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On thermomechanical properties of Au–Ag–Pd–Cu–Si bulk metallic glass


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Abstract

The viscosity behavior and formability of the Au49Ag5.5Pd2.3Cu26.9Si16.3 bulk metallic glass within the supercooled liquid temperature region are examined using thermomechanical analyzer (TMA). The viscosity values of the Au-based BMG within 440–470 K lies within 2 × 1010–1 × 1018 Pa s, a reasonable viscosity level for macro- or micro-forming. The low working temperature of ∼450 K and the low working pressure less than 1 MPa, coupled with the sufficient hardness of ∼350 Hv, stress level of ∼1100 MPa, and anti-oxidation and anti-corrosion capability, would be highly promising for micro-forming or micro-imprinting for the micro-electro-mechanical systems.

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phases are present. In fact, as this amorphous alloy is crystallized upon annealing or severe forming, the major XRD crystalline peaks are due to Au₃Cu₈, plus some minor peaks due to AuCu₃. The selected area diffraction pattern (SADP) of the Au-based BMG, as shown in Fig. 1(b), shows a few light spots spreading around amorphous rings indicating that there are partial crystalline phases in the amorphous matrix. The crystalline phases are not discernible owing to the tiny crystalline phase in Fig. 1(b). The results of XRD and TEM are in consistent. Since the current paper is focused on the viscosity and forming aspects, the detailed microstructure characterization will be reported in another paper.

The thermal properties of the Au₄₉Ag₅₅Pd₂₃Cu₂₆.₉Si₁₆.₃ BMGs were determined by DSC with the heating rate of 0.67 K s⁻¹ (40 K min⁻¹), as shown in Fig. 2. The crystallization exothermic reactions for the Au₄₉Ag₅₅Pd₂₃Cu₂₆.₉Si₁₆.₃ BMGs in the DSC curves appear as one single peak, indicating one major phase was induced during DSC heating. The glass transition temperature (T_g), the onset crystallization temperature (T_x), the solidus temperature (T_m) and the liquidus temperature (T_l) are all marked by arrows in the DSC traces, which are 400, 450, 625 and 646 K, respectively. Meanwhile, the main criteria for glass forming ability of this alloy, such as ΔT_x (T_x − T_g), T_rg, γ[T_x/(T_x + T_l)] [12] and γ_m [(T_x − T_g)/T_l] [13,14], can be extracted from the about thermal properties of the alloy, these criteria are commonly adopted in the BMG circle. The values of ΔT_x and ΔT_m (T_l − T_m) are 50 and 21 K. The low glass transition temperature of 400 K (or 127 °C) is even lower than that for the Mg based BMGs (mostly around 410–420 K). The glass forming ability criteria, T_rg, γ and γ_m, for the current Au₄₉Ag₅₅Pd₂₃Cu₂₆.₉Si₁₆.₃ BMG at the heating rate of 0.67 K s⁻¹ are 0.619, 0.430 and 0.774, respectively. All of these values are higher compared with the Mg based BMG systems (with the γ and γ_m values of 0.414 and 0.730 [9,10]), suggesting that the current alloy does possess sufficiently high glass forming ability favorable for future application.

The micro-hardness is about 348 ± 10 in Hᵥ scale which is much higher than ordinary gold alloys. The compressive fracture stress and strain at 1 × 10⁻⁴ s⁻¹ are 1122 MPa and 2%, respectively. Probably due to the presence of partial nanocrystalline phase, the alloy still exhibits brittle nature at room temperature. Note that the hardness and stress level are both higher than the Mg₆₅Cu₂₅Gd₁₀ amorphous counterparts (267 Hᵥ [9] and 800–1000 MPa [15,16]).

3.2 Thermomechanical properties

Fig. 3 illustrates the typical TMA and differential thermo-mechanical analyzer (DTMA) curves under the heating condition measured at a low stress level of 7.1 kPa on the Au-based BMG.

The relationship among temperature, relative displacement, effective viscosity, and effective linear expansion coefficient were measured using a thermomechanical analyzer (TMA, PerkinElmer Diamond) under the isochronal (or non-isothermal) condition at a heating rate of 10 K min⁻¹ and a fixed compression load of 50 mN. The load was applied by a tip with a diameter of 3.8 mm. Temperature was calibrated by using pure In and Zn samples as standards. The diameter of the specimen is 3 mm with aspect ratio around 2. Displacement data under various pressures and temperatures were collected simultaneously upon heating.

3.1 Basic properties

The surface appearances of suction cast Au-based BMGs rods with different diameters all show lustrous and shining surface. This indicates that complete filling of the cavities was obtained during injection casting. Fig. 1(a) shows the XRD patterns of the Au₄₉Ag₅₅Pd₂₃Cu₂₆.₉Si₁₆.₃ alloy rods with diameters of 2 and 3 mm, consisting of a broad diffraction peak over the 2θ range from 30° to 50°, which shows the amorphous nature. However, the peaks are still somewhat sharper than other BMGs, suggesting that there are nano-crystalline phases dispersed in the amorphous matrix. The sharper peak at 2θ ~ 38–42° is consistent with the (1 1 1) peak for crystalline Au₃Cu (38.1° for this ordered face-centered cubic L₁₂ structure with α = 0.4048 Å) and the (1 1 1) peak for AuCu₃ (41.7° for this ordered face-centered cubic L₁₂ structure with α = 3.749 Å). The XRD result suggests that both the Au₃Cu and AuCu₃ nanocrystalline
The DTMA curve is obtained from the derivative of the displacement with respect to time. Note that applied stress in this study was rather low. Parallel research using higher stress levels in the range of 40–400 kPa also gives similar results. The viscosity and forming characteristics are not seen to be highly sensitive to the stress level over the low stress level less than 1 MPa. The homogeneous deformation of BMGs at elevated temperature can be described by a free-volume model developed by Spaepen [18] and Argon and Shi [19]. The stress–strain deformation mechanisms. The homogeneous deformation of BMGs can be simplified to

