Preparation and Thermal Stability of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ Metallic Glass with Good Ductility

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Preparation and Thermal Stability of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ Metallic Glass with Good Ductility

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Abstract. The $Au_{40}Cu_{30}Pd_{10}Si_{20}$ amorphous alloy samples with size of 5mm×0.02mm were prepared by melt-spinning method. The thermal analysis results show that the glass transition temperature T_g, the initial crystallization temperature T_x and the supercooled liquid region ΔT of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ amorphous alloy are 404K, 440K and 36K, respectively, and the calculated glass transition temperature T_{rg} is 0.617, the parameter γ is 0.415. Compared with other Au-based amorphous alloys, the $Au_{40}Cu_{30}Pd_{10}Si_{20}$ alloy has good glass-forming ability (GFA), better thermal stability and good ductility.

1. Introduction

It is well known that amorphous alloys have attracted much attention from materials researchers due to their excellent mechanical, chemical and magnetic properties, and have become a hot research point in the field of materials. Since amorphous alloys was reported [1, 2], the various properties of there have been extensively and deeply studied. For example, the soft magnetic properties of Fe-based and Co-based amorphous alloys have been studied for long time [3, 4, 5]. Recently, another Fe-based amorphous alloy has been found having good magnetic property as well as good plasticity [6]. There are also so many studies and reports on the mechanical properties of Al-based and Mg-based metallic glasses are better than those of corresponding crystalline alloys [7, 8, 9, 10], the superhigh strength of Co-based and Ni-based amorphous alloys [11, 12, 13, 14], superconductivity [15, 16, 17], excellent mechanical properties [18,19] and super-plasticity in supercooled liquid region [20] of Zr-based amorphous alloys, excellent mechanical property [21]of Ti-based amorphous alloy and its application in biomedicine.[22, 23, 24] and the excellent glass forming ability and thermal stability of Pd-based amorphous alloy [25, 26, 27]. However, there are few reports about Au-based amorphous alloys.

Since Duwez, a professor of California Institute of Technology, invented the melt-spinning method and successfully prepared amorphous alloys, this method has been widely used in sample preparation for studying the property of amorphous alloys. Therefore, this study design the alloy composition based on the three empirical principles [28]: ⑴multicomponent systems consisting of more than three elements; ⑵significant difference in atomic size ratios above about 12% among constituent elements; ⑶negative heats of mixing among main constituent elements, and the exchangeability between constituent [29]. With Cu and Pd partially replace Au in $Au_{75}Si_{25}$, $Au_{40}Cu_{30}Pd_{10}Si_{20}$ amorphous alloy for properties testing was prepared by melt-spinning method.

2. Experimental

An ingot of experimental alloy was prepared by melting the mixture of high purity(higher than 99.9%)Pd, Au, Cu and Si 3-5 times under high purity Ar protection. Then, put the alloy prepared earlier into the quartz glass tube. Under the condition of argon gas protection, the alloy is heated through high frequency induction until melting. Finally, the molten alloy is sprayed onto the high-speed rotating copper roller to cool rapidly, and the glassy alloy of about 5mm×0.02mm were prepared.

The sructure of the samples was examined by X-ray diffraction (XRD) (Cu K_{α}) using a SmartLab (Rigaku, Japan). The thermal properties of the prepered glassy alloy were examined by differential scanning calorimetry (DSC) using a STA449-F1 at different heating rate of 10, 20, 40 and 60K/min. The microsructure of the glassy alloy sample was examined by a JEM-2100 transmission electron microscope (TEM). The thin TEM foil samples were prepared through standard twin-jet electropolishing method under the liquid nitrogen protection. Bending the sample to judge the plasticity of the sample. The fracture surface was examined with EDAX-TSL scanning electron microscopy (SEM).

3. Result and Discussion

Figure 1(a) and 1(b)show the picture and XRD pattern of the as-prepared glassy alloy ribbon, respectively. It is seen that the pattern of the sample consists of two broad diffraction peaks (2θ≈40° and 2θ≈71°) without any detectable sharp crystalline peaks. It is typical XRD spectra of amorphous alloy structure, indicating that the as-prepared alloy sample is amorphous structure.

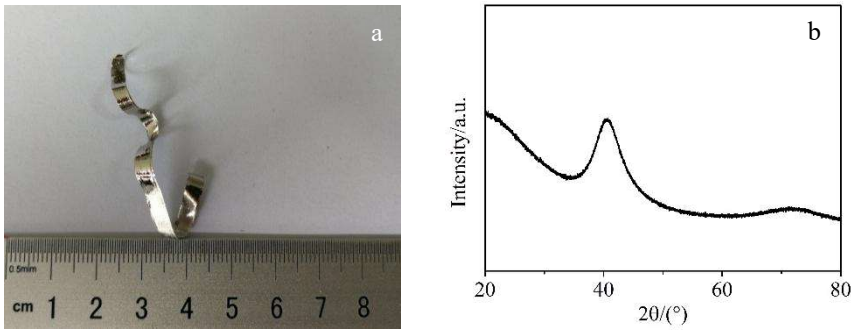

Figure 1. The picture of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ prepared by melt-spinning method (a) and XRD pattern (b)

Figure 2 shows a bright field TEM image of as-prepared ribbon sample. It is a typical TEM image of glassy alloy, showing uniform contrast and sand-like appearance, no detectable crystal structure. The related selected area electron diffraction (SAED) pattern is shown at the upper-right coner of Figure 2. There is no sharp diffraction spot or sharp diffraction ring except for the wide diffracton rings, futher proved that the as-prepared alloy sample possesses amorphous structrue.

