APPLIED PHYSICS LETTERS **87**, 061912 (2005)

Gold based bulk metallic glass

Jan Schroers[a)]
Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91125 and Liquidmetal Technologies, Lake Forest, California 92630

Boonrat Lohwongwatana and William L. Johnson
Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91125

Atakan Peker
Liquidmetal Technologies, Lake Forest, California 92630

(Received 7 February 2005; accepted 2 June 2005; published online 3 August 2005)

Gold-based bulk metallic glass alloys based on Au–Cu–Si are introduced. The alloys exhibit a gold content comparable to 18-karat gold. They show very low liquidus temperature, large supercooled liquid region, and good processibility. The maximum casting thickness exceeds 5 mm in the best glassformer. $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ has a liquidus temperature of 644 K, a glass transition temperature of 401 K, and a supercooled liquid region of 58 K. The Vickers hardness of the alloys in this system is ~350 Hv, twice that of conventional 18-karat crystalline gold alloys. This combination of properties makes the alloys attractive for many applications including electronic, medical, dental, surface coating, and jewelry. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2008374]

Gold became known to mankind thousands years ago, and has been of inestimable value to civilization ever since. It is the noblest of the noble metals, and has a good combination of high thermal conductivity, high electrical conductivity, and high corrosion resistance. These properties have resulted in extensive use of gold and its alloys in electronic, aerospace, astronomy, medical, and industrial applications. For instance, gold can be found in many of today's sophisticated electronic devices. However, gold has always been most valued as a jewelry material. Gold alloys are easy to fashion, are nonallergenic, have a bright pleasing color, and remain tarnish free indefinitely. Pure gold and higher karat gold alloys, however, are rather soft and therefore vulnerable to wear and scratching. This results in diminished aesthetic appearance, and is a drawback of conventional crystalline gold alloys.

In the last two decades, several alloys based on Pd,[1–3] La,[4] Zr,[5,6] Fe,[7–9] and Pt[10] were found to form bulk amorphous phases. Fully amorphous samples are obtained when the alloys are cast into copper molds of diameter up to centimeters which indicates critical cooling rates for glass formation of 100 K/s or less. These bulk metallic glasses (BMGs) exhibit properties such as high strength, large elastic strain limit, high hardness, and, in some cases, substantial ductility.[11] The compositions of these BMGs are typically close to a deep eutectic composition. Consequently, their melting temperatures are much lower than estimated from interpolation of the alloy constituents' melting temperatures. The resulting low liquidus temperature is an attractive property for casting alloys. The extraordinary stability of BMG forming alloys against crystallization also results in a large supercooled liquid region, ΔT, ($\Delta T = T_x - T_g$, T_x: crystallization temperature, T_g: glass transition temperature), the temperature region in which the amorphous phase first relaxes into a highly viscous liquid before eventually crystallizing. In this temperature region, BMG's are amenable to superplastic processing using netshape processing methods similar to those employed for thermoplastics.[12]

The binary gold silicon eutectic composition was the first alloy found to exhibit metallic glass formation by Duwez and co-workers in 1960.[13] The critical cooling rate for glass formation of this alloy is of the order of 10^6 K/s, resulting in a critical casting thickness, d_c, below 50 microns. In an effort to increase the glass forming ability of this alloy, Si was partially replaced by Ge, which resulted in only moderate increase of the glass forming ability and the width of the supercooled liquid region.[14,15] The poor glassforming ability of these early metallic glasses and the low glass transition temperature make these alloys of marginal interest for most applications and explains the limited interest in these Au-based metallic glasses over the past several decades.

A suitable amorphous gold based alloy for applications such as jewelry, electronics, or dental reguires a T_g of at least 370 K to be stable at ambient temperatures. Other desirable properties include: a large gold content (~18 karat or higher), high hardness, good processibility, and a critical casting thickness that permits fabrication of net shaped articles such as jewelry. From a processing point of view, it is desirable to possess a large supercooled liquid region which gives access to a low forming viscosity, which in turn facilitates superplastic forming.

