Materials Science & Engineering A 651 (2016) 548–555

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Nanoindentation investigation on the creep mechanism in metallic glassy films

Y. Ma [a], G.J. Peng [a], Y.H. Feng [b], T.H. Zhang [a,*]

[a] College of Mechanical Engineering, Zhejiang University of Technology, Hangzhou 310014, China
[b] State Key Laboratory of Nonlinear Mechanics (LNM), Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:
Received 26 May 2015
Received in revised form
5 November 2015
Accepted 6 November 2015
Available online 10 November 2015

Keywords:
Metallic glass
Nanoindentation
Creep
Free volume
Shear transformation zone

ABSTRACT

Using the magnetron sputtering technique, two metallic glassy films namely $Cu_{44.3}Zr_{45.1}Al_{10.6}$ and $Cu_{44.2}Zr_{43}Al_{11.3}Ti_{1.5}$ were prepared by alloy targets. The minor Ti addition effectively induces excess free volume. Upon spherical nanoindentation, the creep behaviors of both films were studied at various peak loads. As the increase of peak load, the creep deformations became more severely in both samples. Interestingly, Cu–Zr–Al–Ti film crept stronger than Cu–Zr–Al at small-load holdings (nominal elastic regimes), whereas it is opposite at high-load holdings (plastic regimes). The creep characteristic could be intrinsically related to the scale variation of the shear transformation zone (STZ) with Ti addition. Statistical analysis was employed to estimate the STZ volume, which increased by 60% with Ti addition in the Cu–Zr–Al film. The finite element modeling indicated that STZs would be activated even at the minimum load we adopted. Higher activation energy of larger STZs in Cu–Zr–Al–Ti enables less flow units, which offsets the creep enhancement by the excess free volume with Ti addition. The deeper the pressed depth of the indenter, the more contribution of the STZ operation on creep deformation. In addition, experimental observation on the creep flow rates implies that STZ could be the dominating mechanism at the steady-state creep. This study reveals that STZ volume could also be important to the time-dependent plastic deformation in metallic glass, besides as a key parameter for instantaneous plasticity.

1. Introduction

For the last several decades, the mechanism of plastic deformation in metallic glasses has been widely investigated [1,2]. This is due to both fundamental and technological importance of these materials in the condensed mater research. Having clear difference in atomic structure from its crystalline counterparts, shear transformation zones (STZs) are usually considered playing a vital role to in allowing irreversible deformation in metallic glasses [3]. The activation and evolution of STZs are pivotal to the shear banding events as well as the instantaneous mechanical response [4,5]. In recent years, following the cooperative shear model (CSM) by Johnson and Samwer [6], Pan et al. estimated the STZ volume experimentally (using rate-jump method) and found a correlation between STZ volume and plasticity of metallic glasses [7,8]. Additionally, free volume is another important atomic-level feature which can intrinsically control plasticity [9–11]. By adding just 2% Ti, plasticity of a Cu–Zr–Al metallic glass can be greatly enhanced due to the induced excess free volume [12]. The creation and annihilation of free volume could sustain the homogeneous creep flow at high temperature [13] or/and nanoscale [14].

Based on nanoindentation, creep behaviors of metallic glasses can be studied at small region, ignoring the limit of required standard size in traditional creep testing. In addition, the holding stage could be time-saving due to the high accuracy for obtaining the time-dependent plastic deformation. However, the stress distribution beneath the indenter is much more complicated and plastic deformation always occurred before the holding stage [15–18]. Thus, metallic glasses having high glass transition temperature (T_g) can even creep at room temperature in nanoindentation. To authors' best knowledge, the creep behaviors of metallic glasses concerned with loading rate [16], holding load [16,17] and initial strain [18] were qualitatively explained through free volume. In our previous work, the loading rate effect on creep was found to be composition-dependent and apparently related to the STZ size [19]. Though the exact creep response on the variation of STZ size is far from understanding due to the changes of other structural or physical parameters at the same time as the composition changes. With this in mind, creep behaviors of Cu–Zr–Al and Cu–Zr–Al–Ti

