Effect of Minor Au Addition on Glass-Forming Ability and Mechanical Properties of Pd–Cu–Au–Si–P Alloys

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The glass-forming ability (GFA), thermal stability and mechanical properties of bulk glassy Pd$_79$Cu$_6$Au$_{10}$Si$_{10}$P$_3$ ($x = 0$–6 at%) alloys were studied. The results revealed that the minor substitution of Au for Cu strongly affects the thermal stability and GFA of Pd–Cu–Au–Si–P alloys. The alloy in which 2 at% Au was added to substitute Cu (Pd$_{79}$Cu$_4$Au$_{10}$Si$_{10}$P$_3$) exhibits the broadest supercooled liquid region ($\Delta T_x = 80$ K) and possesses the highest GFA among the alloys investigated. The critical diameter for glass formation of this alloy reaches ~7 mm by copper mold casting. The GFA is dramatically reduced when the Au content is more than 5 at%, beyond which no bulk glasses could be formed. The Young’s modulus, yield strength and maximum compressive strength of the best glass former (Pd$_{79}$Cu$_4$Au$_{10}$Si$_{10}$P$_3$) are 87 GPa, 1525 MPa and 1660 MPa, respectively, with a compressive plastic strain over 13%.

1. Introduction

Noble metal-metalloid type metallic glasses have drawn great interest for a long time because of their excellent glass-forming ability (GFA) and good mechanical and chemical properties.1) They are of interest for fundamental scientific investigations and some technological applications.2) Several noble metal-metalloid bulk glasses have been synthesized, e.g., Pd–Cu–Si, Pt–Ni–P, Pd–Ni–P, Pd–Cu–Ni–P, Pt–Cu–P, and Pt–Co–Ni–Cu–P.3–10) These glassy alloys generally contain 20 at% of one, or a combination of the metalloids (Si or P). These metalloids lead to the production of hard and brittle alloys due to the formation of covalent bonds.1) Recently, Pd-based bulk metallic glasses (BMGs) with reduced metalloid content were synthesized in the Pd–Cu–Si–P system. The typical composition is Pd$_{79}$Cu$_6$Si$_{10}$P$_3$, which can be cast into fully amorphous products with a diameter of up to 5 mm by copper mold casting.11) This alloy contains increased amount of the noble element (Pd) and can subject to considerably large plastic deformation (~3.5%) in comparison with the famous Pd$_{79}$Cu$_3$Si$_{10}$P$_2$ glassy alloy (~0%),12) which has been exploited for electrode and jewelry applications.2) In this paper, we have investigated the substitution of Au for a portion of Cu in the Pd$_{79}$Cu$_6$Si$_{10}$P$_3$ alloy in order to further improve its GFA and mechanical behavior.

Experimental observations of atomic size distribution of many BMGs suggest that amorphous alloys typically have at least one alloying element with a larger atomic radius and at least one alloying element with a smaller radius, both relative to the base element.13–15) For the multi-component Pd$_{79}$Cu$_6$Si$_{10}$P$_3$ alloy, the atomic radii of the constituent elements are in the order of Pd (0.137 nm) > Cu (0.128 nm) > Si (0.117 nm) > P (0.109 nm).16) It has a great probability that the addition of a proper alloying element with a larger atomic size compared to the base element, Pd, to the Pd$_{79}$Cu$_6$Si$_{10}$P$_3$ alloy should improve its GFA. Au and Cu are in the same group (IB) in the periodic table, while Au has an atomic radius 0.144 nm, larger than that of Pd. Therefore, it is reasonably expected that addition of Au could improve the GFA. By fixing the Pd, Si and P concentrations and substituting appropriate amounts of Au for Cu in Pd$_{79}$Cu$_6$Si$_{10}$P$_3$, we have developed new high GFA alloys in a multi-component Pd–Cu–Au–Si–P system. Glassy alloy rods as large as 7 mm in diameter have been produced by copper mold casting. This paper aims to present the thermal and mechanical properties of the new glassy alloy and to discuss the origin of the high GFA of the multi-component alloy.

