Microindentation of a Zr$_{57}$Ti$_{15}$Cu$_{20}$Ni$_{8}$Al$_{10}$ Bulk Metallic Glass

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Using microindentation technique, the indentation behavior of a Zr$_{57}$Ti$_{15}$Cu$_{20}$Ni$_{8}$Al$_{10}$ bulk-metallic glass is studied over a range of the indentation load from 200 mN to 5000 mN. For the indentation load larger than 1000 mN, the indentation load-depth curves during unloading display three regions, a) a fast unloading phase at the onset of unloading, b) a linear phase at which the indentation load is proportional to the indentation depth, and c) a slow unloading phase after the linear phase. The size of the linear region increases with the increase in the indentation load, and the slope is independent of the indentation load. The indentation hardness decreases slightly with the increase in the indentation load. The plastic energy dissipated in an indentation cycle is proportional to the 3/2 power of the indentation load. The effect of the indentation loading rate on the indentation behavior is discussed. [doi:10.2320/matertrans.MJ200733]

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1. Introduction

Metallic glasses, which have unique mechanical properties, such as high yield stress and high ductility, were first discovered by Duwez in 1960.$^1$ The first Au-Si binary metallic glass was formed at a cooling rate of 10$^6$ K/s with a characteristic dimension of less than 100 μm. Recently, new techniques and compositions have made it possible to produce bulk metallic glasses (BMGs) with thickness greater than 10 mm at a cooling rate as low as 10 K/s.$^2$–$^8$ This has renewed interest in characterizing the mechanical properties of BMGs.$^9$–$^{21}$ In general, it is believed that the plastic deformation initiated in BMGs localizes in the narrow zones called shear bands$^9$ for high strain rates and low temperatures. Bei et al.$^9$ and Zhang et al.$^{10}$ investigated the effect of the length to diameter aspect ratio on the compression deformation of Zr-based BMGs. They suggested that specimens with low aspect ratios have higher ductility than those with high aspect ratios. Conner et al.$^{12}$ measured the mechanical and thermal properties of a Zr$_{57}$Nb$_{3}$Al$_{10}$-Cu$_{15}$-Ni$_{12}$ BMG with different oxygen contents. Wesseling et al.$^{13,14}$ assessed the mechanical behavior of Cu-based BMGs at elevated temperatures and observed significant softening near the glass-transition temperature ($T_g$).

Indentation test has recently been used to characterize mechanical properties of BMGs.$^{22}$–$^{28}$ The advantages of using the indentation test involve the use of a small amount of material and possibly evaluate the local behavior of heterogeneous materials. The presence of the serrated flow and the formation of shear bands underneath indents have been reported. Schuh and Nieh$^{23}$ observed the dependence of the serrated flow on the loading rate and suggested that the serrated flow in BMGs during indentation is associated with the activation of shear bands. Zhang et al.$^{24}$ revealed the formation of shear bands in a Zr-based BMG indented by a Vickers indenter and found the creation of secondary and tertiary shear bands inside the plastic zone when subjected to a high-indentation load. They developed a modified-expanding cavity model to determine the plastic zone size created by the shear bands. Su and Anand$^{25}$ examined the plane-strain indentation of a Zr-based BMG by a cylindrical indenter, in which they used a bonded-interface technique to assess the evolution of the shear-bands underneath the indentation. Murali and Ramamurty$^{26}$ studied the effect of sub-$T_g$ annealing on the embrittlement of a Zr$_{41.2}$Ti$_{37.5}$Cu$_{12.5}$-Ni$_{10}$Be$_{22.5}$ BMG, and they observed up to a 90% loss in the impact toughness and a relatively high indentation strain necessary for the initiation of shear bands in the annealed glass. They suggested that the reduction of the free volume during annealing is the reason for the embrittlement. Recently, Schuh and Nieh$^{27}$ summarized the indentation deformation of BMGs, including the role of shear bands, the measurement of hardness, structural changes underneath indentations, and rate-dependent effects. The review of literature indicates that the majority of work in the nano-indentation of BMGs has focused on the characterization of hardness and Young’s modulus and on the observation of serrated flow. Little work has paid attention to the energy dissipation in each indentation.

