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Stress-induced mechanical heterogeneity in metallic glasses revealed by spatial nano-indentation

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ABSTRACT

The heterogeneity plays a key role in physical and mechanical properties of a material. The nature of lacking long-range order in metallic glasses (MGs) causes the local atomic rearrangement to vary significantly in space when compressed. Different configurations of an ensemble of atoms in a MG lead, therefore, to a distribution of nanohardness, which also changes in space. The effects of pressure on the mechanical heterogeneity of MGs induced by a stress have been investigated by spatial nanoindentation. The mechanical heterogeneity is quantified by calculating shear-transformation zone volumes. Here, we demonstrate that the spatial nanohardness experimentally reveals very well on pressure-induced local mechanical heterogeneity in MGs.

1. Introduction

Metallic glasses (MGs) have attracted much research interest due to their particular structure, mechanical, electrical, and magnetic properties [1]. Many properties are sensitive to the local atomic structure [1–6]. When compressed, the local atomic rearrangement in MGs leads to a distribution of nanohardness changes in space. However, the atomic-scale mechanism of plastic deformation of MGs is far from being fully understood. The shear transformation zone (STZ) [7–9] is a widely-accepted model for the plastic deformation in MGs. During deformation, the amorphous solids undergo cascades of local atomic rearrangements [10–14]. As a result of the local atomic rearrangement, it has been theoretically postulated that MGs should exhibit a scale-dependent distribution of mechanical constants [15]. These local variations in the stress state of individual atoms lead to a more cooperative motion on a larger scale and are often observed as dynamical heterogeneities in studying relaxation modes [13]. Vacancy, defect, and grain boundary usually result in micro-scale heterogeneity of a material [16]. The nature without defects, such as grain boundaries in metallic glasses (MGs), causes its heterogeneity defying accurate experimental and theoretical analyses [14]. Experimental observations reveal that MGs are intrinsically and structurally inhomogeneous [17,18]. However, there is still a lack of a simple and efficient means to demonstrate the heterogeneity of MGs on a nano-scale. Recently, using atomic force microscopy imaging and quantitative mechanical mapping, structural and mechanical heterogeneity of key components of the erythrocyte membrane was revealed at the nanometer resolution [19]. Therefore, it is reasonable to believe that the heterogeneity in MG can be detected on the nanoscale by testing the interactions of atoms. The nanoindentation method has been widely used for the investigation of mechanical properties and deformation behavior in a small volume of materials [20]. For instance, nano-indentation-creep tests have been used to study the creep behavior of nanocrystalline materials [21] and bulk metallic glasses (BMGs) [22]. It is known that the stress-induced local atomic rearrangement gives rise to long-range elastic fields. Every local atomic rearrangement can alter the stress-field surroundings [23–25], and shear localization and strain hardening are closely related to the number density of STZs [10–14]. Therefore, the heterogeneity of MGs induced by stresses is supposed to be quantified, based on the spatial nanohardness, activation energy, and calculated STZs volumes.

The aim of the present work is to seek the experimentally-accessible way to reveal the pressure/stress (ranging from 0 to 4 GPa) induced local atomic rearrangement in MGs. We find that spatial nanohardness can be used to effectively detect the structural inhomogeneity, and the heterogeneity of MGs induced by stress was explained by calculating the activation energy and STZs volumes.

2. Material and methods

The amorphous $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$(at.%) rod was cut into a length of 5 mm with the diameter about 6 mm, and its ends were carefully polished to the flat and parallel surface or the pressure treatment by a conventional cubic-anvil-type high-pressure facility. The effect of pressure (up to 4 GPa) on the structural heterogeneity

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of$Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$(atomic percent, at.%) MG has been investigated. Based on the Hysitron NanoIndenter system, a Hysitron NanoIndenter (TI-900) was employed to detect the structural inhomogeneity. The experimental characterization of STZs for plastic flow of bulk metallic glasses (BMGs) based on a cooperative shearing model (CSM) [3]. A differential scanning calorimeter (DSC), with heating rates ranging from 10 k/s to 80 K/s was used to determine the effective crystallization-activation energy parameters in both as-cast and compressed MGs at various pressures.

3. Experimental

The amorphous alloy with the composition of $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$(at %) was prepared by arc melting. The amorphous nature before and after compressive loading was ascertained by the X-ray diffraction (XRD) using a D/MAX-RB diffractometer with Cu Kα radiation. A pyrophyllite bulk was used as the pressure-transmitting medium. The high-pressure process was carried out at 0 GPa, 3 GPa, 3.5 GPa, and 4 GPa at room temperature for 1 h. To ensure the ultrahigh mechanical sensitivity in the dynamic tests, the nanoindentation method, which is based on the Hysitron NanoIndenter system, was employed. To make sure of nanoindentation measuring the same area before and after compression, we notch 1 × 1 mm on the sample surface with diameter of 3 mm. An arrays with 10 × 13 indents has been measured with the constant loading rate of 1000 $\mu N\ s^{-1}$ to a maximum load of 5000 μN on each sample after different high pressure treatment. For nanoindetations under changing loading rates, the loading rates of 5000, 1000, 500, 100 $\mu N\ s^{-1}$ with a maximum load of 5000 μN were applied to calculate the STZs volume. This nanoindentation system possesses an achievable resolution of ~1 nm in displacement and ~1 μN in load after calibration.