2. Experimental Procedures

Multicomponent alloys with nominal compositions of Pd$_{79}$Cu$_{6-x}$Au$_x$Si$_{10}$P$_3$ ($x = 0$–6 at%) were prepared by induction melting the mixture of pure elements of Pd, Cu, Au, Si and P in an Ar atmosphere. The weight loss of ingots was measured to be less than 0.1 mass%. It is therefore judged that the compositions of the ingots are very close to the designed compositions. From the alloy ingots, ribbon samples with a cross section of 0.02 × 1 mm$^2$ were prepared by a single-roller melt-spinning technique in an argon atmosphere. Cylindrical rods with diameters up to 8 mm were produced by copper mold casting. The structure of the ribbon and rod samples was examined by X-ray diffraction (XRD) using Cu Kα radiation. The thermal characteristics (glass transition temperature, $T_g$, and crystallization temperature, $T_c$, as well as supercooled liquid region, $\Delta T_g = T_g - T_f$) were measured at a heating rate of 0.67 K s$^{-1}$ with a differential scanning calorimeter (DSC). Mechanical properties under uni-axial compression were examined at a strain rate of 4.1 × 10$^{-4}$ s$^{-1}$ with an Instron load frame. The glassy alloy rods for the compression test were 2 mm in diameter and 4 mm in height. Prior to the compression test, both the top and the bottom of the specimens were examined with XRD to rule out crystallization. The fracture surface was observed by scanning electron microscopy (SEM).

3. Results

Figure 1 shows the DSC curves of the Pd$_{79}$Cu$_{6-x}$Au$_x$Si$_{10}$P$_3$ ($x = 0$–6 at%) glassy alloy ribbons. As the
increased Au affects the thermal stability of the supercooled liquids. With further increase in Au, maximum of 80 K at 2 at% Au, and then decreases slightly as the calculated critical cooling rate ($R_c$) of Pd$_{79}$Cu$_{6-x}$Au$_x$Si$_{10}$P$_5$ (x = 0–6 at%) alloys.

Table 1 Some thermal parameters and the critical diameters ($t_{max}$) as well as the calculated critical cooling rate ($R_c$) of Pd$_{79}$Cu$_{6-x}$Au$_x$Si$_{10}$P$_5$ (x = 0–6 at%) alloys.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$t_{max}$ (mm)</th>
<th>$R_c$ (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{79}$Cu$</em>{6}$Si$_{10}$P$_5$</td>
<td>615</td>
<td>685</td>
<td>70</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>Pd$<em>{79}$Cu$</em>{5}$Au$<em>2$Si$</em>{10}$P$_5$</td>
<td>626</td>
<td>694</td>
<td>68</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pd$<em>{79}$Cu$</em>{4}$Au$<em>2$Si$</em>{10}$P$_5$</td>
<td>617</td>
<td>697</td>
<td>80</td>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td>Pd$<em>{79}$Cu$</em>{3}$Au$<em>2$Si$</em>{10}$P$_5$</td>
<td>620</td>
<td>674</td>
<td>54</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pd$<em>{79}$Cu$</em>{2}$Au$<em>2$Si$</em>{10}$P$_5$</td>
<td>617</td>
<td>665</td>
<td>48</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>Pd$_{79}$Cu$_1$Au$<em>2$Si$</em>{10}$P$_5$</td>
<td>621</td>
<td>663</td>
<td>42</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pd$_{79}$Au$<em>6$Si$</em>{10}$P$_5$</td>
<td>616</td>
<td>638</td>
<td>22</td>
<td>—</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

temperature ramps up, all samples exhibit glass transition, followed first by a wide supercooled liquid region ($\Delta T_x = T_x - T_g$) and then by crystallization. The $T_g$, $T_x$, and $\Delta T_x$ derived from the DSC curves are summarized in Table 1. It is evident that the substitution of Au for Cu greatly affects the thermal stability of the supercooled liquids. With increased Au $\Delta T_x$ increases and eventually reaches the maximum of 80 K at 2 at% Au, and then decreases slightly with further increase in Au.

