy. The Poisson ratio v can be calculated by  $v^{-1} = \sum (x_i v_i^{-1}) [7] (x_i \text{ and } v_i \text{ are})$ mole fraction and Poisson ratio of the *i*-th element, respectively) and large v would generally be related with good plasticity [2,7,16]. The calculated v values for the present Zr-based BMGs are listed in Table 1. The v values are 0.34 for Zr, 0.35 for Al, 0.31 for Ni, and 0.34 for Cu, respectively [7]. Figure 4(a) presents the relationship between the v and the  $\varepsilon_p$ . It is clear from Fig. 4(a) that large v does not lead to good plasticity for the present Zr-based BMGs. However, the plasticity increases with increasing v for the BMG II, as shown in Fig. 4(a) and Table 1. In addition, LEE et al [15] found that low  $E_x$  generally resulted in good plasticity for Cu-Zr-based BMGs due to the crystallization under external stress. The relationship between the plasticity and the  $E_x$  for the present Zr-based BMGs was



**Fig. 3** SEM images of fracture surfaces (a–d) and side surfaces (e–h) of fractured specimens for BMG I (a, e), BMG II (b, f), BMG III (c, g), and BMG IV (d, h)



**Fig. 4** Relationship of plastic strain  $\varepsilon_p$  vs Poisson ratio v (a) and activation energy for crystallization  $E_x$  (b)

investigated and the results are presented in Fig. 4(b). One can observe from Fig. 4(b) that low  $E_x$  does not result in good plasticity for the present Zr-based BMGs even for the BMG II. This indicates that the mechanism of the plasticity for these Zr-based BMGs is not due to the crystallization which is not observed for these Zr-based BMGs during the compression.

In addition, the critical dimension  $(\Phi_c)$  is a direct indicator for glass forming ability (GFA) of glass forming alloys. The higher the GFA of the BMG, the more homogeneous the distribution of the atoms [7]. This indicates that the structural heterogeneity is difficult for the appearance in the BMG with high GFA. Thus, the relationships of the  $\Phi_{\rm c}$  with  $d_{\rm c}$  and  $W_{\rm c}$  were investigated and the results are shown in Fig. 5(a). One can clearly observe from Fig. 5(a) that both  $d_c$  and  $W_c$  decrease with increasing  $\Phi_c$ , indicating that large  $\Phi_c$  generally results in higher homogeneity for the present Zr-based BMGs. It is found that the heterogeneity would generally result in good plasticity [2,7,9,10]. However, Fig. 5(b) indicates that there is not a clear correlation of the  $\varepsilon_{\rm p}$  and  $\Phi_{\rm c}$  or  $d_{\rm c}$ for the present Zr-based BMGs but the  $\varepsilon_p$  increases with decreasing  $\Phi_c$  or  $d_c$  for the BMG II. These results indicate that the heterogeneity plays a critical role for the

