Homogeneous deformation of Au-based metallic glass micropillars in compression at elevated temperatures

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We performed high-temperature microcompression tests on micron-sized pillar samples fabricated from Au49Ag5.5Pd2.3Cu26.9Si16.3 metallic glass near the glass transition temperature to investigate the homogeneous deformation behavior. Samples were invariably deformed uniformly. The strength was observed to decrease with increasing temperature and decreasing strain rate. Plastic flow behavior can be described by a shear transition zone model. The activation energy and the size of the basic flow unit were both deduced and compared favorably with the theory. © 2009 American Institute of Physics. [DOI: 10.1063/1.3081111]

Bulk metallic glasses (BMGs) have unique mechanical properties, such as large elastic limits (2%), high strength at low temperatures (< ~0.87,Tg, where Tg is the glass transition temperature).1–4 However, plastic deformation of this class of materials is highly localized in shear bands, which usually propagate rapidly through the sample because of strain softening.5–7 At high temperatures (> ~0.75,Tg), BMGs deform in a homogeneous fashion and exhibit high deformability comparable to plastic materials,8,9 but with a significant reduction in flow stresses.10,11 Stress overshoot was often observed in BMGs deformed at high strain rates as a result of the creation of excessive free volume during deformation.12–14

Recently, room-temperature compression was carried out with micron-sized pillars fabricated from various BMGs to study the sample size effect.15–19 Localized shear was always revealed as the dominant deformation mode, except in samples with a diameter smaller than 440 nm.18 Strain bursts were observed in the stress-strain behavior as indications of localized shear. Deformation of micron-sized metallic glasses under uniaxial compression at high temperatures has not yet been performed. In the present letter, micropillar specimens fabricated initially from an Au-based BMG were tested in compression at high temperatures. The data were subsequently analyzed based on a shear transition zone (STZ) model. The selection of the Au-based BMG was mainly to minimize the oxidation effect at high temperatures.

The BMG material used in the present study was Au49Ag5.5Pd2.3Cu26.9Si16.3.20 Alloy rods of 3 mm diameter were prepared by arc melting and suction casting. X-ray diffraction and differential scanning calorimetry measurements were conducted on the cast rods and the amorphous nature was verified. The glass transition temperature, Tg, of this material is about 401 K.20 Micron-sized pillars with a diameter of about 3.7 μm and the sample aspect ratio of about 2.4 were machined from the cast rod using the dual focus ion beam system (FIB) of Seiko, SM13050 SE, following the method developed previously.15,21 A typical FIBed pillar, as shown in Fig. 1(a), is noted to be slightly tapered with a taper angle of about 2.5°.

High temperature microcompression tests were performed with a Hysitron Triboindenter under the displacement control mode using a flat punch, which was machined out of a standard Berkovich indenter with MACOR holder. The projected area of the tip of the punch is an equilateral triangle of 12 μm. Test samples attached with a thermal couple were glued on a thin atomic force microscope (AFM) specimen disk using a high temperature glue, and the disk assembly was further clamped onto the heating stage. After stabilizing at a prescribed temperature for at least 15 min, the indenter tip was moved onto the sample surface in AFM imaging mode so that the tip could also be heated and reach a steady-state temperature distribution. A temperature variation of <0.1 K within 15 min was achieved and thermal drift rate was also monitored before every experiment. Taking advantage of having a high yield strength, the position of the test BMG pillar was precisely located by AFM imaging in Hysitron Triboindenter using the same flat punch tip at high temperatures. A low set point force of 2 μN and slow scan frequency of 0.4 Hz were used during the AFM imaging. Once the test was ready, the flat punch began to compress without losing contact with the sample surface. This continuous contact between sample and punch results in a negligible temperature variation (<0.1 K) and low thermal drift rate (<1 nm/s).22 The load-displacement data were recorded during microcompression at 393.6–401.2 K. Constant displacement rate and displacement change tests were both performed at the nominal strain rates ranging from 10−3

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FIG. 1. SEM images of a typical Au-BMG micropillar (a) before and (b) after compression.

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TABLE I. Pillar sample height change and thermal drift in microcompression tests.

