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Flow units perspective on sensitivity and reliability of metallic glass properties

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ABSTRACT

The metastability of metallic glasses (MGs) can be well described by the Weibull distribution function. We study the relationship between flow units and mechanical properties and find that the concentration of flow units also follows the Weibull distribution function as do other properties of MG. The results suggest that the properties' sensitivity and metastability of MGs described by the Weibull distribution function can be explained by the structural heterogeneity (or flow unit) perspective and attributed to the variation of the flow units.

1. Introduction

The amorphous structure of a metallic glass (MG) produced from the rapid quenching of its melt, is a typical example of metastable state [1–4]. Although MGs have unique and better properties but these properties are quite sensitive to the preparation conditions [5–14]. For instance, the mechanical properties of MGs to some extent are controlled by the casting temperature [5]. Lovas et al. [6] observed that when melt overheating and subsequent cooling rate is changed then there is considerable change in chemical, magnetic and mechanical properties. Chen et al. [7] showed that when the casting atmosphere was changed from Ar gas to He gas, a significant change appears in exothermic heat flow before the glass transition temperature T_g during differential scanning calorimetric (DSC) measurements, and the plasticity of the MG also increases. Sun et al. [8] reported that higher casting vacuum can improve glass forming ability, thermal properties, corrosion resistance and solubility of certain elements in Fe-based MG. Das et al. [9] explored an unusual combination of high compression strength and ductility at room temperature which sensitively depends upon the casting technique employed. Besides preparation conditions, there are other factors and parameters which can sensitively influence the MG properties [15–20] including localized chemical or/and structural heterogeneity, raw material impurities, casting defects (porosity, oxide inclusions etc.) and sample geometry imperfections.

The Weibull distribution analysis has been widely used in materials science and engineering fields to assess the reliability of mechanical and physical properties of various materials [15,20–29]. The Weibull analysis is also widely applied to evaluate the sensitivity and variation of mechanical properties of MGs [15,20,23,25,26,28,29] because of their importance for engineering applications. It is known that any change (intrinsic or extrinsic) in the structure of MGs will definitely change their properties. However, the structural origin for the sensitivity and the mechanism for the Weibull distribution of the MG properties remain unclear.

Recently, the flow unit model in metallic glass has been proposed [30–40] to explain different MG properties. According to the model, the localized nano-scaled liquid like regions of lower density, lower modulus and higher energy, called flow units, exist and embed in the elastic matrix of MG. The concentration and distribution of flow units is quite stochastic rather than uniform due to heterogeneous nature of MG structure, and the plastic deformation and other mechanical properties of MGs are generally attributed to activation process of the flow units. This model has been successfully used to describe the thermal and mechanical properties of

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MGs. It is intriguing to know the relationship between the structural flow units and the Weibull distribution of the MG properties.

In this paper, we show that even under the similar conditions of casting process, the variation in mechanical properties of MG is related to the stochastic activation and concentration of the flow units which also follow the Weibull distribution function like other properties of MGs. The results suggest that the sensitivity and metastability of the MG properties is closely correlated with the features of flow units and can be well explained from the flow unit perspective. The results are helpful for the understanding the deformation behavior of glass and desirable properties for material design.

2. Experimental procedures

We selected $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ bulk metallic glass as a model system due to its good glass forming ability (GFA), thermal stability and reasonable compression plasticity. The master alloy ingots of $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ (at. %) were prepared from pure constituent elements by melting them in an electric arc furnace under Ti getter Ar gas atmosphere. The amorphous alloy rods with 2 mm diameter were prepared using Cu mold suction casting technique by carefully controlling the same ingot weight, vacuum level, arc current and time. The glassy structure of each rod was assured by the X-ray diffraction (XRD) using Cu-K_α radiations on a Bruker D8 AA25 diffractometer. The surface of each rod was polished to eliminate the possibility of nano-crystallization at the interface of Cu mold inner surface and casting rod surface. The polished rods were cut into small compression samples of length 4 mm each and maintaining the gauge aspect ratio of 2:1. The both ends of each compression sample were also carefully polished to ensure parallel and flat surfaces so that any ambiguity in compression test could be avoided. Compression tests were performed on MTS 809 universal testing machine with a strain rate of 1×10^{-4}/s and the yield stress for each sample was determined with the help of 0.2% off-set method. The thermal analyses were done using Perkin–Elmer DSC 8000 in Ar atmosphere at a heating rate of 0.33 K/s. The Weibull analysis of measured properties was carried out using at least 20 samples for each.