plasticity of the present Zr-based BMGs. It is well known that there are mainly two factors influencing the plasticity of the BMG. One is the extrinsic factors, including sand blasting [17], hydrogen absorption [18,19], stress/strain state [20,21], which are not related with the present work. The other is the intrinsic factors such as the composition and the heterogeneity [2-4]. It is found that the composition plays an important role for the plasticity of the BMG. For example,  $\varepsilon_p$  can reach up to 14.5% for Zr<sub>53</sub>Cu<sub>18.7</sub>Ni<sub>12</sub>Al<sub>16.3</sub> BMG [22], while zero for the present  $Zr_{54}Al_{13}Cu_{18}Ni_{15}$  BMG (see Table 1). Nevertheless, QU et al [22] claimed that the plasticity of Zr<sub>53</sub>Cu<sub>18.7</sub>Ni<sub>12</sub>Al<sub>16.3</sub> BMG was due to the stress/ strain-induced atom-scale compositional/structural heterogeneity. More interestingly, Zr<sub>61.88</sub>Cu<sub>18</sub>Ni<sub>10.12</sub>Al<sub>10</sub>,  $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10} \mbox{ and } Zr_{62}Cu_{15.5}Ni_{12.5}Al_{10} \mbox{ BMGs [2]}$ all characterize in super plasticity but the plasticity is zero for Zr<sub>61.5</sub>Al<sub>10.7</sub>Cu<sub>13.65</sub>Ni<sub>14.15</sub> BMG, 1.0% for  $Zr_{64}Al_{10,1}Cu_{11,7}Ni_{14,2}$  BMG, and 1.2% for Zr<sub>62</sub>Al<sub>10</sub>Cu<sub>15</sub>Ni<sub>13</sub> BMG (see Table 1). The former characterize in nano-scale heterogeneity [7], while micro-scale heterogeneity for the latter (see Table 1). In addition, the  $d_c$  values of  $Zr_{64}Al_{10.1}Cu_{11.7}Ni_{14.2}$  and Zr<sub>62</sub>Al<sub>10</sub>Cu<sub>15</sub>Ni<sub>13</sub> BMGs are smaller than those of Zr<sub>61.5</sub>Al<sub>10.7</sub>Cu<sub>13.65</sub>Ni<sub>14.15</sub> BMG. These results indicate that the compositional/structural heterogeneity is crucial for the plasticity of the BMG and  $\varepsilon_p$  is related to the size of the heterogeneous structure. Increasing efforts have clarified that the inherent heterogeneity is of advantages of the plasticity of the BMG [2,7,9,10]. The structure is homogeneous for the BMG I, while inversely for the other BMGs (see Table 1). Thus, the plasticity cannot be observed for the BMG I, as shown in Fig. 2 and Table 1. However, the plasticities of BMGs III and IV are zero, indicating that the plasticity would be related with other factors besides the structural heterogeneity. The plastic deformation for the BMG can be regarded as a glass to supercooled liquid transition by external stress [7]. In addition, the activation energy for glass transition  $(E_g)$  is equal to that for plastic flow [7]. As shown in Table 1, the  $E_{g}$  of the BMG IV is the largest among the networking BMGs, indicating its difficult plastic flow. However, the  $E_{g}$  of the BMG II is quite similar with that of the BMG III. Why does the plasticity occur in the former not in the latter? It is well known that the plastic deformation needs the compatibility of deformation among each part in the material. Since the hardness of the cell (hard region) is larger than that of the cell wall (soft region), the shear strength is larger for the cell than for the cell wall [7]. The plastic flow would preferentially occur in the soft regions [7], resulting in inharmonic deformation between the soft regions and the hard regions. Both  $d_{\rm c}$  and  $W_{\rm c}$  are larger for the BMG III than for the BMG II (see Table 1), resulting in more



**Fig. 5** Relationships of critical dimension  $\Phi_c$  with cell size  $d_c$  and width of cell wall  $W_c$  (a), and plastic strain  $\varepsilon_p$  vs cell size  $d_c$  and critical dimension  $\Phi_c$  (b) (The inset in Fig. 5(b) presents the relationships of plastic strain  $\varepsilon_p$  vs cell size  $d_c$  and critical dimension  $\Phi_c$  for the BMG II)

inharmonic deformation in the former than in the latter.

On the other hand, the deformation and the propagating direction of shear bands for the present Zr-based BMGs are schematically presented in Fig. 6 in order to clearly clarify the transition of the fracture

