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Nanoindentation study of size effect and loading rate effect on mechanical properties of a thin film metallic glass $Cu_{49.3}Zr_{50.7}$

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ABSTRACT

A binary metallic glass (MG) $Cu_{49.3}Zr_{50.7}$ in the form of thin film was successfully grown on a Si (1 0 0) substrate by magnetron sputtering. The mechanical properties, specifically, hardness and modulus at various peak loads and loading rates were characterized through instrumented nanoindentation. Unlike other metallic glasses showing an indentation size effect (ISE), the composition of this study does not have an ISE, which is phenomenologically the result of the negligible length scale according to the strain gradient plasticity model. The proportional specimen resistance model is applicable to the load–displacement behaviors and suggests that the frictional effect is too small to contribute to the ISE. The occurrence of plasticity depends on loading rates and can be delayed so that the displacement during the load holding segment increases logarithmically. In addition, the hardness and modulus are both dependent on the loading rates as well, i.e., they increase as the loading rate increases up to 0.1 mN/s and then hold constant, which is independent of creep time (≤ 100 s). These loading-rate-dependent behaviors are interpreted as the result of viscoelastic effect rather than free volume kinetics.

1. Introduction

Strength and plasticity are the mechanical properties of focus in the field of metallic glasses (MGs), which are governed by shear bands (SBs). The formation of SBs is achieved by localization and coalescence of flow defects, i.e., free volume or shear transformation zone (STZ). The strain rate response of SBs and mechanical properties have been investigated under a variety of loading modes. In uniaxial tension, a single SB tends to nucleate and grow rapidly along the maximum shear plane, resulting in the brittle fracture of MGs. In uniaxial compression, due to the geometrical constraints, MGs exhibit a limited plasticity through a series of shear banding events. Under both modes, the strength of MGs at room temperature is usually observed to display independence on strain rates over a broad range, at least six orders of magnitude from a quasi-static mode up to a low-velocity impact mode [1]. In contrast, some other experiments under these conventional modes distinctly revealed either positive or negative effects of strain rates [2–5]. Meanwhile, some computational work supports the strength scaling with rate for MGs at the nanometer scale [6,7]. These contradictory results might lie for two reasons: firstly, as predicted in the theories [1,8], MGs have an extremely low strain rate sensitivity beyond the resolution ability of these traditional loading methods; secondly, the strain rate effect could be influenced by a few factors, such as material composition, sample geometry, test temperature and loading mode.

Unlike these traditional loading techniques, instrumented nanoindentation is an important investigative technique with high spatiotemporal and force resolution, allowing for the precise measurement of stress drops or displacement bursts in materials [9]. Additionally, under conventional loading modes, MGs are usually brittle, leading to the poor understanding of their plastic deformation. In these respects, nanoindentation is more helpful to study the deformation behavior of MGs. Recently, experiments under this mode have been widely conducted to probe the loading/strain rate effects [10–13]. Pan and Chen [11] employed an artfully designed method termed rate-change indentation and found that the hardness of both Ni-based MG and nanocrystalline nickel increases slightly with elevated loading/strain rates when measured at high loading rates (≥ 13.2 mN/s) underneath large depths (>1 μm), while Sort et al. [10] observed the opposite effect of loading rates over a large range at a depth less than 300 nm, which is attributed to the enhancement of free volume therein. Indentation size effect (ISE) is another issue worth noting in nanoindentation tests, which is manifested as the increasing hardness with reduction of the indentation depth. The ISE exists in both crystalline and amorphous solids and was well

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documented [14,15]. The early experiment on a Zr-based BMG by Wright et al. [16] attributed such an increase to the lower SB density at a smaller indentation load, while recent studies demonstrate that strain gradient plasticity (SGP) [17] or surface frictional effect [18] might be sufficient to figure out the problem.

In this work a binary metallic glass $Cu_{49.3}Zr_{50.7}$ was prepared in the form of thin film so that the good surface quality was attained to minimize the experimental errors from surface defects and roughness. To date, little work has been done on thin films to characterize the plastic deformation in MGs. The understanding of deformation mechanism can be applied to establish the constitutive deformation model and then to predict the fracture behavior of MGs, which is very important for structural applications. Instrumented nanoindentation was performed to investigate the mechanical properties at various loading rates and under various peak loads. The loading rate effect and ISE are both discussed on the basis of theories available.

2. Experimental method

CuZr thin films were deposited on Si (1 0 0) substrates in a magnetron sputtering system under an argon (Ar) atmosphere. The base pressure was 1.5×10^{-6} Torr, and the sputtering process Ar pressure was 2.5 mTorr. To achieve the desired composition, two targets were used; one is a CuZr alloy target under the direct-current power of 250 W and the other is a Cu target under the radio-frequency power of 25 W. The Si substrates were placed on a holder rotating around a central axis at a constant speed. To strike off the possibly existing oxide layer on the target surface, pre-sputtering was carried out for 2 min, followed by a sputtering process for 220 min. The thickness of the thin films is on average 3.5 μm.