The purpose of this work is to study the indentation-deformation behavior of a Zr$_{57}$Ti$_{15}$Cu$_{20}$Ni$_{8}$Al$_{10}$ BMG, using a Vickers indenter. The indentation hardness is studied in order to assess the effects of the indentation load and indentation-loading rate. The dependence of the dissipated plastic energy on the indentation load is also analyzed.

2. Analysis of Indentation Behavior

It has been reported that metallic glasses do not obey either the Tresca or the von-Mises yield criterion.$^{29}$ Instead, metallic glasses exhibit some pressure or normal-stress dependence to the yield criterion, such as the Mohr-Coulomb criterion and the Drucker-Prager yield criterion, in which the pressure-dependent flow stress represents the effect of the excess free volume on plastic deformation of metallic glasses. Vaidyanathan et al.$^{28}$ used the Mohr-Coulomb criterion to simulate the indentation of Vitreloy 1$^{7}$ bulk metallic glass and observed that the simulation result was in agreement with the experimental data with the indentation load being proportional to the square of the indentation depth. Thus, it
would be reasonable to express the indentation load, $F$, as a power function of the indentation depth, $\delta$,

$$ F = K_m \delta^n $$

where $K_m$ is a constant related to the properties of the material and the geometry of the indenter, and $n$ is an exponent constant. Equation (1) gives the maximum indentation depth, $\delta_m$, as

$$ \delta_m = (F_m/K_m)^{1/n} $$

where $F_m$ is the peak indentation load. For a Vickers indentation, the relation between the diagonal size and the indentation load can be expressed as a Meyer line relation:

$$ \log F_m = m \log D + \log a $$

which gives

$$ D = (F_m/a)^{1/m} $$

Here $D$ is the diagonal length of the indentation mark, $m$ is the Meyer index, and $a$ is a constant. According to the principle of geometrical similarity, the residual indentation depth, $\delta_r$, is proportional to $D$. Using eq. (4), one obtains

$$ \delta_r = (F_m/K_r)^{1/m} $$

where $K_r$ is a constant, depending on the properties of the material.

For the Vickers indentation, the indentation hardness, $H_V$, can be calculated, using the following expression:

$$ H_V = 1.854F_m/D^2 $$

Substitution of eq. (4) into eq. (6) gives

$$ H_V = 1.854a^{2/m}F_m^{(m-2)/m} $$

The indentation hardness is a function of the Meyer index and becomes independent of the indentation load for $m = 2$.

During the indentation loading process, the total energy, $E_{total}$, given to a specimen can be calculated as:

$$ E_{total} = \int_0^{\delta_m} Fd\delta $$

which is represented as the area under the loading curve. Substituting eqs. (1 and 2) into eq. (8), one obtains the total energy as

$$ E_{total} = F_m^{(n+1)/n}/[(n + 1)K_m^{2/n}] $$

During the unloading process, the elastic recovery occurs and the elastic energy released, $E_{elastic}$, can be calculated by

$$ E_{elastic} = \int_{\delta_m}^{\delta_r} Fd\delta $$

Thus, the plastic energy dissipated during an indentation cycle is given by

$$ E_{plastic} = \int_0^{\delta_r} Fd\delta - \int_{\delta_m}^{\delta_r} Fd\delta $$

Based on experiment data, Menčík et al. and Cheng et al. give a linear relationship between the energy ratio, $E_{plastic}/E_{total}$, and the depth ratio, $\delta_r/\delta_m$, for $\delta_r/\delta_m > 0.4$. Blau et al. and Loubet et al. found that the energy ratio, $E_{plastic}/E_{total}$, is proportional to the depth ratio, $\delta_r/\delta_m$, in some materials. Here, we assume that the relationship between the energy ratio, $E_{plastic}/E_{total}$, and the depth ratio, $\delta_r/\delta_m$, can be expressed as

$$ \frac{E_{plastic}}{E_{total}} = A \frac{\delta_r}{\delta_m} $$

where $A$ is a constant. Substituting eqs. (2 and 5) into eq. (12), one obtains

$$ \frac{E_{plastic}}{E_{total}} = \frac{AK_r^{1/m}F_m^{(n-2)/m}}{K_m^{1/m}F_m^{(n-1)/m}} $$