In this letter we report gold based bulk metallic glass forming compositions of various complexities, with a gold content comparable to 18-karat gold alloys. Samples were prepared by alloying the elements (Au: 99.95%, Cu: 99.9%, Ag: 99.5%, Pd: 99.95%, Si: 99.95% purity) in an arc-melter. Copper mold quenching was performed to solidify the alloy in its amorphous state, and to determine the critical casting thickness. Thermal analysis was performed in a differential scanning calorimeter (DSC) Netzsch DSC 404c. X-ray diffraction (XRD) was carried out on an Inel XRG 3000 using

---

[a)] Electronic mail: jan.schroers@liquidmetal.com

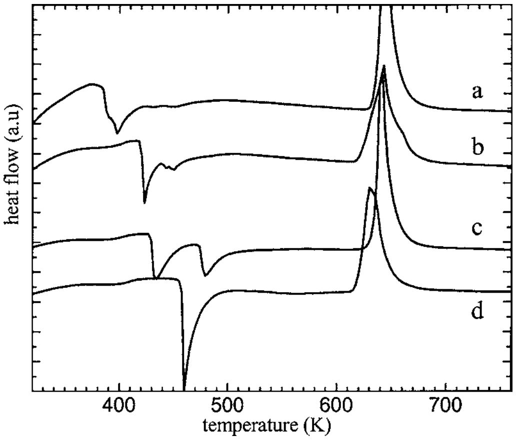

FIG. 1. DSC thermogram determined by heating with 20 K/min of gold based alloys of various compositions that were cast in copper molds of various sizes. (a) $Au_{55}Cu_{25}Si_{20}$ cast in 0.5 mm copper mold; (b) $Au_{46}Ag_5Cu_{29}Si_{20}$ cast in 1 mm copper mold; (c) $Au_{52}Pd_{2.3}Cu_{29.2}Si_{16.5}$ cast in 2 mm copper mold; (d) $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ cast in 5 mm copper mold.

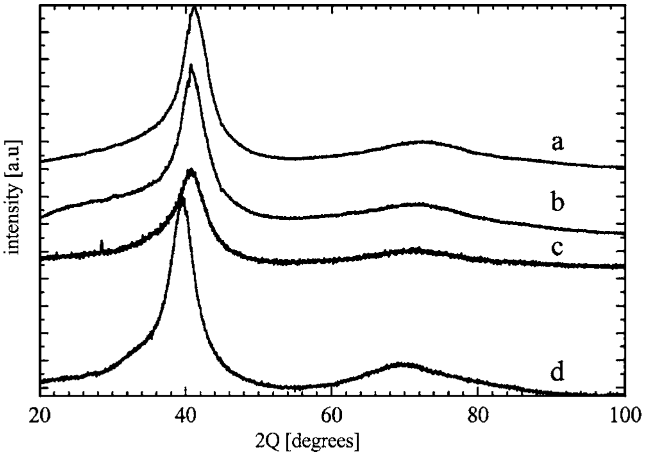

FIG. 2. X-ray diffraction thermogram of gold based alloys of various compositions that were cast in copper molds with various diameters. (a) $Au_{55}Cu_{25}Si_{20}$ cast in 0.5 mm copper mold; (b) $Au_{46}Ag_5Cu_{29}Si_{20}$ cast in 1 mm copper mold; (c) $Au_{52}Pd_{2.3}Cu_{29.2}Si_{16.5}$ cast in 2 mm copper mold; (d) $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ cast in 5 mm copper mold.

Cu $K\alpha$ radiation. Hardness tests were performed on a Leco R-600.

Within this alloy development work a large number of compositions was studied from various families of alloys. The alloys that are explicitly introduced represents the compositions in each alloy family with the highest glass forming ability. Figure 1 shows the DSC thermogram obtained by heating at a rate of 20 K/min for four gold alloys. The thermogram in Fig. 1(a) is that of $Au_{55}Cu_{25}Si_{20}$ which was cast in a 0.5 mm copper mold, Fig. 1(b) shows $Au_{46}Ag_5Cu_{29}Si_{20}$, cast at 1 mm, Fig. 1(c) shows $Au_{52}Pd_{2.3}Cu_{29.2}Si_{16.5}$ cast at 2 mm, and Fig. 1(d) shows $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ cast at 5 mm. All compositions are in atomic percent. All alloys show a glass transition and a crystallization peak suggesting that at least some fraction of the material was amorphous. A comparison of the heat of crystallization, ΔH, and the heat of fusion, H_f, which are summarized for the various alloys in Table I gives approximately $\Delta H/H_f = 0.6$, a value typical for an entirely amorphous sample. When comparing with the T_g of the early gold alloys of about 300 K (Refs. 13–15) all alloys have surprisingly high T_g. Their T_g is higher than 370 K with the exception of $Au_{55}Cu_{25}Si_{20}$, thereby exceeding requirements for most jewelry applications.