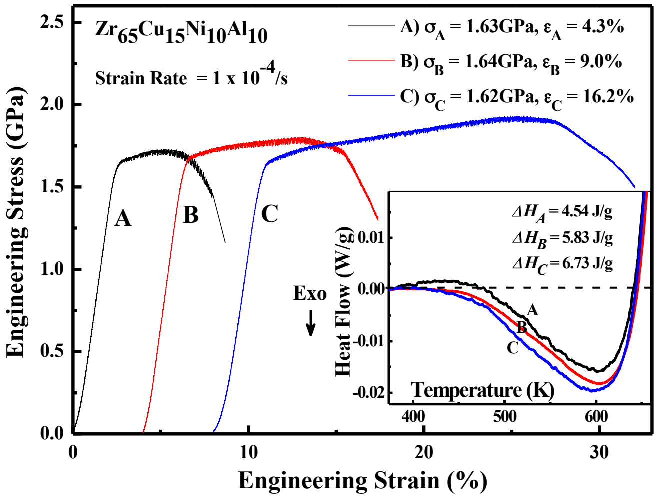

Fig. 1. Typical compressional engineering stress versus engineering strain curves of 03 as-cast $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ BMG samples (*A*, *B* and *C*) under similar conditions but showing different plasticity, σ and ε denote the yield stress and the plastic strain, respectively. The inset represents the portions of DSC scans just before T_g of respective samples and areas bound by the dashed line and DSC scan lines correspond to the exothermic heat ΔH flow.

3. Results and discussion

The typical compressional engineering stress versus engineering strain of three as-cast $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ BMG samples (*A*, *B* and *C*) is shown in Fig. 1. Although these are chemically identical samples and were carefully cast under similar conditions including the similar casting temperature and cooling rate, large variation in plasticity (about 3–16% for 20 samples) with small variation in yield stress (about 1.5–1.7 GPa for 20 samples) can be seen in Fig. 1. Yu et al. [25] also reported even more variation in plasticity from less than 5% to larger than 30%, and as well small variation in yield stress for MG system. The inset of Fig. 1 shows the portions of DSC scans of these three samples just before T_g and the dashed line is a guide to eyes. One can see that area under the dashed line corresponding to the exothermic heat ΔH (4.54, 5.83 and 6.73 J/g for sample *A*, *B* and *C*, respectively) increases gradually for three samples. The larger value of ΔH indicates larger amount of structural defects or free volume in MG, and vice versa [7,41,42]. Zhao et al. [39] proposed a linear relationship between the concentration of free volume and flow units embedded in densely packed elastic matrix. Thus, the samples *A*, *B* and *C* contain increasing relative concentration of flow units. It also confirms that the sample with high concentration of flow units represents good plasticity [7,32]. Zhu et al. [40] mentioned that annealing at sub-T_g will decrease the concentration of flow units and considerable increase of ΔH was noted due to annihilation of flow units. It is also consistent with the DSC results just recently reported by Li et al. [43]. They did not find any significant change in crystallization temperature and enthalpy after sub-T_g annealing but a closer look just before T_g reveals a detectable ΔH.

The Weibull distribution function $W(x_i)$ for *i* th value of any quantity *x*, is defined as,

$$W(x_i) = 1 - \exp\left[-(x_i/\beta)^m\right], \tag{1}$$

where *m* is the Weibull modulus and β is the fitting parameter. The value of *m* is determined from the slope of linear fit of data between probability function $F(P_i) = ln[-ln(1-P_i)]$ and natural log of measured quantity while the intercept gives the value of β as: $intercept = -mln(\beta)$. The characteristic distribution parameter *m* indicates the dispersion of flaws and the extent of variation in that quantity [24,25]. The lower value of *m* demonstrates broader distribution in the measured property due to large variation in flaw concentration, while a higher value illustrates narrower distribution due to small variation in flaw concentration in all the tested samples. The Weibull analysis is based on some assumptions: (1) 'weakest link' failure is responsible for catastrophic fracture and there is no redistribution of load among other links; (2) the probability of finding a critical defect in a given volume is same as in the entire volume of the sample; (3) samples can fracture due to different mechanisms or reasons and each has its own probability of failure [44]. The Weibull distribution functions of plasticity $W(\varepsilon_i)$, yield stress $W(\sigma_i)$ and exothermic heat $W(\Delta H_i)$ for 20 as-cast BMG samples are plotted against respective quantity in Fig. 2 (a)–(c). The insets represent the linear fit of data between two mentioned quantities and the Weibull analysis utilizes this linear relation. It assumes only one type of defect ('weakest link') whereas there may be other defects depending upon composition and preparation conditions. The non-linear behavior of actual data is due to the simultaneous presence of several types of defects [44]. The value of *m* is not a material constant and it significantly depends upon loading conditions and geometrical factors [28]. The smaller value $m = 7.21$ for exothermic heat and $m = 2.07$ for plasticity indicate large variation, while larger value of $m = 39.13$ for yield stress