Glass-Forming Ability and Properties of New Au-Based Glassy Alloys with Low Au Concentrations

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Au₄₀Si₁₇₋₂₀Cu₂₈₋₃₀Ag₅₋₇Pd₅ glassy alloys showed a wide supercooled liquid region of 42–53 K and a large reduced glass transition temperature of 0.568–0.605, indicating high stabilization of supercooled liquid and high glass-forming ability (GFA). The best GFA was obtained from Au₄₀Si₂₀Cu₂₈Ag₇Pd₅ alloy, and a fully glassy sample with a diameter of 6 mm could be fabricated by copper mold casting. The bulk glassy alloys exhibited very low T_g of 400–424 K, high fracture strength of over 1100 MPa, and corrosion resistance superior to SUS316L in 1 N H₂SO₄ solution. [doi:10.2320/matertrans.ME200809]

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1. Introduction

Since the synthesis of bulk glassy alloys (BGAs) in multi-component Ln⁻¹ (Ln: lanthanide metal) and Mg⁻² based alloys by copper mold casting in 1989, much effort has been devoted to the development of a new BGA exhibiting high glass-forming ability (GFA) and other useful engineering properties. As a result, BGA systems have been widely extended to Zr-,³⁻⁵ Fe-,⁶ Pd-,⁷ Ti-,⁸ Co-,⁹ Ni-,¹⁰⁻¹² Cu-,¹³⁻¹⁵ Pt-,¹⁶ and Au-¹⁷ based alloys. These BGAs are expected to be useful in a wide variety of applications, because they exhibit unique properties such as high strength, high elastic strain limit, high hardness, good soft magnetic properties, viscous flow workability in the supercooled liquid region, homogeneity on the nanometer scale, and excellent corrosion resistance.^{18,19} For practical applications, BGA requirements include high GFA, good mechanical properties, high corrosion resistance, and low cost.

Recently, Schroers *et al.*¹⁷ reported that the Au-based glassy alloys exhibited high GFA (maximum sample thickness of 5 mm), very low glass transition temperature (T_g) of about 400 K, large supercooled liquid region ($\Delta T_x = T_x - T_g$, T_x : crystallization temperature) of over 50 K, and good processability. This combination of properties makes the alloys attractive for many applications, including electronic, medical, dental, surface coating, and superplastic formation. However, the alloys contained about 50 at% Au, leading to a high material cost. In addition, little is known about the mechanical properties or corrosion resistance of the Au-based BGAs. For broader engineering applications, as well as further scientific studies on the Au-based glassy alloys, it is important to reduce the Au content in the BGAs without detrimentally affecting their unique properties, and also to clarify their mechanical properties and corrosion resistance. In this paper, we report the formation, thermal stability of supercooled liquid, mechanical properties, and corrosion resistance of new Au-based BGAs with 40 at% Au content in the Au-Si-Cu-Ag-Pd system.

2. Experimental Procedure

Alloy ingots were prepared by arc melting mixtures of Au, Cu, Ag, Pd and Si with purities of over 99.5 mass% in an argon atmosphere. The alloy ingots were re-melted four times to ensure chemical homogeneity. The mass losses were measured for each ingot after melting and were less than 0.1 mass%. The glassy alloy was produced by copper mold casting for bulk cylindrical rods with diameters of 2 to 8 mm. The thermal stability of the glassy alloy was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Mechanical properties were measured with an Instron testing machine. The gauge dimension of specimens was 2 mm in diameter and 4 mm in height for compressive test and the strain rate was $5 \times 10^{-4} \text{ s}^{-1}$. The fracture surface was examined by SEM. Corrosion resistance was evaluated by electrochemical measurements in 1 N H₂SO₄ solution open to air at room temperature. Electrochemical measurements were conducted in a three-electrode cell using a platinum counter electrode and an Ag/AgCl reference electrode. Potentiodynamic polarization curves were measured at a potential sweep rate of 50 mV·min⁻¹ after open-circuit immersion for about 20 min when the open-circuit potential became almost steady.

