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Letter

Correlations between the relaxed excess free volume and the plasticity in Zr-based bulk metallic glasses

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ABSTRACT

Zr-based bulk metallic glasses (BMGs) with Nb minor alloying have been fabricated with different free volume (FV) trapped in. FV is evaluated by the relaxed excess free volume (REFV) after annealing just below T_g through loop thermal expansion tests. The results show that there is a qualitative correlation between the plasticity and REFV in Zr-based BMGs. The larger amount of excess FV the BMGs relax, the better plasticity they exhibit. With 1.5% Nb addition, the brittle $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ BMGs possess REFV up to about 0.428% and exhibit the relatively good plasticity up to 25.6%. This provides a promising way to estimate the plasticity of BMGs and design new ductile BMGs through the minor alloying.

1. Introduction

Due to the special structure trait, which is different from the ordinary crystalline alloys, BMGs exhibit the unique mechanical properties, such as high strength, large elastic limit and good resistance to abrasion. However, the limited plasticity at room temperature restricts the engineering application of this unique class of materials [1–3]. The plastic flow in BMGs is believed to occur via atoms' diffusion and migration that are characterised by the shear bands in the samples. Ordinarily, the plastic flow is highly localized in a few shear bands at the ambient temperature, and thus the main cracks occur. This results in a limited plastic strain (less than 2%) and catastrophic failure [2,3]. It is widely recognized that the plasticity in BMGs can be largely enhanced by introducing interior heterogeneity into BMGs, which can facilitate the initiation, the bifurcation and the intersection of the shear bands. Usually, the heterogeneity, such as nano-crystalline or nano-quasicrystalline, phase separation, deforming-induced crystallization and micrometer-sized ductile phases, is adopted as effective heterogeneous source to improve the plasticity in BMGs [4–11]. The large compression strain of BMGs is achieved, and even the superplasiticity occurs in the condition of a particular nanometer-sized non-homogeneous structure [12]. But these sophisticated structures are often difficult to be controlled. Sometimes they have little positive effect or even negative effect on the strength of BMGs [13–15]. It is also reported that FV can act as the beneficial site to initiate and bifurcate the shear bands. Therefore the plasticity in BMGs is enhanced [16,17]. But the intrinsic relationship between FV and the plasticity and the ways to obtain more FV still need further intensive investigation. Recently, some theories, for example, Poisson ratio rules and the nonuniform stress-induced plasticity are brought forward [18–21], but they are not suitable to all BMG systems. Also the mechanisms of these theories are still not clear. In this paper, we will examine the uniaxial compression nature of the brittle monolithic $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ BMGs with (ZrCu) substituted by Nb, and thus the good plasticity is achieved when the minor Nb is added. The REFV after annealing just below T_g is got through dilatometric measurements, and it correlates steadily with the plasticity of Zr-based BMGs. Those above show that the plasticity in BMGs is closely related to the change in REFV. Due to the facility in measuring REFV, this closely relationship between the plasticity and the change in REFV might offer a convenient way to design new ductile BMG systems and improve the plasticity in the brittle BMGs in existence.

2. Experimental details

The $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ (x = 0, 0.5, 1, 1.5, 2, 4 and 6) master alloys were prepared by arc melting mixtures of the pure elements (>99.9%) with the appropriate portions of Zr, Cu, Ni, Al and the Zr–Nb intermediate alloy that was arc-melted in advance in the Ti-gettered argon atmosphere with 99.999% purity. The alloys were remelted four times to ensure the compositional homogeneity. Finally, the cylindrical rods of 2 mm in diameter were casted by injecting the alloy melt into a copper mold under the argon atmosphere with 99.999% purity. The phase structures were investigated by X-ray diffraction (XRD) using a Bruker D8 Advance 18 kW X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm). The glass transition and the

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crystallization behavior were determined by the differential scanning calorimetry (DSC) using a Netzsch DSC 200 F3 under a continuous argon flow at the heating rate of $0.33\,K\,s^{-1}$. The quasi-static-compression tests were carried out on the cylindrical rods (2 mm in diameter and 4 mm in length) using a universal testing machine (Regr5500 Reger, China) with a strain rate of $5 \times 10^{-5}\,s^{-1}$ at room temperature. The samples for the quasi-static-compression tests were cut from the long rods. The ends of the samples were polished to make them parallel to each other and perpendicular to the axis of the rod prior to compression tests using a carefully designed jig. The stress and the strain quantities presented here are the engineering stress and engineering strain data. The morphology of the side surfaces of the fractured samples was observed by the scanning electron microscope (SEM) and the stereo-optical microscope (KEYENCE digital microscope VHX-600). The cylinder samples (2 mm in diameter and 25 mm in length) are used for linear thermal dilatometric measurements, which were performed on a NETZSCH DIL 402C dilatometer with a resolution of $\Delta L = 1.25$ nm at the heating rate of $0.083\,K\,s^{-1}$ under a compressive load of 0.3 N.

