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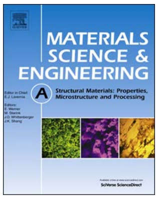

Decoding flow unit evolution upon annealing from fracture morphology in metallic glasses

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ABSTRACT

The intrinsic correlation between the fracture morphology evolution and the structural heterogeneity of flow units in a typical $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ (vit105) metallic glass (MG) upon annealing was investigated. By systematically tuning the annealing time at temperature below the glass transition temperature, a series of dimple-like fracture morphology were obtained, which is the unique fingerprint-like pattern for every annealing state. Based on the structural relaxation model of flow units, the evolution of the typical dimple sizes, the largest and smallest dimple size, with annealing were well fitted. Then the evolution of flow unit density was estimated from the fracture morphology evolution, which displays the same evolution trend with that measured from thermal relaxation. A stochastic dynamic model considering the interaction of activated flow units was proposed to analyze the effect of the initial flow unit density and the flow unit interaction intensity on the dynamic evolution of dimple distribution. Our work may provide a novel scheme to investigate the structural fingerprint information on flow units from fracture morphology, and enlighten the microscopic structural origin of the ductile-to-brittle transition during structural relaxation in MGs.

1. Introduction

Metallic glasses (MGs) have been studied extensively as potential structural and functional materials in view of their excellent physical properties compared to traditional crystalline counterparts [1,2]. The unique amorphous structure and tunable composition endow MGs ultrahigh strength, large elastic limit, high fracture toughness, good corrosion resistance, excellent soft magnetic property and unique thermoforming capability like plastics [3–5]. However, the practical applications of MGs still face many challenges [2]. One major obstacle is the physical property unreliability, especially for the embrittlement problem at room temperature, which intrinsically origins from the metastable nature of MGs [6]. Since the metastable materials are trapped in local free energy minima, they tend to change their structure progressively towards the crystalline state or more stable glassy states when they are stimulated with the external energy. This process is referred to as structural relaxation or aging, and various physical properties significantly evolve with the structural relaxation, such as elastic modulus, density, hardness, plasticity and fracture toughness [7–11]. Low temperature (the temperature below the glass transition temperature T_g, sub-T_g) annealing induced ductile-to-brittle transition (DBT) is one of the most critical problems in practical applications [10,12]. In spite of decades-long investigations, the nature of this phenomenon remains a matter of debates. The popular interpretation of DBT is based on the free volume model [12,13]. These interpretations think that the decrease of free volume upon annealing reduces the propensity for formation of multiple shear bands (SBs) and hence deteriorates plastic deformation ability. However, the free volume model is just phenomenological physical concept and the intrinsically microscopic structure origin of structural relaxation induced embrittlement is still unclear.

Recently, there have been a large number of experimental results implying that the MGs are not completely homogeneous in nanoscale and there exist a lot of dynamic or property defects of flow units (also termed as liquid-like zones or weakly bonded regions) [14–17]. These dynamic defects show low modulus, low viscosity and high atomic mobility. Based on the above experimental results, the structure of MGs can be considered as a random distribution of flow units in the elastic matrix [18]. Thus, the dynamic relaxations, aging, and the evolution of many physical properties with structural relaxation in MGs could be well understood based on the flow unit model, such as the elastic modulus, the density, the strength, the plasticity and the viscoelasticity [8,19–23]. However, little work has been done on the relationship between the structural relaxation induced DBT and the structural heterogeneity of flow units. Although the evolution of structural heterogeneity or flow units with annealing could be studied

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by high-resolution atomic force microscopy (HRAFM) technique [14,24], this technique is only suitable for the MG systems with the ultra-low surface roughness, such as the MG films, which largely limits the research on the embrittlement of MGs. Meanwhile, previous research indicates that the fracture morphology represents a one-to-one relationship with the annealing state in MGs [12], which reminds us of the human fingerprint as the unique identification. It is noted that spatiotemporal patterns in nature, such as the various leaves, sweeping loops of meandering rivers, crescentic and star-shaped patterns of sand dunes, and convective patterns of normal fluids, offer a direct clue to identify the natural plants and understand the dynamic behaviors of non-equilibrium systems [25–27]. Particularly, for MGs combining the glassy structure and metallic bonds, various and plentiful dynamic fracture patterns like dimple structures, periodic corrugations, and river patterns appear selectively in different regions of their fracture surface [28–30]. And different MG systems display the different fracture morphology correlating with their unique physical properties [31]. Therefore, it implies that the fracture morphology may be a fingerprint-like tool to study the intrinsic correlation between the flow unit and the structural relaxation, and then encode the microscopic structural origin of the embrittlement induced by structural relaxation.

In this work, we systematically studied the spatial distribution evolution of the typical fracture morphology (represented by dimple structures) with the sub-T_g annealing in typical Zr-based MG. The evolution of the typical size of dimple structures (the largest and smallest size) with the increase of the annealing time can be well fitted by the structural relaxation model based on the flow unit image. What is more, the spatial distribution of dimple structures appears a transition from the power-law distribution to Gaussian-like distribution. To further understand this transition behavior, a stochastic dynamic model is proposed to theoretically understand the fracture morphology evolution upon annealing by considering the influences of the initial flow unit density and the flow unit interaction intensity. Finally, a physical scheme is presented to elaborate how to encode the intrinsic flow unit evolution information from fracture morphology.