* Corresponding author.
E-mail address: zhangth@zjut.edu.cn (T.H. Zhang).

http://dx.doi.org/10.1016/j.msea.2015.11.014
0921-5093/© 2015 Elsevier B.V. All rights reserved.

metallic glassy films were investigated in the present work. The minor Ti addition was confirmed to effectively increase free volume content while not changing the intrinsic parameters such as Poisson's ratio or elastic modulus [12]. The STZ volumes of both films were carefully estimated in nanoindentation based on a popular statistical method. Here, we aim to study the effect of Ti addition on creep deformation for further revealing the creep mechanism in metallic glasses.

2. Experimental procedures

The Cu–Zr–Al and Cu–Zr–Al–Ti thin films were deposited on clean silicon wafer in a DC magnetron sputtering system (Kurt J. Lesker PVD75) at room temperature in pure argon gas. The 2-in. alloy targets adopt in the chamber were $Cu_{45}Zr_{48}Al_7$ and $Cu_{45}Zr_{46}Al_7Ti_2$, respectively. The target is installed at the bottom while the silicon wafer is stick on the sample platform, which is right above the target. The target-to-substrate distance is kept constant, which is equal to 100 mm. The base pressure of the chamber was kept about $5*10^{-7}$ Torr before deposition and working argon pressure was set at about 1 mTorr. The power on the target was fixed at 180 W during the deposition and the sputtering time was for 1 h. The structures of both films were detected by X-ray diffraction (XRD, PANalytical X'Pert PRO) with Cu K_α radiation. The thicknesses of the as-deposited films were measured from cross-sections by scanning electron microscope (SEM, MOI-ZEISS). By means of X-ray energy dispersive spectrometer (EDS) attached on the SEM, the chemical compositions of both films can be accurately detected. The thermal properties of the samples (peeled from the substrate) were estimated using the differential scanning calorimetry (DSC, NETZSCH) with heating rate of 20 K/min.

The nanoindentation experiments were conducted at constant temperature of 20 °C on Agilent Nano Indenter G200 with a spherical indenter, with an effective radius of 3.15 µm upon calibrating on standard fused silica. The displacement and load resolutions of the machine are 0.01 nm and 50 nN, respectively. The as-deposited films could be directly applied on nanoindentation testing due to the ultralow roughness of metallic glassy film surface [19]. For the creep tests, a constant-load holding method was used, and the displacement of indenter into the surface at a prescribed load could be continuously recorded. The indenter was held for 500 s at maximum loads of 1 mN, 2 mN, 4 mN, 8 mN, 12 mN and 16 mN in both samples. The loading rate was a constant value, which was equal to 0.5 mN/s. The reliability of the creep results was confirmed by conducting ten independent measurements. The STZ volume was estimated by a statistical measurement, in which 64 loading tests were conducted on each sample. The loading rate and the maximum load were 0.5 mN/s and 15 mN, respectively. All the nanoindentation tests were carried out until thermal drift reduced to below 0.02 nm/s. Furthermore, drift correction which was calibrated at 10% of the maximum load during the unloading process would be strictly performed.

3. Results and discussion

The chemical compositions of the as-deposited films were $Cu_{44.3}Zr_{45.1}Al_{10.6}$ and $Cu_{44.2}Zr_{43}Al_{11.3}Ti_{1.5}$, which were much close to the target alloys. Each elements were uniformly distributed as shown in the layer probes in Supplementary material. Fig. 1 (a) shows the typical X-ray diffraction patterns of the as-prepared Cu–Zr–Al and Cu–Zr–Al–Ti films. It is clear that only a broad diffraction peak can be detected in each sample, which represents a