A large value of $\Delta T_x$ generally implies a high GFA because the supercooled liquid can steadily exist in a wide temperature interval without crystallization and has a high resistance against the nucleation of crystalline phases. It is expected that the Pd$_{79}$Cu$_4$Au$_2$Si$_{10}$P$_5$ alloy with the largest $\Delta T_x$ possesses relatively high GFA. Cylindrical rods with various diameters (up to 8 mm) were produced for this alloy by copper mold casting. Figure 2 shows a rod of the Pd$_{79}$Cu$_4$Au$_2$Si$_{10}$P$_5$ with a diameter of 7 mm. The surface of the cast rod is smooth, with no evidence of concavity or porosity. Figure 3 presents the XRD results of the 7 mm cast rod along with the data of the 8 mm rod. The XRD of the 7 mm rod exhibits a principal hump, with no peaks corresponding to any crystalline phase, indicating its amorphous nature. The XRD of the 8 mm rod shows some crystalline peaks on the broad diffraction background. The complete amorphous nature of the Pd$_{79}$Cu$_4$Au$_2$Si$_{10}$P$_5$ rod (diameter 2 to 7 mm) was confirmed by comparing their DSC curves with that of the corresponding melt spun ribbon as shown in Fig. 4. It is noticed that there is no distinct difference in the $T_g$, $T_x$ and the exothermal peak of crystallization among the bulk and ribbon samples. Therefore, it is concluded that the critical diameter ($t_{max}$) for glass formation for the Pd$_{79}$Cu$_4$Au$_2$Si$_{10}$P$_5$ alloy is estimated to be 7 mm in the case of copper mold casting, larger than that of the Au-free Pd$_{79}$Cu$_4$Au$_2$Si$_{10}$P$_5$ alloy. The critical cooling rate for glass formation ($R_c$) of the Pd$_{79}$Cu$_4$Au$_2$Si$_{10}$P$_5$ alloy is evaluated to be 20 K s$^{-1}$ by $R_c = 10 \cdot t_{max}^{-2}$ (where the unite of $t_{max}$ is cm). The $t_{max}$ and the calculated $R_c$ of the studied
alloy rods with 2 mm in diameter. The data of the Pd$_{79}$Cu$_{4}$Au$_{2}$Si$_{10}$P$_{5}$ alloys are also summarized in Table 1. It is clear that the Pd$_{79}$Cu$_{4}$Au$_{2}$Si$_{10}$P$_{5}$ alloy possesses the highest GFA in the present alloy system.

Figure 5 shows a compressive engineering stress-engineering stain curve of the bulk glassy Pd$_{79}$Cu$_{4}$Au$_{2}$Si$_{10}$P$_{5}$ alloy rods with 2 mm in diameter. The data of the Pd$_{79}$Cu$_{4}$Au$_{2}$Si$_{10}$P$_{5}$ alloys is also included for comparison. Note that the compression test was stopped when the plastic strain is beyond 3.5%, but the fractured segments of the glassy Pd$_{79}$Cu$_{4}$Au$_{2}$Si$_{10}$P$_{5}$ alloy after compression were jointed together after the test and could not be easily detached. Figure 6 displays the side appearance of the jointed segments. It is clear that the failure takes place along the maximum shear stress plane, which is inclined by about 45-degree to the loading axis. There appears a large step caused by the relative sliding of the two segments on the main shear band, suggesting highly localized shearing in the specimen.

4. Discussion

We have reported a number of interesting observation in this work. The most notable is that the GFA is significantly enhanced by a minor substitution of Au for Cu (2 at%) in the Pd$_{79}$Cu$_{6}$Si$_{10}$P$_{5}$ alloy. As a result of this substitution, the critical thickness increases from 1.5 to 12 mm by adding only 2 at% Er to Fe–Cr–Mo–C–B$^{(19)}$ (Fe$_{48}$Cr$_{15}$–Mo$_{14}$C$_{15}$B$_{5}$Er$_{2}$), and from less than 7 to 12 mm by adding 1.5 at% Y to Fe–Cr–Co–Mo–Nn–C–B$^{(20)}$ ((Fe$_{54.3}$Cr$_{15.5}$Co$_{5}$–Mo$_{12.8}$Mn$_{11.2}$C$_{15.8}$B$_{5.9}$)98.5Y$_{1.5}$). Another example is the critical thickness increase from 2.2 mm for the Si-free alloy (Ti$_{32.5}$Zr$_{23.5}$Hf$_{3}$Cu$_{22.5}$Ni$_{7.5}$) to 5 mm for the 1% Si-modified alloy (Ti$_{31.5}$Zr$_{23.5}$Hf$_{3}$Cu$_{22.5}$Ni$_{7.5}$)$.^{21}$ Several mechanisms may contribute to the superior GFA of the minor alloying modified glass formers. It has been suggested that the remarkable enhancement in GFA originates from the intrinsic role of the minor alloying elements (Y, Er, Si etc.), i.e. destabilizing the competing crystalline phase and stabilizing the liquid phase.$^{22,23}$ It has also been proposed that the
alloying elements, such as Y, Er and Si, may also act as an oxygen scavenger, which leads to the suppression of heterogeneous nucleation and improve the GFA.