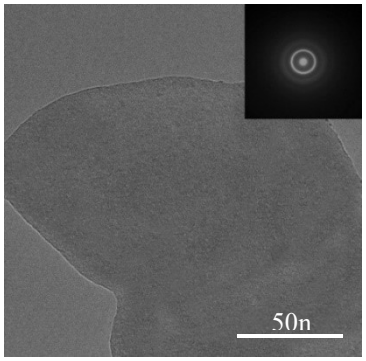

Figure 2. The TEM bright field image of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ sample and the corresponding selected area electron diffraction (SAED) pattern

The microstructure of glassy alloy is a metastable structure, which will change into stable structure slowly with time in normal temperature. But when the temperature rises to a certain value, this metastable structure will be relaxation and rearrangement, and even crystalize and grow to form stable crystalline structure at higher temperature. This process is very important in studying amorphous alloys. Because of the changes in microstructure of alloy could cause the change of material property. Studying this process deeply, the reason for why glassy alloy possesses unique properties would be found out.

Figure 3 shows DSC curves of as-prepared $Au_{40}Cu_{30}Pd_{10}Si_{20}$ amorphous alloy sample at different heating rate. It is observed that the parameters, the glass transition temperature T_g, the initial crystallizing temperature T_x, the crystallizing peak T_p and the supercooled liquid region [30] $\Delta T=Tx-Tg$ increas with the heating rate increases. The reason, as author suggest, is that this process is a process of atomic difusion and migration, which is started when the temperature rises to a certain level. In the case of low heating rate, the atoms have enough time to move, gather and finally crystallize, so when the temperature does not rise to higher level, the inside atoms of the alloy have completed the corresponding "actions". In other words, in the case of faster heating rate, the atoms can not finish these "actions", before the temperature rises to higher. So, faster heating rate makes larger value of T_g, T_x, T_p and ΔT.

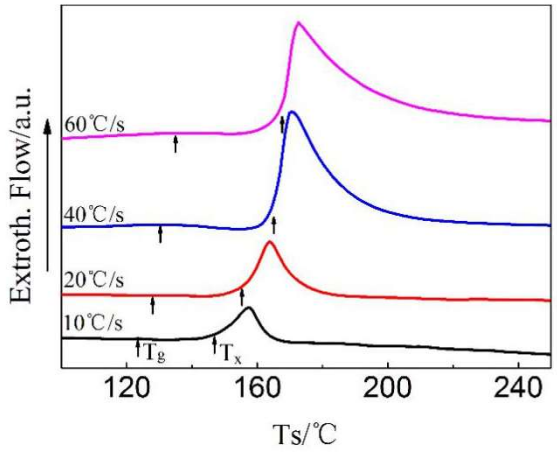

Figure 3. The DSC curves of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ samples at different heating rates

The DSC curves in Figure 3 both exhibit obvious endothermic and exothermic reactions, suggesting the glass transition and crystallization happend during heating. In-depth analysis of DSC curve examined at a heating rate of 40℃/min with extrapolations shows a glass transition temperature T_g of 131℃(404K), an onset temperature of crystallization T_x of 167℃(440K) and peak temperature of crystallization T_p of 172℃(445K). In addition, the liqiudus temperature T_l measured by DTA is 382℃ (655K). So, the caculated supercooled liquid range $\Delta T = T_g - T_x$, the reduced glass transition temperature $T_{rg} = T_g / T_l$ and the $\gamma = T_x / (T_g + T_l)$ are 36, 0.617 and 0.415, respectively.