<table>
<thead>
<tr>
<th>Pillar</th>
<th>$H_1$ (μm)</th>
<th>$H_2$ (μm)</th>
<th>$\Delta H$ (μm)</th>
<th>$\Delta L$ (μm)</th>
<th>$t$ (s)</th>
<th>($\Delta H - \Delta L$)/$t$</th>
<th>Drift rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>8.762</td>
<td>7.936</td>
<td>0.826</td>
<td>0.737</td>
<td>114</td>
<td>0.78</td>
<td>0.82</td>
</tr>
<tr>
<td>P-2</td>
<td>8.849</td>
<td>7.789</td>
<td>1.060</td>
<td>1.045</td>
<td>97</td>
<td>0.91</td>
<td>0.22</td>
</tr>
<tr>
<td>P-3</td>
<td>8.885</td>
<td>7.633</td>
<td>1.198</td>
<td>1.126</td>
<td>79</td>
<td>0.91</td>
<td>0.56</td>
</tr>
<tr>
<td>P-4</td>
<td>9.01</td>
<td>7.812</td>
<td>1.198</td>
<td>1.126</td>
<td>79</td>
<td>0.91</td>
<td>0.22</td>
</tr>
<tr>
<td>P-5</td>
<td>8.195</td>
<td>7.073</td>
<td>1.092</td>
<td>1.062</td>
<td>41</td>
<td>0.73</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Each compression test took less than 100 s for an acceptable error from thermal drift (<10% for 1 μm total displacement).

The typical morphology of a compressed sample is shown in Fig. 1(b). It is apparent that the sample was deformed homogeneously. For easy discussion of mechanical analysis, the compressive displacement ($\Delta L$) recorded from load-displacement curves, as well as the time duration ($t$) and measured drift rate are all listed in Table I. The sample heights before ($H_1$) and after ($H_2$) each test were also measured from scanning electron microscopy (SEM) images and listed in Table I for a direct comparison. It is noted in the table that $\Delta H(=H_1 - H_2)$ is close to $\Delta L$ in all pillar samples, indicating that the strain contribution from the base of the pillar is insignificant. This is in contrast to the deformation of a pillar at room temperature, which often shows significant strain contribution from the pillar base. The difference is caused by the fact that metallic glasses have a high strain rate sensitivity value ($m$) at temperatures near the supercooled region. Thus, the pillar sample is preferentially deformed. It is also noted in Table I that the difference in the length change measured from SEM image and load-displacement curve [i.e., ($\Delta H - \Delta L$)] is comparable to the displacement error caused by thermal drift. This suggests that the strain measurement obtained directly from Hysitron Triboindenter is reliable.

Since the sample was homogeneously deformed, the load-displacement data were readily converted into true stress-strain curves in Fig. 2. As shown in the figure, the strength of the pillars is noted to increase with strain rate and decrease with temperature, and it is consistent with the results previously reported for high temperature nanoindentation on the same alloy. However, in contrast to the stress overshoot often observed in millimeter-size metallic glass samples deformed in the supercooled liquid region at high strain rates, stress overshoot is absent in the compression of the current microscale Au-BMG pillars. The absence of stress overshoot may be associated with the fact that strain rate is too low, thus free volume annihilation occurs too fast, or the response of the indenter is too slow to capture the strain rate change. There is also a possibility of the sample size, thus shear band length, effect. We will address this in the near future. In the present letter, we only focus on the steady-state viscous flow.

The existence of a steady state in stress-strain curves in Fig. 2 is usually regarded as a dynamic equilibrium between strain induced structure disorder (e.g., free volume creation) and structural relaxation (e.g., free volume annihilation). The steady-state flow stress against strain rate is plotted in Fig. 3 to elucidate the deformation mechanism in the current Au-based metallic glass at high temperatures. At low strain rates, the strain rate sensitivity ($m$) is about 0.87, which is close to that for a Newtonian flow ($m=1$ and is indicated in the figure for guidance) but gradually changes to non-Newtonian at high strain rates. This Newtonian to non-Newtonian transition was also observed previously in several other BMG systems.

Based upon a STZ model, the strain rate during homogeneous deformation of BMG can be described by

$$\dot{\varepsilon} = \alpha \varepsilon_0 \nu_G \exp\left(-\frac{\Delta F}{kT}\right) \sinh\left(\frac{\sigma V}{2\sqrt{3}kT}\right),$$