3. Results and Discussion

For developing new Au-based BGAs with lower Au contents, we first examined the effect of substitution Cu for Au on the stability of supercooled liquid and GFA of a Au-Si-Cu-Ag-Pd alloy with 50 at% Au. Figure 1 shows DSC curves of the melt-spun Au_{50-x}Si₁₇Cu_{23+x}Ag₅Pd₅ ($x = 0$ to 15) glassy alloys. It is seen that the T_g increases gradually from 404 to 440 K with decreasing Au content from 50 to 35 at%, while ΔT_x increases from 47 to 59 K with increasing x from 0 to 5 and then decreases to 32 K with a further increase in x to 15. On the other hand, as the Au content decreases, the liquidus temperature (T_l) increases, and multiple endothermic events are observed, indicating that this alloy series go far from the eutectic composition. Table 1 lists the thermal parameters and the critical diameters (d_c) of

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Fig. 1 DSC curves of melt-spun $\text{Au}_{50-x}\text{Si}_{17}\text{Cu}_{23+x}\text{Ag}_5\text{Pd}_5$ ($x = 0$ to 15) glassy alloys.

Fig. 2 DSC curves of melt-spun $\text{Au}_{40}\text{Si}_{55-x-y}\text{Cu}_x\text{Ag}_7\text{Pd}_5$ ($x = 30-33$, $y = 5$ and 7) glassy alloys.

Table 1 The thermal parameters and the critical diameters of newly developed Au-based BGAs with lower Au contents.

Composition (at%)	T_g (K)	T_x (K)	ΔT_x (K)	T_l (K)	T_{rg}	d_c (mm)
$\text{Au}_{50}\text{Si}_{17}\text{Cu}_{23}\text{Ag}_5\text{Pd}_5$	404	451	47	662	0.610	—
$\text{Au}_{45}\text{Si}_{17}\text{Cu}_{28}\text{Ag}_5\text{Pd}_5$	413	472	59	677	0.610	>3
$\text{Au}_{40}\text{Si}_{17}\text{Cu}_{33}\text{Ag}_5\text{Pd}_5$	419	470	51	716	0.585	2
$\text{Au}_{35}\text{Si}_{17}\text{Cu}_{38}\text{Ag}_5\text{Pd}_5$	440	472	32	774	0.568	<2
$\text{Au}_{40}\text{Si}_{20}\text{Cu}_{30}\text{Ag}_5\text{Pd}_5$	400	442	42	683	0.586	3
$\text{Au}_{40}\text{Si}_{17}\text{Cu}_{31}\text{Ag}_7\text{Pd}_5$	424	477	53	703	0.603	4
$\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$	409	456	47	676	0.605	6

newly developed Au-based BGAs with lower Au contents. It is recognized that the reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_l$) decreases gradually from 0.610 to 0.568 with decreasing Au content from 50 to 35, leading to the decrease in GFA. However, the alloy with 40 at% Au possesses sufficient GFA to form a bulk glassy sample with a diameter of 2 mm.

We further optimized the Au-based alloys with 40 at% Au for increasing the GFA, and found that the stabilization of supercooled liquid and GFA can be enhanced with small adjustment in $\text{Au}_{40}\text{Si}_{17}\text{Cu}_{33}\text{Ag}_5\text{Pd}_5$ composition. Figure 2 shows DSC curves of melt-spun $\text{Au}_{40}\text{Si}_{55-x-y}\text{Cu}_x\text{Ag}_7\text{Pd}_5$ ($x = 30-33$, $y = 5$ and 7) alloys. Compared to $\text{Au}_{40}\text{Cu}_{33}\text{Si}_{17}\text{Ag}_5\text{Pd}_5$, the alloy with $x = 28$ and $y = 7$ shows a lower T_g of 400 K, and the alloy with $x = 31$ and $y = 7$ shows a larger ΔT_x of 53 K, which are similar to those of $\text{Au}_{49}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Cu}_{26.9}\text{Si}_{16.3}$ glassy alloy.¹⁷⁾ In addition, all the alloys exhibit lower T_l , resulting in larger T_{rg} . The glassy alloy samples with diameters of over 3 mm (see Table 1) were prepared, and the best GFA was achieved for $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ alloy, which had a d_c of 6 mm.