3. Results and discussion

Fig. 1 shows the XRD patterns of $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ (x = 0, 0.5, 1, 1.5, 2, 4 and 6) alloy rods of 2 mm in diameter. The patterns exhibit a broad maximum with no detectable crystalline Bragg peaks, which is characteristic for glassy structures. The DSC traces of the as-cast ZrCuNiAlNb alloy rods all exhibit an endothermic event characteristic of the glass transition and a supercooled liquid region, followed by the exothermic events characteristic of the crystallization processes, as shown in Fig. 2. The XRD and DSC results show the glass nature of the as-cast alloys.

Fig. 3 shows the stress–strain curves for the $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ (x = 0, 0.5, 1, 1.5, 2, 4 and 6) alloy rods. For each alloy component, five samples, which were cut from three different alloy rods prepared in the same conditions, were selected to undergoing compression to ensure the result reliability. The stress–strain curves shown in Fig. 3 represent the typical ones that exhibit the plasticity closest to the average values of all five ones. It is value to note that the strength remains almost the same in spite of the different plasticity for the five samples with the same alloy component. The origin of the scattering data for the compression plasticity in the same BMGs is still unclear. It is also concluded from Fig. 3 that Nb contents have the main effect on the plasticity but the minor effect on the strength of BMGs. With the (ZrCu) substituted by 0.5–6% Nb, ZrCuNiAlNb BMGs exhibit improved plastic strain, and reach the maximum strain value of 25.6% (the average strain value is 15.14%) at 1.5% Nb content. The original alloy without Nb content exhibits an average plastic strain of 2.22%, which is different from the results of absolutely brittle by Inoue and co-workers [22] and Yan et al. [12]. This may be ascribed to the different purities of the raw materials or the different compression strain rate. The average plastic strain sequence is $\varepsilon_{1.5\%\,Nb} > \varepsilon_{1\%\,Nb} > \varepsilon_{2\%\,Nb} > \varepsilon_{0.5\%\,Nb} > \varepsilon_{4\%\,Nb} > \varepsilon_{6\%\,Nb} > \varepsilon_{0\%\,Nb}$.

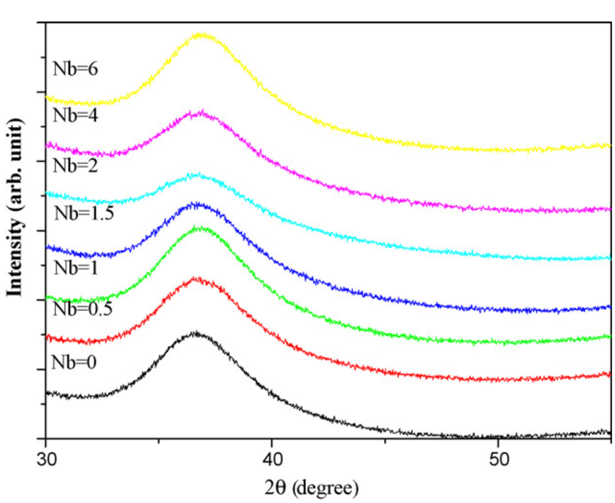

Fig. 1. X-ray diffraction patterns of the as-cast $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ alloy rods with x = 0, 0.5, 1, 1.5, 2, 4 and 6.

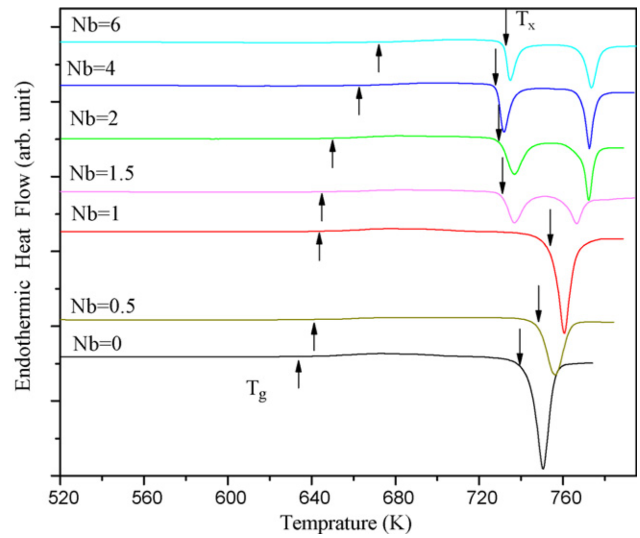

Fig. 2. DSC traces (heating rate of 20 K/min) of the as-cast $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ alloy rods with x = 0, 0.5, 1, 1.5, 2, 4 and 6.