\[ \dot{\gamma} = 2 \exp \left( \frac{\beta v^*}{v_0} \right) \exp \left( -\frac{\Delta G_m}{kT} \right) \sinh \left( \frac{v_0^* T}{kT} \right) + A, \]

where \( \dot{\gamma} \) is the shear strain rate, \( \beta \) is a geometrical factor between 1 and 0.5, \( v^* \) is the effective hard-sphere size of the atom, \( v_0 \) is the average free volume of an atom, \( v_0 \) is the shear strain of a basic flow unit or shear transition zone (STZ), \( \Delta G_m \) is the volume of a flow unit, \( \Omega \) is the atomic volume, \( J \) is the atomic vibration frequency, \( \Delta G_m \) is the thermal activation energy, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature and \( r \) is the applied shear stress. Yang et al. [20] pointed out that Eq. (2), at low stresses and a fixed temperature, can be simplified to

\[ \ln(\dot{\gamma}) = \frac{v_0^*}{2kT} + \ln(\gamma_0 v_0) - \frac{\beta v^*}{v_0} - \frac{\Delta G_m(kT)}{kT} \]

which is a temperature dependent constant. It needs to be noted that the current BMG was conducted under the compressive mode. With the strain rate and the measured stress, the material constant \( \gamma_0 v_0 \) can be determined from the slope in Eq. (3), as shown in Fig. 5(a). Using \( \gamma_0 = 0.125 \) [21], the volume of a basic flow unit STZ during shear, \( v_0 \) is calculated to be 1.3 nm³. That is similar to the value, 1.25 nm³, calculated by Yang et al. [20] for the same Au based BMG by high-temperature nanoindentation experiments with loading rates ranging from 0.1 to 100 mN/s⁻¹. The 1.3 nm³ for STZ size can be calculated to correspond to about a cluster of 60 atoms, which is a reasonable size for STZ.

Besides, at low stresses and a fixed strain rate, Eq. (2) can also be simplified to

\[ \tau = BT + 2\frac{\Delta G_m}{\gamma_0 v_0}, \]

where \( B = (2k/\gamma_0 v_0)\ln(\dot{\gamma} - \ln(\gamma_0 v_0/\Omega^2) + (\beta v^* v_0)) \) is a strain rate dependent constant. The thermal activation energy of a sin-
Single STZ, $\Delta G^m$, can be determined from the intercept of the plot of Eq. (4), as shown in Fig. 5(b) for a representative strain rate of 0.15 s$^{-1}$. The extracted thermal activation energy $\Delta G^m$ for the Au-based BMG is 1.9 eV or 180 kJ mol$^{-1}$, somewhat lower than the extracted value by Yang et al. [20] for the same Au based BMG of about 3.2 eV or 308 kJ mol$^{-1}$. Nevertheless, both results suggest that the activation energy for STZ at elevated temperatures might only be slightly higher than or even compatible to the activation energies of single atom diffusion; the latter are also around 170–200 kJ mol$^{-1}$ for the major Au or Cu atoms in their crystalline structures [22].

Based on the analysis on the activation volume and activation energy of the STZ flow unit over the elevated temperatures, the extracted values of $v_0$ and $\Delta G^m$ are both within the reasonable region. This indirectly suggests that the deformation behavior can be characterized by the free-volume model.

4. Conclusions

(1) The $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ BMGs with different rod diameters from 2 to 3 mm were successfully fabricated by copper mold casting under an argon atmosphere. XRD and TEM results indicate the presence of some nanocrystalline phases in the amorphous matrix.

(2) For the thermal properties of the Au-based BMG, the value of supercooled liquid region $\Delta T_x$ is 50 K and the glass forming criterion values of $T_{fg}$, $\gamma$ and $\gamma_m$ are 0.619, 0.43 and 0.774, respectively. The current Au-based BMG shows better glass forming ability index than most Mg-based amorphous alloys.

(3) The micro-hardness $H_v$ of the current Au-based BMG is 350, which is much higher than pure gold (<50) and the Mg-based BMGs (~280). The Au-based BMG also exhibits compression stress and strain of 1122 MPa and 2%, respectively.

(4) The viscosity values of the Au-based BMG within 440–470 K lie within $2 \times 10^2$ and $1 \times 10^3$ Pa s, a reasonable viscosity level for macro- or micro-forming. The low working temperature of ~450 K (or 177 °C) and the low working pressure (in kPa scale), coupled with the anti-oxidation and anti-corrosion capability, would be highly welcome by the MEMS industry.

(5) Within the viscous flow region, the volume of a basic flow unit STZ during shear, $v_0$, is calculated to be 1.29 nm$^3$. And the thermal activation energy of a single STZ, $\Delta G^m$, is extracted to be 1.9 eV (or 180 kJ mol$^{-1}$).

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References