Fig. 3 X-ray diffraction patterns of as-cast $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ alloy rods with diameter of 5 and 6 mm.

Figure 3 shows the X-ray diffraction patterns of the as-cast $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ alloy rods with diameters of 5 and 6 mm. All XRD patterns consist of only broad peaks, and no diffraction peak corresponding to a crystalline phase is seen,

Fig. 4 Compressive stress-strain curves of as-cast $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ and $\text{Au}_{40}\text{Si}_{17}\text{Cu}_{33}\text{Ag}_5\text{Pd}_5$ glassy alloy rods with a diameter of 2 mm.

Fig. 6 Potentiodynamic polarization curves of $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ glassy alloy in 1 N H_2SO_4 solution open to air at 298 K. The data of the SUS316L stainless steel are also shown for comparison.

Fig. 5 Fracture surface appearance of the as-cast $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ glassy alloy rod with a diameter of 2 mm.

indicating that the alloy rods are full glassy. Its GFA is higher than the previous data.¹⁷⁾ It has been noticed that the best GFA of the present $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ alloy composition is closed to a deep eutectic point (see Fig. 2). From a kinetic point of view, there are multiple ordered phases competing with each other for eutectic alloys in multi-component system, and the crystallization of the liquid requires simultaneous rearrangements of different species of atoms, which significantly suppress the kinetics of the crystallization process and thus promote glass formation.²⁰⁾ In addition, a high T_{rg} above 0.60 implies that the viscosity of the supercooled liquid increases rapidly with decreasing temperature, leading to easy solidification of the supercooled liquid into a glassy solid state under the suppression of the crystallization reaction.¹⁸⁾

Figure 4 shows compressive stress-strain curves of the $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ and $\text{Au}_{40}\text{Si}_{17}\text{Cu}_{33}\text{Ag}_5\text{Pd}_5$ BGAs. The glassy alloys exhibit good mechanical properties, i.e., compressive fracture strength, Young's modulus and Vickers hardness are 1120 MPa, 75 GPa and 340, respectively, for the

former, and 1220 MPa, 78 GPa and 355, respectively, for the latter. Although no distinct plastic strain is observed, the fracture of the samples occurred along the maximum shear stress plane, which is declined by about 45 degrees to the direction of applied load (see Fig. 5(a)), and the fracture surface consists mainly of a well-developed vein pattern typical to other BGAs with good toughness (see Fig. 5(b)).²¹⁾

Figure 6 shows the potentiodynamic polarization curves of the $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ glassy rod with a diameter of 2 mm in 1 N H_2SO_4 solution open to air at 298 K. The data of a SUS316L stainless steel sample are shown for comparison. The present BGA begins with a small active dissolution, followed by a passivation process with a very low passive current density of the order of 10^{-2} A m^{-2} . After the passivation, we can observe that the secondary passive region with a short potential domain occurs with further increasing applied potential. In addition, the $\text{Au}_{40}\text{Si}_{20}\text{Cu}_{28}\text{Ag}_7\text{Pd}_5$ glassy alloy shows much lower anodic current density than SUS316L stainless steel in the entire potential scheme, although the SUS316L is spontaneously passivated

in this solution. As a result, the new Au-based BGA exhibits excellent corrosion resistance in 1 N H₂SO₄ solution and its corrosion resistance is much better than that of the SUS316L.

4. Conclusions

The new series of Au-based BGAs with low Au concentrations had large ΔT_x of 42–53 K, low T_g of 400–424 K and a critical sample diameter range of 2–6 mm. The best GFA appeared around Au₄₀Si₂₀Cu₂₈Ag₇Pd₅ alloy, which is close to a deep eutectic point in the multi-component system. The Au-based BGAs also exhibited high fracture strength of over 1100 MPa, and good corrosion resistance, superior to that of SUS316L in 1 N H₂SO₄ solution. The high GFA, high stabilization of supercooled liquid, low glass transition temperature, good mechanical properties, and high corrosion resistance give the new glassy alloy excellent potential for future scientific and engineering applications.

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