The loop thermal expansion curves of $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ (x = 0, 1, 4) alloy rods are shown in Fig. 4. The other curves are not shown here due to the similarity. The inset in Fig. 4 is the enlargement just above room temperature range. The loop heating processes include two parts: firstly, heating at a rate of $0.083\,K\,s^{-1}$ to the temperature just below the glass transition temperature, holding for 60 min and then cooling down at the same rate to the room temperature; secondly, heating at a rate of $0.083\,K\,s^{-1}$ to the temperature higher than the crystallizing point. The BMGs frozen from the high temperature melts exhibit metastable structures characteristic of relatively low densities and excess FV comparing with the corresponding crystal counterparts [23]. These unstable structures can be transformed into more stable ones with the depletion of FV by external heating, which is called the structure relaxation [24–26]. The structure relaxation below T_g results in the volume shrinkage, which is three times of the linear thermal shrinkage measured by the loop thermal expansion tests [27]. So, it is convenient to take the REFV after annealing just below T_g to quantificationally describe the amount of FV trapped in BMGs. The relationships between REFV after annealing just below T_g and the average plastic strain with Nb contents in ZrCuNiAlNb BMGs are

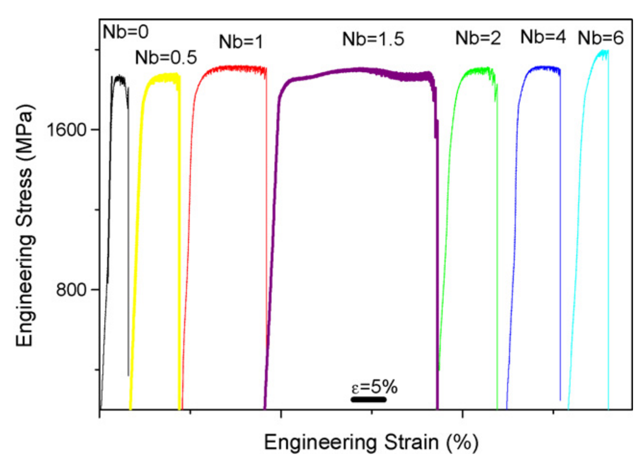

Fig. 3. Stress–strain curves of $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ alloy rods with x = 0, 0.5, 1, 1.5, 2, 4 and 6 under the compression at a initial strain rate of $5 \times 10^{-5}\,s^{-1}$.

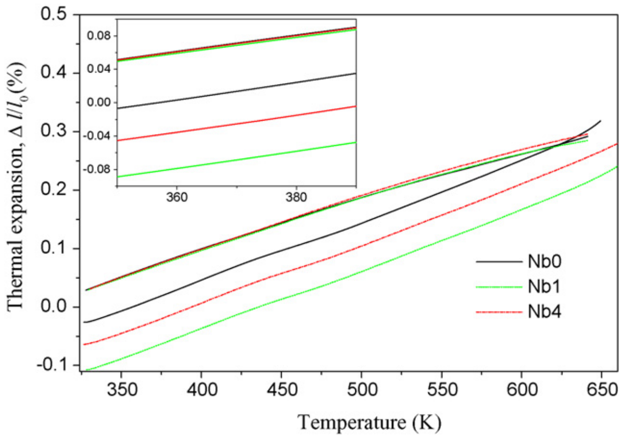

Fig. 4. The loop thermal expansion curves of the $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ (x = 0, 1 and 4) alloy rods, indicating a discrepant linear thermal shrinkage due to the structure relaxation (the holding zones are not visible here due to the temperature reference axis). The inset is the enlargement just above room temperature range.