It is well known that Au has high oxidization resistance, and there is no report about Au as an oxygen scavenger. In this study we believe that the origin for the enhancement of GFA by the minor Au addition is that the small amount of Au may facilitate the formation of a new local atomic structure favoring the supercooled liquid, and as such, dramatically enhances the GFA.

As mentioned in the introduction section, amorphous alloys typically have at least one alloying element with a larger atomic radius than that of the base element. Clearly, Au is the only one element with a larger atomic radius than that of the base element (Pd). On the other hand, the heats of mixing of the pairs Au–Si, Au–P, Au–Pd and Au–Cu are −13, −5, 0 and −9 kJ/mol, respectively. This topological and energetics (thermodynamic) information points to a high degree of dense random packing structure in the supercooled liquid. It may result in high liquid/solid interfacial energies and low atomic mobilities, and consequently retard the nucleation of crystalline phases and hence a high GFA. Obviously, as to the details of how the atomic structure is changed by the small addition of Au, further effort is needed.

The other interesting result is the significantly beneficial effect of Au addition on the plastic deformation of the studied alloy. The ultimate plastic strain increases from 3.5% for the Pd$_79$Cu$_{10}$P$_5$ alloy to 13% for the Au-modified Pd$_79$Cu$_7$-Au$_3$Si$_{10}$P$_3$ alloy. Recently, Schroers et al. reported that bulk glassy alloy P$_{57.5}$Cu$_{14.7}$Ni$_{11.3}$P$_{22.5}$ exhibits a plastic strain to failure of 20% in compression. The large ductility is a consequence of the formation of a high density of shear bands. In the present study, as shown in Fig. 6, the density of shear bands is not high, but a large step caused by the relative sliding of the two segments on the main shear band is seen. It is indicative of highly localized shearing in the specimen subject to compressive straining. It should be of interest as to the reason for the highly localized shear deformation, and yet the sample did not failed into pieces. It is known that two mechanisms of free volume and adiabatic heating are generally used to explain the formation and development of shear bands. Both the free volume and adiabatic heating cause the decrease in viscosity of materials in shear bands. The difference in the localized shear deformation behavior for the Au-free and Au-containing glassy alloys may be reflected in part by the difference in the free volume and adiabatic heating behavior of the two glassy alloys. It should be further elaborated to clarify the underlying mechanism responsible for the experimental observations. The corresponding investigation of the glassy Pd–Cu–Au–Si–P system alloys is under way in this lab.

5. Conclusions

The strong effect of Au replacement for 0–6 at% Cu in the Pd$_{79}$Cu$_{10}$Si$_{10}$P$_5$ alloy on the glass-forming ability, thermal stability and mechanical properties was observed by various techniques. Substitution of Au for 2 at% Cu results in the widest supercooled liquid region ($\Delta T_g = 80$ K) and the highest glass-forming ability. The critical diameter for glass formation of the Au modified alloy reaches as large as 7 mm by copper mold casting. The $\Delta T_g$ decreases with further addition of Au (>2 at%), and when the Au content is more than 5 at%, the glass-forming ability is dramatically reduced and no bulk glasses can be formed. The Young’s modulus, yield strength and maximum compressive strength of the best glass former (Pd$_{79}$Cu$_7$Au$_3$Si$_{10}$P$_3$) are 87 GPA, 1525 and 1660 MPa, respectively. The ultimate compressive plastic strain is over 13%.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 50225103 and No. 50471001).

REFERENCES