mode. It is well known that the drum deformation (see Fig. 6(a) would generally occur more or less due to the shear induced dilatation and softening [23,24]. The shear bands would propagate along with 45° shear planes to the loading direction (see Fig. 6(b)). The propagation of the shear bands would be altered even stopped by the barriers. In addition, it should bear in mind that the velocity of the shear band can reach up to 10 m/s [25] or even more [26] and increases with increasing temperature [26]. Since the BMG I is homogeneous, its shear bands can easily propagate along with 45° shear planes to the loading direction, resulting in single macroscopic smooth fracture surface (see the insets of Fig. 2). As for the networking BMGs, the resistance of the propagation of the shear bands would increase with increasing  $d_c$  and/or  $W_c$ . The shear bands can penetrate throughout the sample along with 45° shear planes because the  $d_{\rm c}$  and  $W_{\rm c}$  for the BMG  $\Pi$  are too small to stop the propagation of the shear bands. However, the propagating direction of shear bands would be changed due to the resistance of the cell and/or the cell wall. These effects would result in the zigzag propagation of the shear bands (see Fig. 6(c)), leading to the macroscopic rough fracture surface (see the insets of Fig. 2). The propagation of the primary shear bands in the BMG III would be stopped by the enough large soft and/or hard regions located in the center. At the same time, the conjugated shear bands [27,28] nucleate and propagate along with 45° shear plane from the surface to the center until two shear planes meet each other (see Fig. 6(d)), resulting in double shear planes (see the insets of Fig. 2). When the  $W_c$  reaches up a critical value, the correlation of two adjacent cells would be weakened. Several small cells even one large cell can be considered as an independent deformed unit, resulting in the destabilization of these independent deformed units under a critical external stress. Factually, the destabilization indeed occurs in the BMG IV because the



**Fig. 6** Schematic diagrams for drums deformation (a), and propagating directions of shear bands for BMG I (b), BMG II (c), BMG II (d), and BMG IV (e) (Red regions and white regions in (c)–(e) represent soft regions and hard regions, respectively. Blue dotted lines in (e) indicate the direction of Domino effect)

small serrate can be clearly observed in the region of so-called elastic deformation (see Fig. 2). In addition, the amount of the free volume would increase and the  $E_g$ would decrease in the condition of the tension or the compression [29,30], resulting in the decrease of the resistance for the propagation of the shear bands. The shear bands would directly propagate along with the large soft and/or hard regions (see Fig. 6(e)), then so-called Domino effect would happen, resulting in cleavage failure for the BMG IV (see the insets of Fig. 2).

#### **5** Conclusions

1) The plasticity cannot be observed in the studied Zr-based BMGs without the network structures. The plasticity can be clearly observed in the networking Zr-based BMGs with  $d_c \sim 3 \mu m$ , while not for the other networking Zr-based BMGs whose  $d_c$  is large than 4  $\mu m$ .

2) The fracture mode is related with the  $d_c$ ,  $W_c$ , and  $W_c/d_c$  of the network structure. The Zr-based BMGs fracture along with single 45° shear plane to the loading direction when the  $d_c$ ,  $W_c$ , and  $W_c/d_c$  are less than 4.7 µm, 0.3 µm, and  $6.4 \times 10^{-2}$ , respectively. Double 45° shear fracture occurs in the Zr-based BMGs whose  $d_c$ ,  $W_c$ , and  $W_c/d_c$  are 4.7 µm, 0.3 µm, and  $6.4 \times 10^{-2}$ , respectively. However, the cleavage fracture occurs in the Zr-based BMGs whose  $d_c$ ,  $W_c$ , and  $W_c/d_c$  are larger than 4.7 µm, 0.3 µm, and  $6.4 \times 10^{-2}$ , respectively. In addition, the plasticity would be related with the fracture mode for the present Zr-based BMGs.

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# 具有网络结构的 Zr-Al-Ni-Cu 块体金属玻璃的 塑性和断裂模式转变

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摘 要:研究网络结构对 Zr-Al-Ni-Cu 块体金属玻璃的塑性和断裂模式的影响。采用化学腐蚀法显示并用 SEM 观察横截面和纵截面的微观结构,采用室温单向压缩试验测定力学性能。结果表明,网络结构显著地影响 Zr-Al-Ni-Cu 块体金属的塑性和断裂模式,当网络结构的尺寸达到某一临界值时,塑性和断裂模式发生转变。当 胞状结构的尺寸约为 3 μm 时,Zr 基块体金属玻璃表现出塑性,并且塑性随胞状尺寸的增加而降低。断裂模式随 胞状尺寸的增加逐渐由单一 45° 剪切面断裂向双 45° 剪切面断裂,最后转变为劈裂断裂。另外,探讨这些 Zr 基块体金属玻璃的塑性和断裂模式发生改变的机理。

关键词: 块体金属玻璃; 塑性; 断裂模式; 网络结构

(Edited by Yun-bin HE)