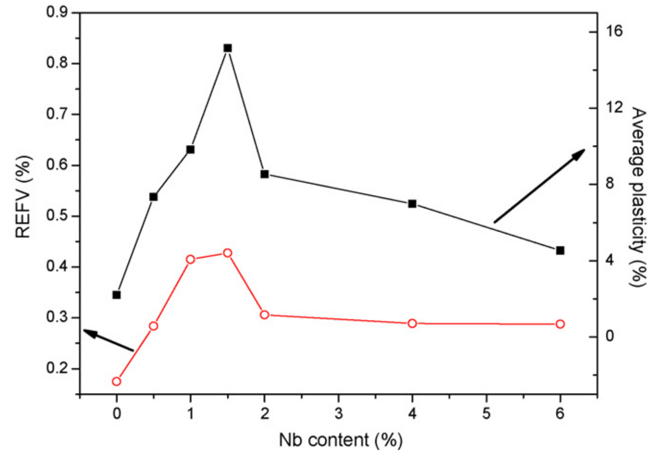

Fig. 5. The relationships of REFV after annealing just below T_g and the average plastic strain with Nb content in ZrCuNiAlNb BMGs.

shown in Fig. 5. It is clearly concluded from Fig. 5 that there are similar tendencies for the REFV and the plastic strain relating with Nb contents in ZrCuNiAlNb BMGs. The larger amount of FV the BMGs relax, the better plasticity they exhibit. With 1–2% Nb additions, the ZrCuNiAlNb BMGs exhibit the large average plastic strain more than 8% at the condition of REFV more than 0.3%. The maximum of the plastic strain reaches 25.6% for the 1.5% Nb content alloys, which have REFV of 0.428%. The FV trapped in BMGs acts as the site for the shear band initiation and branching, therefore, it results in more plastic deformation in BMGs. So, it can be experimentally

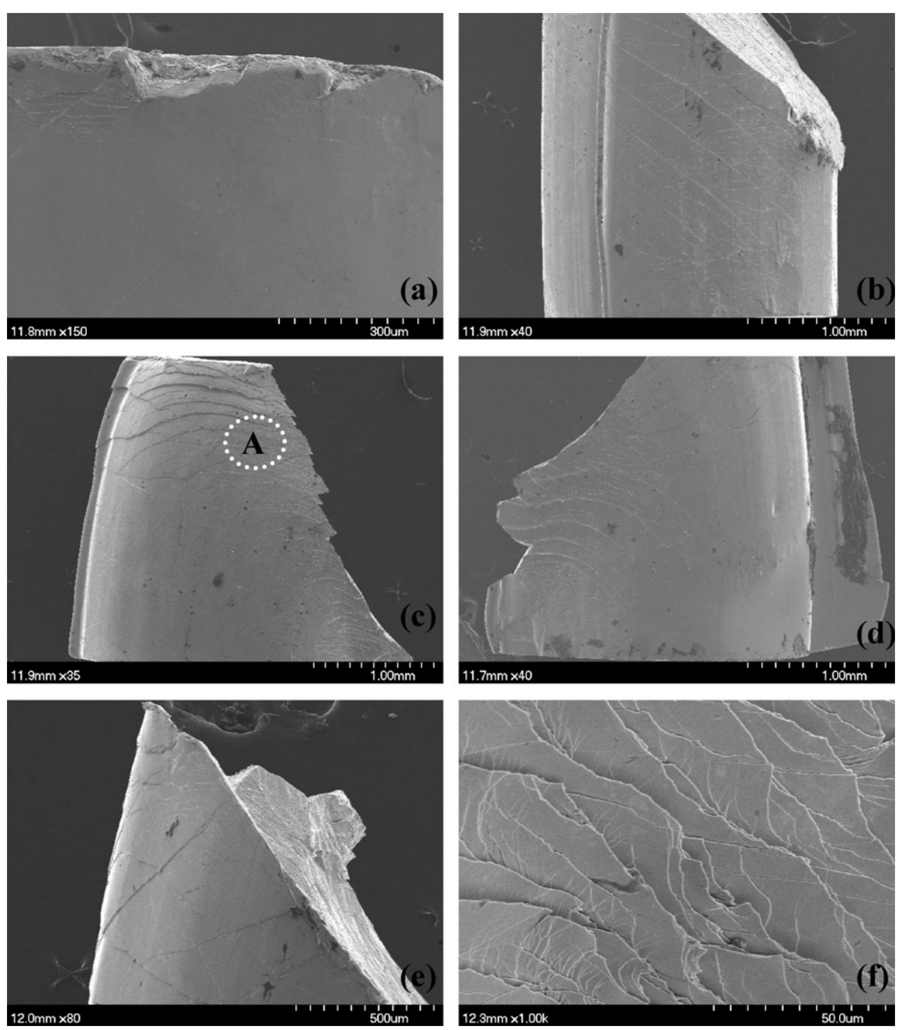

Fig. 6. SEM images showing the morphology of side surfaces of the fractured rods of $(Zr_{0.8125}Cu_{0.1875})_{80-x}Ni_{10}Al_{10}Nb_x$ alloy rods with x = 0 (a), x = 0.5 (b), x = 1.5 (c), x = 4 (d) and x = 6 (e). (f) is the enlargement of (c) at the area A.