The amorphous structure was examined by X-ray diffraction (XRD) with a CuKα radiation. Energy dispersive X-ray (EDX) technique was used for compositional analysis. Five points were measured for statistical calculation. Line scanning analysis was performed to ensure the compositional homogeneity.

Mechanical properties were characterized by nanoindentation with a diamond berkovich indenter on an MTS Nanoindenter® XP system. The force resolution and vertical displacement resolution are estimated to be less than 0.1 μN and 1 nm, respectively. Prior to the beginning of tests, the contact area function was calibrated using a standard fused silica material. The nanoindentation measurements were performed under a load-control mode at room temperature and consisted of 6 sequential segments.

The indenter drift rate control segment is to reach the allowable drift rate limit 0.05 nm/s. The surface find segment is to identify the surface contact point. These two segments are designed to guarantee the stable and reliable measurements. The loading segment reaches the preset maximum loads of 1, 2, 4, 6, 9 and 12 mN at loading rates of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1 mN/s, followed by a holding segment where the peak loads are kept for 2–100 s. Loads are removed in the unloading segment at an unloading rate of 1 mN/s until the unload limit (10% of the peak load) was reached for all the tests. Finally, thermal drift correction segment takes place where the absolute values of the thermal drift rates were usually well kept below 0.05 nm/s. The thermal drift effect was excluded from the resulting displacement data. Five indents were made in each test for statistical analysis and consistency inspection.

The hardness and the reduced elastic modulus were calculated by fitting the load–displacement (P–h) curve using the Oliver–Pharr method. Specifically, the hardness was determined by the maximum load divided by the projected contact area. The elastic modulus is associated with the unloading stiffness and the projected contact area. The unloading stiffness reflects the resistant ability of surface to bending and equivalent to the initial gradient of the unloading curve. As the reduced elastic modulus is measured, the Young's modulus of the material investigated can be derived as follows:

$$\frac{1}{E_r}=\frac{1-\nu_i^2}{E_i}+\frac{1-\nu^2}{E} \quad (1)$$

where E_r, E_i and E are, respectively, the reduced elastic modulus, the Young's modulus for diamond and the Young's modulus for the test material. ν_i and ν are the Poisson's ratios for diamond and test material, respectively.

3. Results and discussion

The nominal composition is $Cu_{49.3}Zr_{50.7}$ ($\pm1\%$). The XRD profile of the as-deposited thin films is presented in Fig. 1. There exists a broad diffraction peak, which represents the fully amorphous structure. No crystalline phases can be detected across the whole diffraction angle range.

3.1. Indentation size effect

Fig. 2 shows the P–h curves of $Cu_{49.3}Zr_{50.7}$ under various maximum loads at a loading rate of 1 mN/s. Instead of the serrated flow often observed in MGs, the load increases smoothly as the indenter advances, which may be attributed to the quite small shearing displacement beyond the instrumental resolving ability. The indentation load as a function of the indentation depth can be well fitted by a parabolic function [19]:

$$P(h)=a_0+a_1h+a_2h^2 \quad (2)$$

where a_0, a_1 and a_2 are fitting parameters dependent on the experimental error and the true hardness. From the viewpoint of energy balance, the first term on the right side is related to the surface residual stress, the second term is related to the surface energy and the third term is related to the volume energy of deformation. It is not true but reasonable to assume $a_0=0$, due to the ideal boundary condition: $P=0$ when $h=0$. Thus, the equation is reformulated as

$$P(h)=a_1h+a_2h^2 \quad (3)$$

Fig. 3 presents the maximum load dependence of the unloading stiffness at the loading rate of 1 mN/s. As the maximum load increases, the stiffness increases nonlinearly. According to the

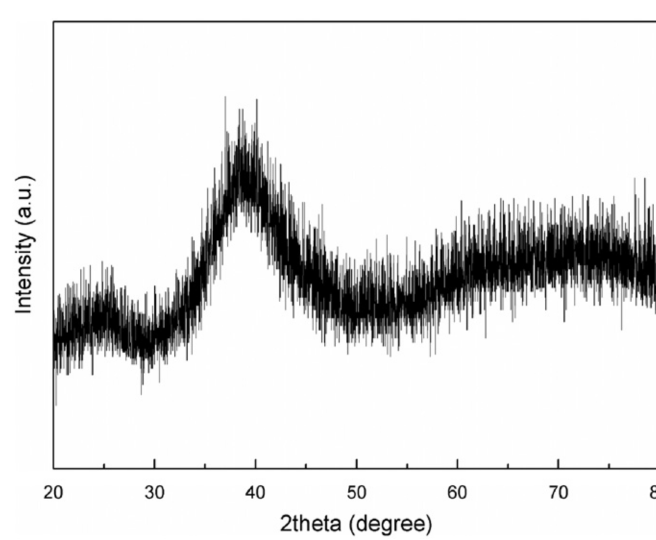

Fig. 1. XRD profile of the as-deposited thin film $Cu_{49.3}Zr_{50.7}$ on the substrate of Si (1 0 0).