Figure 2 shows the x-ray diffractogram of the four alloys. The diffractogram in Fig. 2(a) is that of $Au_{55}Cu_{25}Si_{20}$ cast in a 0.5 mm copper mold, Fig. 2(b) shows $Au_{56}Ag_5Cu_{29}Si_{20}$ cast at 1 mm, Fig. 2(c) shows $Au_{52}Pd_{2.3}Cu_{29.2}Si_{16.5}$ cast at 2 mm, and Fig. 2(d) shows $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ cast at 5 mm. All spectra show broad maxima typical for entirely amorphous material, supporting the DSC results.

TABLE I. Summary of the properties of the various gold based alloys. The maximum thickness the alloy could be cast amorphous, d_c, was determined for copper mold quenching.

Composition (at %)	T_g (K)	T_x (K)	ΔT (K)	T_l (K)	Trg T_g/T_l	d_c (mm)	ΔH (J/g)	H_f (J/g)
$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$	401	459	58	644	0.62	5	35	46
$Au_{52}Pd_{2.3}Cu_{29.2}Si_{16.5}$	393	427	34	651	0.6	2	33	49
$Au_{46}Ag_5Cu_{29}Si_{20}$	395	420	25	664	0.59	1	28	46
$Au_{55}Cu_{25}Si_{20}$	348	383	35	654	0.53	0.5	32	57

The results are summarized in Table I. All alloys show liquidus temperatures of below 700 K. $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ has a liquidus temperature as low as 644 K. With the glass transition temperature of 401 K, the alloy has the reduced glass transition temperature, $T_{rg} = T_g/T_l$, of 0.62, a value only seen among excellent bulk metallic glassformers.[16] The supercooled liquid region for $Au_{55}Cu_{25}Si_{20}$, $Au_{56}Ag_5Cu_{29}Si_{20}$, and $Au_{52}Pd_{2.3}Cu_{29.2}Si_{16.5}$ is approximately 30 K. For $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$, the supercooled liquid region reaches 58 K.

ΔT is often used as a parameter that describes the super plastic formability of a BMG.[17,18] However, when comparing the formability of different alloy systems, ΔT should be normalized to the width of the undercooled liquid region, $T_l - T_g$ (T_l: liquidus temperature). The parameter, $S = \Delta T/(T_l - T_g)$, shows better correlation with formability, even though the assumption of identical fragility of the liquid and viscosity at T_l is oversimplified.[19] The S parameter for $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ of 0.24 exceeds even the one for $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ of 0.2, an alloy frequently used and known for its super plastic formability,[20] but is below the

FIG. 3. $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$, superplastically formed from a rod shape into this article. The forming was carried out in air at 423 K for 200 s under a forming pressure of 100 MPa. The amorphous structure of the plastically formed article was confirmed by DSC and x ray. Note that the as-formed article is shown with no subsequent finishing. The flash and overflows have not been removed.