2. Experimental details

The typical Zr-based MG ($Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$, vit 105) was chosen as the model material for its good glass forming ability and high thermal stability. The plate-like samples with 2×10×60 mm^3 (thickness×width×length) in geometric size were prepared from a master alloy with normal composition of $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ by water-cooled copper mold casting. The glass nature of all samples was checked by X-ray diffraction (XRD, Bruker D8) and differential scanning calorimetry (DSC). The DSC experiment was performed with a power compensated Perkin-Elemer DSC 8000 with a heating rate of 0.33 K/s under a constant flow of high purity argon gas. The MG plates were then cut into the rectangular cubes with the dimensions of 2×4×12 mm^3 (thickness×width×length) for three-point bending tests. All MG rectangular cubes were polished using 200, 600 and 1200 grit SiC paper successively to remove the surface defects from the casting process.

To systematically study the structural relaxation of Zr-based MGs, we annealed specimens at the temperature T_a of 543 K (0.8 T_g) with different annealing times t_a: 0 min (*as*-cast), 20, 40, 60, 120, 240, 720, 1465, 4986, 7200 and 14,400 min. To avoid the oxidation effect during annealing, the above rectangular specimens for three-point bending tests were encapsulated in a quart crucible with vacuum of 10^{-4} Pa. Then these encapsulated specimens were put into the Box type resistance-heated furnace (FNS Electric Furnace Co.) for annealing treatment.

Before three-point bending, the notches (250 µm in width and 1.5 mm in depth) were introduced into the middle of these rectangular specimens by a diamond saw for confirming the flatness of fracture surfaces. The three-point bending tests were carried out in an Instron 3384 machine (Norwood, MA) with a cross-head moving speed of 0.5 mm min^{-1} at room temperature. The generated fracture surfaces were observed by scanning electron microscopy (SEM) conducted in a Philips XL30 instrument.

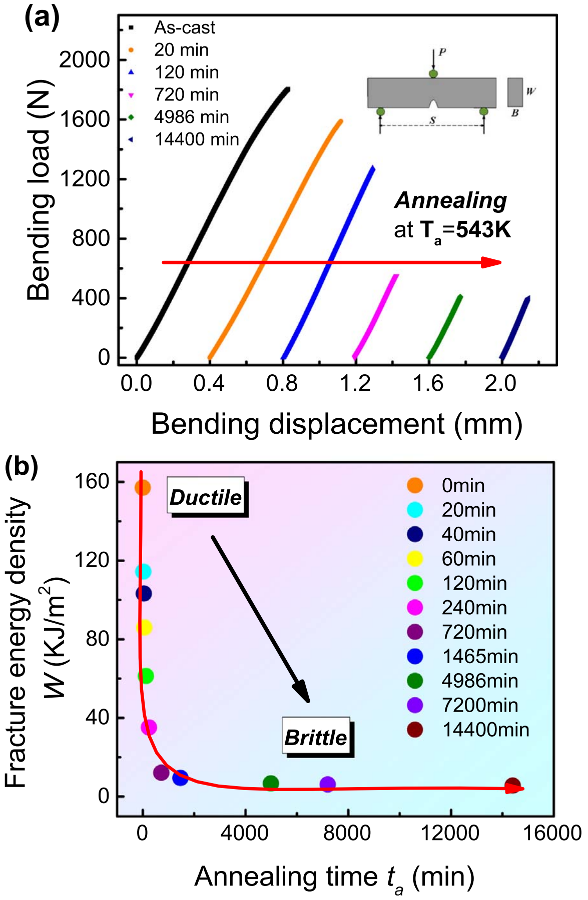

Fig. 1. (a) The evolution of bending-load and bending-displacement curve with the increase of annealing time at annealing temperature T_a of 543 K. The inserted graph gives the set-up of the three-point bending test. (b) The evolution of fracture energy density W with the increase of annealing time. The black arrow points the ductile-to-brittle transition and the red arrowed curve gives the evolution trend of W with annealing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussions

3.1. Mechanical property evolution with structural relaxation

Three point bending tests were conducted on a series of MG specimens with different annealing times at T_a =543 K (sub-T_g, 0.8 T_g) and the detailed set-up of three point bending tests is shown in the inserted graph of Fig. 1a. Fig. 1a displays the bending load-bending displacement curves for the annealed specimens and the as-cast specimen. For as-cast specimen, the load-displacement curve initially follows a linear relation at low loads, and then starts to become nonlinear at about 1400 N, which is one of the experimental evidences of the ductile fracture. In contrast, for various annealed MG specimens, there is nearly no nonlinear behavior and the fracture bending displacement and load gradually decrease with the increase of the annealing time. Especially, for the specimen with the annealing time of 720 min, the bend fracture load reduces to 600 N, which is about 75% lower than that of the as-cast one. With the continuing increase of the annealing time, the decrease amplitude of the bending fracture load gradually becomes smaller and reaches the saturation value. The above results indicate that these annealed specimens have been changed into