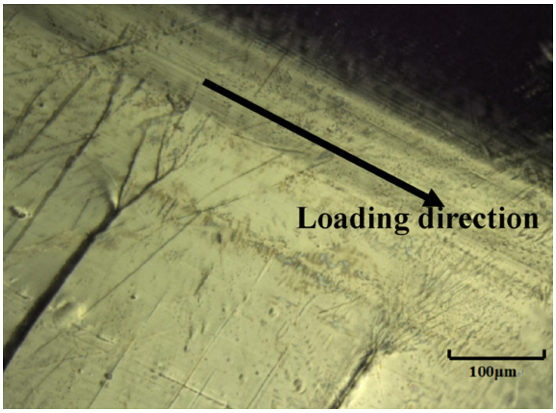

Fig. 7. Stereo-optical microscope image showing the cracks blunted by the multiple shear bands on the side surface of ZrCuNiAlNb alloy rods with 1.5% Nb content at 25.6% plastic strain.

conclude that REFV after annealing just below T_g acts as an effective clue to scale the plasticity in monolithic BMGs. The REFV of brittle FeBYNb BMGs was also measured at the same technological condition and its value is small (no more than 0.15%). This also presents the evidence of beneficial effects of REFV on the plasticity in BMGs. The minor Nb additions to the ZrCuNiAl alloys induce the large amount of FV changes in the as-cast ZrCuNiAlNb BMGs. This can be understood as follows: the values of heat of mixing for Nb–Al, Nb–Cu and Nb–Ni atom pairs are −18, 3 and −32 kJ/mol, respectively, which are remarkably positive comparing with −44, −23 and −51 kJ/mol for Zr–Al, Zr–Cu and Zr–Ni atom pairs, respectively [28]. The Zr and Nb can form a substitution solid solution at the high temperature and they can both bond more easily with Ni atoms [29]. On the other hand, the atomic radius of Nb (0.143 nm) is relatively smaller than that of Zr (0.162 nm) [29]. So, it is reasonable to assure that Nb atoms can substitute Zr to form Nb–Ni atom pairs instead of Zr–Ni pairs at the condition of minor Nb additions, therefore, it result in more excess FV. With further increasing the Nb content, redundant Nb may substitute Cu, which has relatively small atomic radius of 0.128 nm [29], and this substitution results in the depletion of excess FV.

The morphology of the side surfaces of the fractured rods is shown in Fig. 6. All the evidences indicate that the shear bands increase with increasing REFV after annealing just below T_g. A few shear bands are found for the rods with little REFV. However, multiple shear bands exist on the side surfaces of the rods with more REFV. It is also shown in Fig. 6(f) that the shear bands can bifurcate and interact, resulting in dense secondary and tertiary shear bands in the rods with more REFV. The concurrent nucleation of multiple shear bands and the occurrence of secondary and tertiary shear bands directly result in the enhancement of the plastic deformation for the proper Nb content samples, which have more REFV.

The side surface of the fractured rods with 1.5% Nb content (with the compression strain of 25.6%) recorded by a stereo-optical microscope (shown in Fig. 7) indicates that the cracks can also be blunted by the multiple shear bands. The large amount of FV also reduces the barrier to the atomic movement, i.e. it enhances the mobility of atoms. When the cracks extend into the sites with excess FV accumulation, they change the propagation directions in a divergence form due to the high mobility of the atoms, and deplete the energy. The viscoplastic flow of the atoms results in the dense shear bands formation around the crack tips, and eases the stress relaxation of the crack tips, thus blunts the cracks. It is also confirm the availability of excess FV in enhancing the plasticity in BMGs.

4. Conclusions

In summary, $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ BMGs with (ZrCu) substituted by 0–6% Nb contents can be casted with monolithic amorphous structures within the experimental uncertainty of XRD and DSC. The Nb additions can change the FV trapped in BMGs, and thus influence the compression plastic deformation. There is a qualitative correlation between REFV after annealing just below T_g and the plasticity in Zr-based bulk metallic glass. The larger amount of excess FV the BMGs relax, the better plasticity they exhibit. With 1.5% Nb addition, the brittle $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ BMGs possess REFV up to 0.428% and exhibit the relatively good plastic strain up to 25.6%. This provides a promising way to estimate the plasticity in BMGs and design new ductile BMG systems through minor alloying. Whether this way is adapt to other BMG systems or not still need further investigation.

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