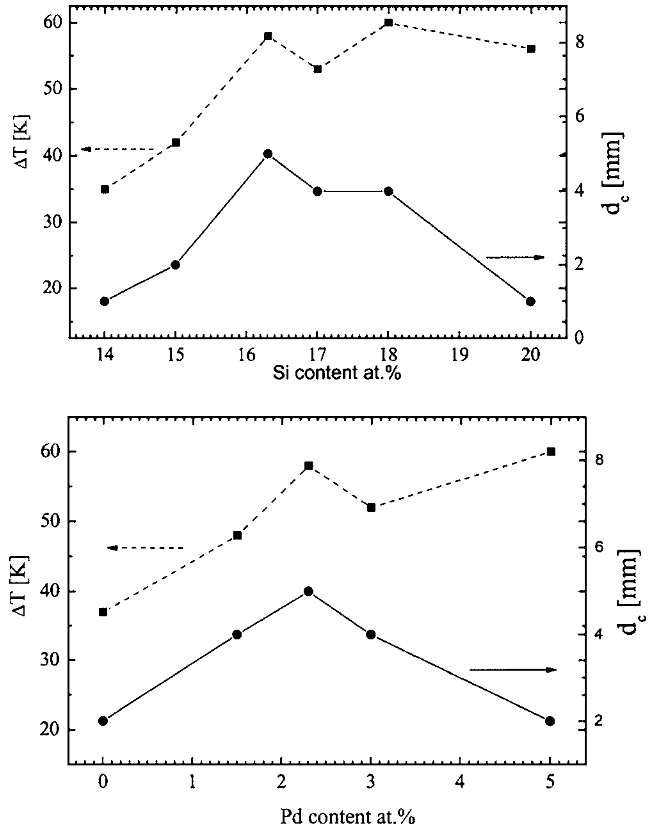

FIG. 4. Composition dependence of ΔT and d_c for $(\mathrm{Au}_{58.5}\mathrm{Ag}_{6.6}\mathrm{Pd}_{2.8}\mathrm{Cu}_{32.1})_{86-x}\mathrm{Si}_{14+x}$ for $x=0-6$ (top); $(\mathrm{Au}_{60.1}\mathrm{Ag}_{6.8}\mathrm{Cu}_{33.1})_{83.7-y}\mathrm{Pd}_y\mathrm{Si}_{16.3}$ for $y=0-5\%$ (bottom). A strong dependence on the Si and Pd content of both, d_c and ΔT is observed. No obvious correlation of d_c and ΔT is seen.

parameter for $\mathrm{Pt}_{57.5}\mathrm{Cu}_{14.7}\mathrm{Ni}_{5.3}\mathrm{P}_{22.5}$ (Ref. 10) of $S=0.34$, the highest S value among all bulk metallic glass forming alloys. The large S parameter for $\mathrm{Au}_{49}\mathrm{Ag}_{5.5}\mathrm{Pd}_{2.3}\mathrm{Cu}_{26.9}\mathrm{Si}_{16.3}$ suggests good formability. Superplastic forming of $\mathrm{Au}_{49}\mathrm{Ag}_{5.5}\mathrm{Pd}_{2.3}\mathrm{Cu}_{26.9}\mathrm{Si}_{16.3}$ was demonstrated by forming rod shaped material into various geometries. Figure 3 shows an article that was formed in air at 423 K for 200 s using an applied pressure of 100 MPa. The amorphous structure of the plastically formed articles was confirmed by DSC and x-ray. The precise replication of the complex geometry confirms the excellent formability as suggested already by the S parameter.

For the three bulk glassforming alloys, $\mathrm{Au}_{56}\mathrm{Ag}_5\mathrm{Cu}_{29}\mathrm{Si}_{20}$, $\mathrm{Au}_{52}\mathrm{Pd}_{2.3}\mathrm{Cu}_{29.2}\mathrm{Si}_{16.5}$, and $\mathrm{Au}_{49}\mathrm{Ag}_{5.5}\mathrm{Pd}_{2.3}\mathrm{Cu}_{26.9}\mathrm{Si}_{16.3}$, Vickers hardness was determined to be approximately 360 Hv. This is an extraordinarily high value when compared with conventional 18-karat gold alloys which have Vickers hardness around 150–200 Hv.[21] Ultrasonic measurements were carried out to determine the elastic constants of amorphous $\mathrm{Au}_{49}\mathrm{Ag}_{5.5}\mathrm{Pd}_{2.3}\mathrm{Cu}_{26.9}\mathrm{Si}_{16.3}$. Youngs modulus was determined to be 74.4 GPa, shear modulus to be 26.45 GPa, and bulk modulus to be 132.31 GPa which results in Poisson ratio of 0.406.