The energy ratio is a function of the indentation load, as expected. For $n = m$, the energy ratio is independent of the indentation load, while it decreases with the increase in the indentation load for $n < m$. From eqs. (9 and 13), one obtains the dependence of the plastic energy on the indentation load as

$$ E_{plastic} = \frac{A}{(n + 1)K_r^{1/m}F_m^{(n+1)/m}} $$

3. Experimental

The BMG used in the experiments had a composition of Zr57Ti13Cu20Ni10 in atomic percent (at%). The ingots of the master alloy were prepared by arc-melting mixtures of pure Zr, Ti, Cu, Ni, and Al metals in a Ti-gettered high-purity argon atmosphere. A special Zr crystal rod was used to maintain the low-oxygen concentration of the alloy. The ingot alloys were remelted for several times to ensure homogeneity. The cast rod of 5 mm in diameter and 60 mm in length was made using a suction-casting method in an arc furnace via a pseudo-floating-melt state before casting to obtain a completely melted state. The samples were cut into a disk shape with a diameter of 5 mm and thickness of 1.5 mm. The samples were ground and polished to a mirror-like surface to avoid surface effects.

Microindentation tests were performed, using a Vickers indenter on a Micro-Combi Tester (CSM Instruments, Needham, MA). Indentations were made along a circle of 1.5 mm in radius over the surface of the sample. The indentation loads were ranged from 200 mN to 5000 mN. Prior to full indentation, a pre-load of 5 mN was applied to the indenter in order to maintain the contact between the indenter and the surface of the sample and to avoid the effect of impact. Both loading time and unloading time were set to be 30 s without intermediate holding at the peak load. The loading-unloading curves were recorded, from which the plastic energy dissipated in an indentation cycle was calculated. The sizes of the indentation marks were measured by an optical microscope to calculate the Vickers hardness. For the indentation load of 1500 mN, indentations of four different loading-unloading times, 10 s, 30 s, 60 s, and 120 s, were performed to investigate the effect of the loading rate on the indentation behavior, which respectively corresponded to the loading rate of 150 mN/s, 50 mN/s, 25 mN/s, and 12.5 mN/s.
4. Results and Discussion

4.1 Loading-unloading curves

Microindentation tests were carried out using constant loading and unloading rates over a load range from 200 mN to 5000 mN. Both loading and unloading times are 30 s. The typical loading-unloading curves are shown in Fig. 1 for the indentations of different peak indentation loads. The loading curves overlap, as expected. No serrated flow is observed from the loading curves under the indentation conditions. The unloading curve for the indentation load of 2500 mN displays three regions, a) a fast unloading phase at the beginning of the unloading, b) a linear phase at which the load is proportional to the indentation depth, and c) a slow unloading phase after the linear phase. It should be pointed out that the unloading curve displays the three regions only for the peak indentation load larger than 1000 mN. The mechanism for the presence of the linear unloading phase is unclear, which might be due to the competition between the unloading rate and the rate of elastoplastic recovery created by the severe plastic deformation underneath the indentation. Figure 2 shows the dependence of the length of the linear region on the indentation load.

The length of the linear region increases with the indentation load; and the slope of the linear region is \(0.69 \pm 0.04\) mN/nm, independent of the indentation load.

Figure 3 shows the dependences of the maximum indentation depth and residual depth on the indentation load. Using the curve fitting of eqs. (2 and 5), one obtains \(n = 1.43\), \(K_m = 8.36 \times 10^{-3}\), \(m = 1.95\) and \(K_v = 5.58 \times 10^{-4}\). The value of the exponential index, \(n\), is different from 2 obtained by using dimensional analyses for a geometrically similar indenter. This is because both the Tresca and the von-Mises criterions may not suit for the description of the plastic deformation in BMGs.