where $\dot{\varepsilon}$ is the strain rate, $\alpha$ is a temperature-dependent rate constant, $\varepsilon_0$ is the steady state fraction of matter capable of undergoing shear transformations, $\nu_G$ is the normal mode frequency of the flow unit along the activation path, $\nu_0 \nu_G$ is 1011 s⁻¹, $\Delta F/kT$ is its usual meaning, and $V$ is the activation volume ($V=\nu_0 \nu_G$, in which $\nu_0$ is the volume of a flow unit or STZ which undergoes a strain $\varepsilon_0$ [−0.125 (Refs. 10 and 28) during deformation]). The stress versus strain rate data in Fig. 3 can be fitted by Eq. (1) and plotted as solid lines at the three given temperatures. The fitting parameters, $\dot{\varepsilon}_r$, $V$, and $\nu_0$, are listed in Table II. The activation volume $V$ is about 43–62 Å³, which has a similar magnitude as reported in other BMG [60 Å³ for a Zr-BMG (Ref. 13) 105 Å³ for a Pd-BMG (Ref. 10)]. The volume of the basic flow unit (STZ) $\nu_0$ in this Au-BMG is then estimated to be 346–496 Å³. Since the present Au-BMG has a density of 13.72 g/cm³ and an atomic weight of 126.5 g/mol, the average atomic

FIG. 2. (Color online) True stress-strain curves from microcompression of Au-BMG pillars at high temperatures: (a) P-1 (constant strain rate: 10⁻³ s⁻¹), and (b) P-2 (strain rate change: 10⁻³−5×10⁻³ s⁻¹), P-3 (3×10⁻³−8×10⁻³−5×10⁻⁴ s⁻¹), P-4 (10⁻³−10⁻²−5×10⁻³), and P-5 (3×10⁻³−8×10⁻³ s⁻¹).

FIG. 3. (Color online) Stress vs strain rate for Au-BMG pillars at different temperatures with curves fitted by Eq. (1). The slope ($m=1$) is for eye guidance of Newtonian flow.
TABLE II. Fitted parameters in Eq. (1) from the results of micro-compression of Au-BMG pillars.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\varepsilon_T$ (s$^{-1}$)</th>
<th>$V$ (Å$^3$)</th>
<th>$V_0$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>393.6</td>
<td>0.0025 ± 0.0001</td>
<td>43 ± 2</td>
<td>344 ± 15</td>
</tr>
<tr>
<td>395.9</td>
<td>0.0026 ± 0.0001</td>
<td>55 ± 2</td>
<td>440 ± 15</td>
</tr>
<tr>
<td>401.2</td>
<td>0.0027 ± 0.0001</td>
<td>62 ± 2</td>
<td>496 ± 15</td>
</tr>
</tbody>
</table>

The volume of the basic flow unit during homogeneous deformation. Argon pointed out that STZ is in a disk shape during inhomogeneous deformation but is more reasonably in spherical shape during homogeneous deformation. Assuming a spherical shape, the radius of the sphere would be about 4.4–4.9 Å which is particularly noted to be similar to the radius where the second peak occurs in the pair distribution functions (PDF) in an amorphous Au–Si alloy (~5 Å) and that in other BMGs (4–6 Å). Since the peaks in PDF indicate the density fluctuation, or multirange order in glass, with the first one being the distance between two neighbor atoms, and the second peak being the smallest range order (e.g., STZ), the present result is consistent with the PDF measurements.

According to Argon’s model, the Helmholtz free energy barrier or the activation energy $\Delta F$ in Eq. (1) can be calculated by

$$\Delta F = \left[ \frac{7 - 5\nu}{30(1 - \nu)} + \frac{2(1 + \nu)}{9(1 - \nu)} \right] \mu V,$$

where $\nu=0.406$ is the Poisson's ratio for Au-BMG, $\sigma$ is the ideal shear resistance, $\mu$ is the shear modulus [26.45 GPa for Au-BMG (Ref. 20)], and $\sigma/\mu \approx 0.03$. Thus, the activation energy is theoretically estimated from Eq. (2) to be 80–114 kJ/mol. Using the fitted data in Table II, we can also experimentally estimate the Helmholtz free energy barrier for viscous flow from the pre-hyperbolic sine term $\varepsilon_T = \sigma V_0 c exp(-\Delta F/kT)$. It is about 102–104 kJ/mol, which agrees remarkably with the theoretical prediction.

In summary, we performed high temperature uniaxial compression tests on micron-sized pillars fabricated from an Au-based metallic glass. Homogeneous deformation of the Au$_{49}$Ag$_{5}$Pd$_{2}$Cu$_{26.5}$Si$_{16.5}$ glass alloy was observed and no stress overshoot was detected at 393.6–401.2 K. The strain rate sensitivity was 0.87 at a strain rate of $10^{-3}$ s$^{-1}$. The volume of the basic flow unit (STZ) was calculated to be 346–496 Å$^3$, equivalent to about 30 atoms. The Helmholtz free energy barrier was also estimated to be 80–114 kJ/mol, compared favorably with the theoretical prediction.

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