A larger composition range in the composition space around the four alloys was studied and characterized to determine the correlation of glass forming ability and ΔT with composition. As an example, during the development of the $\mathrm{Au}_{49}\mathrm{Ag}_{5.5}\mathrm{Pd}_{2.3}\mathrm{Cu}_{26.9}\mathrm{Si}_{16.3}$ alloy, the Au content was varied between 40% and 60%, Ag content was varied from 0 to 20%, Pd from 0 to 5%, Cu from 0 to 35%, and Si from 14% to 20%. Among the constituents of these alloys, the Si and Pd content have the strongest influence on the glass forming ability and ΔT. This is illustrated in Fig. 4 which shows the dependence of the critical casting thickness and ΔT on Si and Pd content. The Si content was varied between 14% and 20% resulting in a variation of d_c from 1 mm to 5 mm, and a variation of ΔT from 35 K to 60 K. By varying the Pd content from 0 to 5%, ΔT increases continuously with some scatter whereas d_c reaches a maximum at Pd=2.3%. In both cases, a strong dependence of ΔT and d_c on the composition variations can be observed. However, no obvious correlation between ΔT and d_c, as previously reported to be positive[22,23] or negative,[20,24] was observed.

In conclusion, gold based bulk metallic glass forming alloys were developed with a weight content of ~18 karat gold. The alloys show low liquidus temperature, large supercooled liquid region, large maximum casting thickness and good processibility for both casting and thermoplastic processing in a similar manner like thermo plastics. The combination of these properties together with their high hardness and esthetical appearance make them ideal for jewelry, dental, medical, and electronic applications.

[1] H. W. Kui, A. L. Greer, and D. Turnbull, Appl. Phys. Lett. **45**, 615 (1984).
[2] N. Nishiyama and A. Inoue, Mater. Trans., JIM **37**, 1531 (1996).
[3] I.-R. Lu, G. Wilde, G. P. Görler, and R. Willnecker, J. Non-Cryst. Solids **250–252**, 577 (1999).
[4] A. Inoue, H. Yamaguchi, T. Zhang, and T. Masumoto, Mater. Trans., JIM **31**, 104 (1990).
[5] A. Inoue, T. Zhang, and T. Masumoto, Mater. Trans., JIM **31**, 177 (1990).
[6] A. Peker and W. L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993).
[7] V. Ponnambalam, S. J. Poon, G. J. Shiftlet, V. M. Keppens, R. Taylor, and G. Petculescu, Appl. Phys. Lett. **83**, 1131 (2003).
[8] V. Ponnambalam, S. J. Poon, and G. J. Shiftlet, J. Mater. Res. **19**, 1320 (2004).
[9] Z. P. Lu, C. T. Liu, J. R. Thompson, and W. D. Porter, Phys. Rev. Lett. **92**, 245503 (2004).
[10] J. Schroers and W. L. Johnson, Appl. Phys. Lett. **84**, 3666 (2004).
[11] J. Schroers and W. L. Johnson, Phys. Rev. Lett. **93**, 255506 (2004).
[12] J. Schroers, JOM **5**, 34 (2005).
[13] W. Klement, R. H. Willens, and P. Duwez, Nature (London) **187**, 869 (1960).
[14] H. S. Chen and D. Turnbull, Appl. Phys. Lett. **10**, 284 (1967).
[15] H. S. Chen and D. Turnbull, J. Chem. Phys. **48**, 2560 (1969).
[16] Z. P. Lu, H. Tan, Y. Li., and S. C. Ng, Scr. Mater. **42**, 667 (2000).
[17] T. Zhang and A. Inoue, Mater. Trans., JIM **44**, 1143 (2003).
[18] V. Ponnambalam, S. J. Poon, and G. J. Shiftlet, J. Mater. Res. **19**, 3046 (2004).
[19] S. Mukherjee, Z. Zhou, J. Schroers, W. L. Johnson, and W. K. Rhim, Acta Mater. **52**, 3689 (2004).
[20] T. A. Waniuk, J. Schroers, and W. L. Johnson, Appl. Phys. Lett. **78**, 1213 (2001).
[21] *Metals Handbook*, 9th ed. (American Society for Metals, Metals Park, Ohio).
[22] A. Inoue, T. Zhang, and T. Masumoto, J. Non-Cryst. Solids **156**, 473 (1993).
[23] T. D. Shen and R. B. Schwarz, Appl. Phys. Lett. **75**, 49 (1999).
[24] Y. C. Kim, W. T. Kim, and D. H. Kim, Mater. Sci. Eng., A **A375**, 127 (2004).