4. Results

4.1. Effect of pressure on amorphous structure stability of $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG

The XRD patterns for the $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG compressed under 0 GPa, 3 GPa, 3.5 GPa, and 4 GPa, are shown in Fig. 1. Some researchers suggest the materials showing X-ray patterns like those (no detectable crystallization phases) shown in Fig. 1 exhibit incipient, although stochastic, crystalline order [26,27]. In our previous study, the amorphous structure of Zr-based BMG keeps stable up to 31 GPa [28]. According to differential scanning calorimeter (DSC) traces (with different heating rates) of the as-cast and compressed MGs at various pressures, we can determine the effective crystallization-activation energy, E_x, and glass-transition-activation energy, E_p, for the $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG at various pressures by Kissinger's equation. Both E_x and E_p decrease with increasing the pressure, reach their minimum around 3.5 GPa, and then increase with a further increase of the applied pressure.

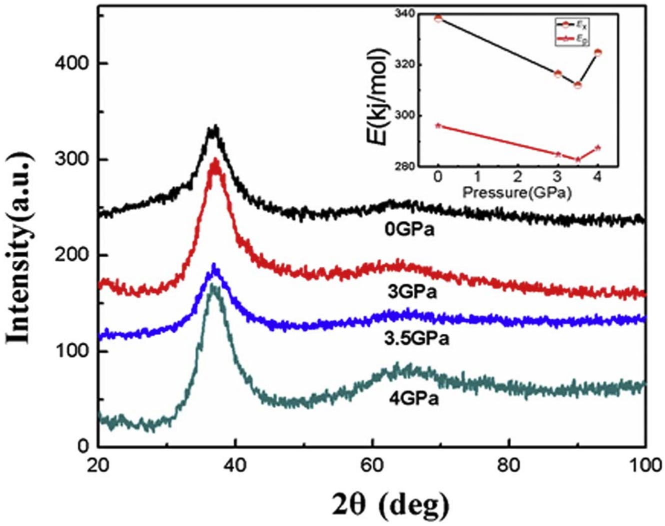

Fig. 1. The XRD patterns for the $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG compressed under different pressures at room temperature. Inset is calculated glass transition and crystallization activation energy.

4.2. Effect of pressure on spatial distribution hardness of $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG

Following the Oliver–Pharr [29] method, hardness values, H, and residual depths, h_f, can be obtained by nanoindentation. The contour map in Fig. 2 shows the spatial distribution of hardness values, H, of the $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG under different pressures over a $100 \times 120\ \mu m^2$ square area. The H values of 0 GPa and 3 GPa pressured samples (shown in Fig. 2(a) and (b)) distribute less heterogeneously along both X and Y directions, than that of 3.5 GPa and 4 GPa pressured samples [shown in Fig. 2(c) and (d)]. "Loops" in the Fig. 2(c) and (d) indicate different distributions of hardness values within the test area. The partially-enlarged loop is shown in Fig. 3. In the size range of about $16 \times 12\ \mu m^2$, 18 loops can be observed. Therefore, the scale of the inhomogeneity of the $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG is about several hundreds of nanometers.

4.3. Effect of pressure on plasticity of $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG.

Plasticity is the tendency of a material to undergo permanent deformation under load. Plastic deformation process material mechanics properties of the change is inevitable because material changes caused by the microscopic structure. Therefore, the mechanical properties of materials research will lead to changes in the structure of the micro material. From the load-displacement curves, the residual depth, h_f, for the $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ BMG in HP pretreated state under 0 GPa, 3 GPa, 3.5 GPa and 4 GPa are 166.6 nm, 184.4 nm, 191.7 nm, and 188.1 nm, respectively, as shown in Fig. 4. Compared with the as-cast $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ BMG (pretreated pressure of 0 GPa), the maximum residual depth increase from 10.7% to 15.1%. That is to say, after the HP pretreated, the plasticity of the $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG significantly increases.

5. Discussion

The room-temperature plastic deformation of MGs is known to be inhomogeneous and achieved by highly localized shear bands [30–32]. Based on the Johnson–Sawmer CSM [3], Pan et al. [33] show that STZs of MGs can be calculated by the experimental data according to the Fischer-Cripps' [34], Mayo's [35], and Chengetal's [36] research work:

$$\Omega = \left(\frac{\mathrm{kT}}{G_0 \gamma_C^2}\right) \frac{1}{6R\varsigma} \frac{1}{m\left(,\frac{\tau}{\tau_C}\right)\left(1-\frac{\tau}{\tau_C}\right)^{1/2}} \tag{1}$$

where G_0 and τ_C are theshear modulus and the threshold shear resistance of an alloy at 0 K, respectively, the average elastic limit, $\gamma_C \approx 0.02$ [3], the constants, $R \approx 1/4$, and $\zeta \approx 3$ [3], m is the strain-rate sensitivity in determining the STZ volumes of MGs by means of nanoindentation. In a nanoindentation hardness test, the corresponding strain-rate sensitivity, m, of hardness is, hence, extracted by lining up the hardness vs. equivalent strain rate on a log–log scale and measuring the slope of the line [33–36].

From the above equation, the Ω for the $Zr_{62}Ti_5Cu_{16}Ni_{10}Al_7$ MG under different pressures of 0 GPa, 3 GPa, 3.5 GPa, and 4 GPa are calculated to be $1.37\ nm^3$, $2.36\ nm^3$, $4.23\ nm^3$ and $2.19\ nm^3$, respectively. The STZs include 95 atoms, 110 atoms, 293 atoms, and 152 atoms with an average atomic radius statistically estimated as