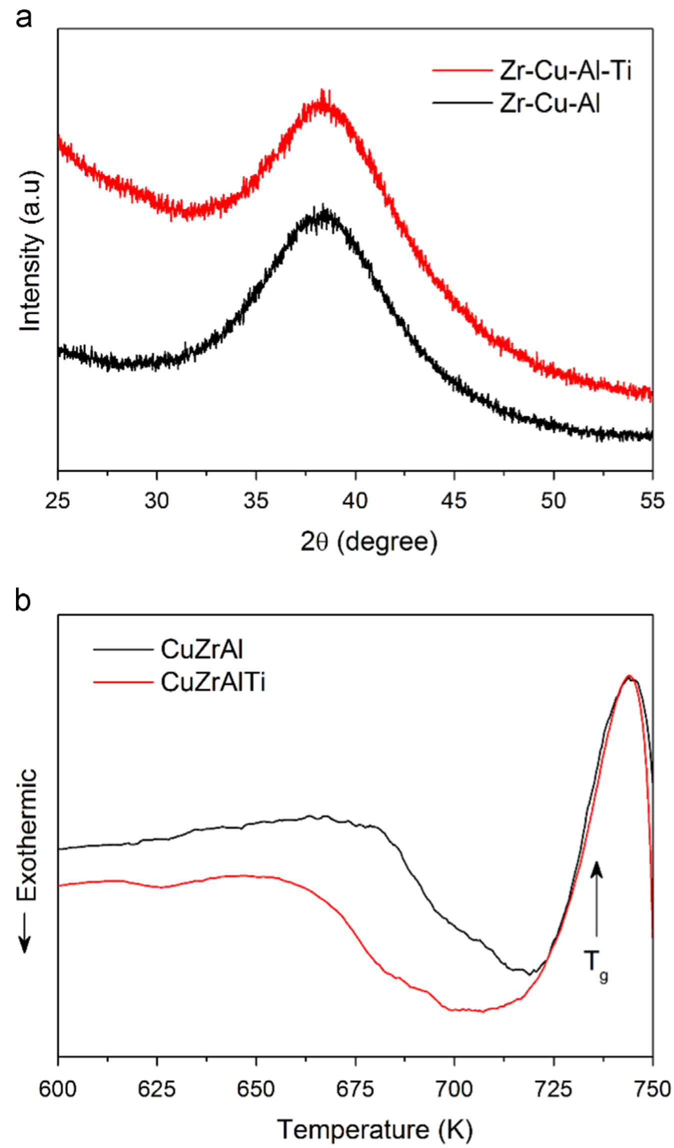

Fig. 1. (a) Typical XRD patterns and (b) the details of the sub-T_g regions for the DSC traces of the Cu–Zr–Al and Cu–Zr–Al–Ti films.

crystal-free structure. Fig. 1(b) shows an enlargement of the sub-T_g region for the DSC curves, which corresponds to the enthalpy released during structure relaxation and can be strongly linked with the free volume content. It clearly shows the structure relaxation process occurred more pronounced in the Cu–Zr–Al–Ti compared with the Cu–Zr–Al, confirming the effect of Ti addition on inducing large amount of free volume. Meanwhile, the glass transition temperature T_g of the films can be obviously observed at about 735 K, as the arrow indicates.

With cleavage cracking of the Si substrate by a diamond knife, a rapid tensile fracture occurs in the film. The thicknesses of Cu–Zr–Al and Cu–Zr–Al–Ti films can be directly measured to be about 1.60 µm and 1.48 µm, from cross-sections in Fig. 2. The thickness discrepancy between the two films could be largely induced by the external configurations, such as the thickness of target alloy, the intensity of magnetic core or the target-to-sample orientation. For the shear-dominated fracture in metallic glass, the final fracture surface usually consists of a smooth region caused by slid shear and a vein pattern region caused by subsequent crack. As shown in Fig. 2(a), a smooth region with width of 500–1000 nm and vein pattern with about 500 nm diameter can be observed in Cu–Zr–Al