Table 1. The parameters of sevieral Au-based metallic glasses measured at a heating rate of 40℃/min

Component	T_g^{max}/T_g^{min} (K)	T_x^{max}/T_x^{min} (K)	$\Delta T_{max}/\Delta T_{min}$ (K)	$T_{rg}^{max}/T_{rg}^{min}$	$\gamma_{max}/\gamma_{min}$
$(Au, Cu, Si)_{90}Ag_5Pd_5$[31]	440/400	472/442	59/32	0.610/0.568	—
$(Au, Si, Cu)_{88}Ag_7Pd_5$[31]	424/409	477/456	53/47	0.605/0.603	—
$(Au, Cu)_{75.5}Ag_{7.5}Si_{17}$[32]	377/339	419/375	50/36	0.578/0.499	0.407/0.368
$Au_{50}Cu_{33}Si_{17}$[32]	383	405	22	0.564	0.381
$Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$[32]	401	459	58	0.62	0.439
$Au_{40}Cu_{30}Pd_{10}Si_{20}$	404	440	36	0.617	0.415

Parameters ΔT, T_{rg} [33] and γ [34] are indicator of glass forming ability (GFA) of alloy. When the parameters are biger, the GFA of the alloy is larger. To compare GFA parameters with other Au-based glassy alloys preparaed by copper mold casting, $Au_{40}Cu_{30}Pd_{10}Si_{20}$ has pretty good GFA. As author thought, the bulk metallic glass of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ could be prepared by water quenching after fluxing techniue.

Figure 4 shows a picture of as-prepared $Au_{40}Cu_{30}Pd_{10}Si_{20}$ glassy alloy after being fold. It can be seen that the fold alloy sample has not fracture, preliminarily suggesting $Au_{40}Cu_{30}Pd_{10}Si_{20}$ amorphous alloy has good plasticity.

Figure 4. The pictrue of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ alloy ribbons after bending deformation through 180°

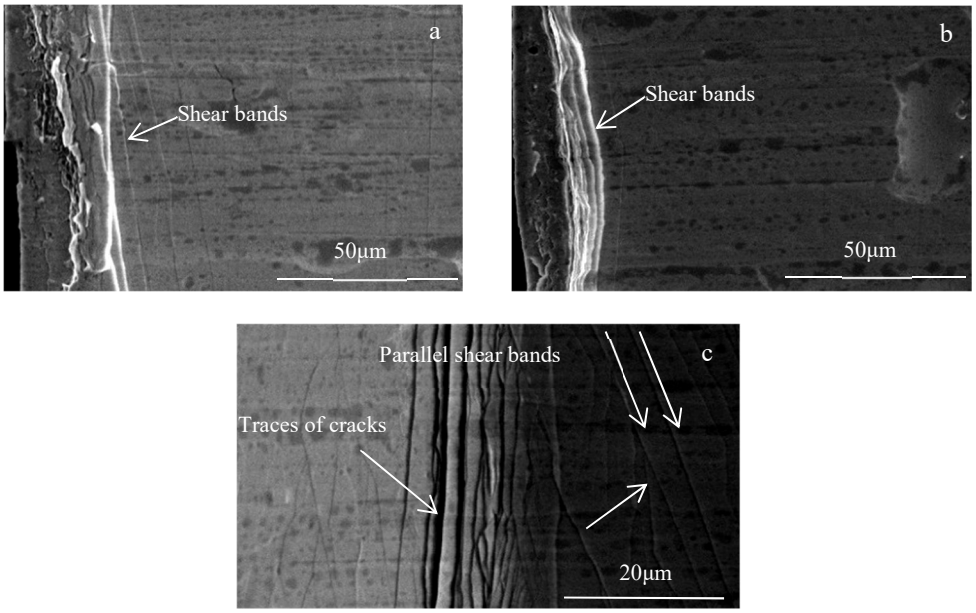

Figure 5. SEM images of the surface near the fracture

Figure 5(a) and (b) show the SEM images on both sides of fracture after several folds. Figure 5(c) is a local enlarged drawing of fracture. From Fig. 5a-5c, it can be seen that plastic deformation took place before fracture, resulting in a large number of shear bands. The shear bands moved from the deformation zone to the undeformed zone in the form of parallel lines. In order to coordinate the plastic deformation, shear band branching occurs during the shear band movement, which enhances the plastic deformation ability of the samples. With the increase of deformation, more and more shear bands are produced, forming a shear band accumulation area. When the shear band can not move to the low density area, the

sample will produce surface cracks, and the sample will fracture with further deformation. As shown in Figure 5(c), surface cracks occur in the shear zone. It can be seen that the specimen has plastic deformation before fracture and has good plasticity.

4. Conclusion

$Au_{40}Cu_{30}Pd_{10}Si_{20}$ amorphous alloy was successfully prepared by melt-spinning method. Thermal analysis showed that the crystallization temperature of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ amorphous alloy was higher than most of other Au-based amorphous alloys, which indicated that $Au_{40}Cu_{30}Pd_{10}Si_{20}$ had good thermal stability. According to the calculation results of reduced glass transition temperature T_{rg}, parameter γ and supercooled liquid region ΔT, it can be concluded that $Au_{40}Cu_{30}Pd_{10}Si_{20}$ alloy has better glass forming ability and plasticity. Good plasticity provides strong support for the application of $Au_{40}Cu_{30}Pd_{10}Si_{20}$ amorphous alloy in more fields. In addition, this study provides supplementary data for the follow-up study of Au based amorphous alloys.

Acknowledgments

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