4.2 Indentation hardness

Figure 4 shows the effect of the indentation load on the diagonal length of the indentation mark. No shear bands and pile-up are observed over the surface of the specimen, which is different from the report...
on the nanoindentation of Zr-based BMGs. This might be due to the resolution of the light optical microscope. Atomic force microscopy is needed to reveal the pile-up or sink-in behavior at the indents. Using eq. (3) to fit the curve, one obtained $a = 3.842$ and the Meyer index of 1.95. The Meyer index is the same as that obtained from the residual indentation depth, which supports the proportionality between the residual depth and the size of the indentation mark as used in deriving eq. (5).

Using the constant, $a$, and the Meyer index into eq. (7), one obtains the dependence of the indentation hardness on the indentation load as

$$H_V = 7.32 F_m^{-0.0238}$$

Figure 5 shows the dependence of the indentation hardness on the indentation load. The indentation hardness starts at the value of 6.55 GPa for the indentation load of 200 mN and decreases slightly with the increase in the indentation load. For comparison, the results from eq. (15) are also depicted in Fig. 5. Obviously, the experimental results are self-consistent.

4.3 Plastic energy dissipated in the indentation

The plastic energy dissipated, $E_{plastic}$, in an indentation loading-unloading cycle is calculated from the area enclosed by the indentation load vs. indentation depth curve. The dependence of the energy ratio, $E_{plastic}/E_{total}$, on the depth ratio, $\delta_r/\delta_m$, is shown in Fig. 6. The energy ratio is proportional to the depth ratio, which supports our assumption of eq. (12). Using the least-squares curve fitting, one obtains the slope of $A = 1.06$ for eq. (12).

Using the parameter $n = 1.43$, $K_m = 8.36 \times 10^{-3}$, $m = 1.95$, $K_r = 5.58 \times 10^{-4}$ and $A = 1.06$ in eqs. (9 and 14), one obtains the dependence of the total energy and the plastic energy dissipated in an indentation on the indentation load as

$$E_{total} = 1.17 \times 10^{-5} \times F_m^{1.7}$$

$$E_{plastic} = 2.30 \times 10^{-5} \times F_m^{1.5}$$

In contrast to the power of 1.7 for the total energy given to the specimen, the plastic energy dissipated in the indentation is proportional to the 3/2 power of the indentation load. To our surprise, the power of 3/2 coincidently is the same as that derived from the dislocation dynamics for the indentation of metals, even though the defects in BMGs are excessive free volumes. Figure 7 shows the effect of the indentation load on the total energy and the plastic energy dissipated in the indentation on the indentation load as well as the calculated results from eqs. (16 and 17). Both energies increase with the increase in the indentation load and are consistent with the calculation results by using the indentation load and other experimental data. It should be pointed out that the analysis is phenomenological without considering the evolution of defects in BMGs, and eqs. (9 and 14) can be applied to both BMGs and metals. The analysis provides us a new approach to evaluate the important parameters, including the exponent, $n$, and the Meyer index, $m$, from the calculation of the total energy and the plastic energy dissipated in the indentation.

4.4 Effect of the indentation loading rate

To understand the effect of the indentation loading rate on the indentation behavior of the Zr$_{57}$Ti$_{15}$Cu$_{20}$Ni$_{8}$Al$_{10}$ BMG, indentations were performed using the indentation load of 1500 mN with different loading/unloading rates of 150
The indentation hardness decreased with the increase in the indentation load, which suggests the presence of the indentation-size effect in the Zr$_{57}$Ti$_3$Cu$_{20}$Ni$_8$Al$_{10}$ BMG and supports the analysis.

The plastic energy dissipated in the indentation of the Zr$_{57}$Ti$_3$Cu$_{20}$Ni$_8$Al$_{10}$ BMG was found to be proportional to the 3/2 power of the indentation load in agreement with the calculated results, using the indentation load, the exponential constant, $n$, and the Meyer index, $m$. The indentation-loading rate has no significant effect on the indentation deformation of the Zr$_{57}$Ti$_3$Cu$_{20}$Ni$_8$Al$_{10}$ BMG.

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