Effect of minor elements addition on glass formation and properties of gold alloys

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Abstract. In this work the effect of 1 % at additions of Ti or In on structural and thermal properties of the Au₄₉Ag₅.₅Pd₂₃Cu₂₆.₉Si₁₆.₃ [1] alloy is presented. Formation of a glassy phase was confirmed using X-ray diffraction for rods up to 3 mm in diameter. Data on glass transition, T_g, and crystallization, T_x, temperatures as well as on colour and Vickers microhardness are reported.

1. Introduction

The topic of gold based amorphous alloys, early prototypes of glass-forming systems (Au-Si [1], Au-Ge-Si [2]), has seen renewed interest with the discovery of a bulk metallic glass at the Caltech [3] with atomic content Au₄₉Ag₅.₅Pd₂₃Cu₂₆.₉Si₁₆.₃ and containing 18-karat gold. It has maximum amorphization thickness close to 5 mm, low melting temperature, high hardness [3] and good workability in the undercooled liquid regime [4], therefore, the alloy has been proposed for jewellery application [5].

Minor addition of alloy components can improve the glass forming ability (GFA). The reasons for such improvement are various: the scavenging effect of oxygen from the liquid, the appropriate atomic-size mismatch and/or large negative heat of mixing with respect to the constitutive elements [6].

The aim of this work is to probe minor additions of selected elements on the GFA of the above alloy for improved thermal stability or colour modification. Ti is used because of its strongly negative heat mixing with Au. It was shown earlier that the glass transition became apparent when it was added to the Au-Cu-Si system, however formation of titanium silicides decreased the GFA [7]. Having tested various amounts of Ti addition (up to 8 % at.), a suitable content is set at 1 % at. Indium is then tested because of its large size (0.155 nm) among all of the alloy constitutive elements. Its affinity to Au in the liquid state is shown by the occurrence of low melting eutectics in the binary phase diagram. In the present work its content as been set to 1 %at. as for Ti.

2. Experimental

A master alloy of nominal composition Au₄₉Ag₅.₅Pd₂₃Cu₂₆.₉Si₁₆.₃ (named A5) was prepared by arc-melting the pure elements (Au, Cu, Ag: 99.99%, Si: 99.9995%, Pd: >99%) in Ar atmosphere with Ti and Zr getters. Portions of it were alloyed with Ti and In (purity of 99.99% and 99.99%, respectively) to obtain (Au₄₉Ag₅.₅Pd₂₃Cu₂₆.₉Si₁₆.₃)₉₉Ti₁ and (Au₄₉Ag₅.₅Pd₂₃Cu₂₆.₉Si₁₆.₃)₉₉In₁, respectively (named A5Ti and A5In). Portions of the alloys were melt spun under Ar as ribbons, 2-3 mm wide and some tens of micron thick.
Bulk samples were obtained by injection casting in a truncated cone mould of 1 mm diameter at the tip, 5 mm at the base, and 50 mm in height. The structure of samples was determined by X-ray diffraction (XRD) with Cu-Kα radiation and compositions by energy dispersive X-ray spectroscopy (EDS). Thermal data were obtained by Differential Scanning Calorimetry (DSC) under Ar with a cell calibrated with the temperatures and heats of fusion of In and Zn. Vickers microhardness was tested with a load of 50 gf.

3. Results and Discussion
The microstructure of A5 master alloy (Fig. 1a) is constituted by five zones. Three of them are single phases, called A, B, and C of composition (EDS analyses in % at.): A: Pd$_{55}$Au$_{7}$Cu$_{9}$Si$_{29}$; B: Si$_{67}$Au$_{15}$Cu$_{18}$; C: Au$_{67}$Cu$_{16}$Ag$_{17}$. The other two zones present limited phase contrast and form the matrix of composition ranging from Au$_{50}$Cu$_{32}$Ag$_{13}$ to Au$_{55}$Cu$_{28}$Ag$_{4}$Si$_{12}$. It is likely A derives from Pd silicides of the binary system. The composition of B must be taken with caution due to the small size of crystals, it can well be

![Figure 1](image.png)

**Figure 1.** Backscattered electron (BE) images of polished ingots of A5 (a) and A5In (b). Letters are explained in the text.

![Figure 2](image.png)

**Figure 2.** XRD patterns of: as cast alloys (a, b and c), the corresponding ribbons on the air side (a1, b1 and c1), sections of bulk cones taken at the maximum amorphization thickness (a2, b2 and c2).
free Si, with contributions of metals from adjacent or embedded phases. C is a Au rich solid solution. The matrix appears to contain two silicides based on Au and Cu. The microstructure of A5In (Fig. 1b) is clearly different from that of A5, although they share four phases: the “palladium silicide” (A) is missing in A5In. B is close in composition to the black phase in Fig. 1b. C to the white one and the matrix of A5 corresponds to the dark gray and light gray phases of Fig. 1b. With XRD it has been possible to index only C as a Au rich solid solution with lattice parameter \( a \approx 4.02 \, \text{Å} \). The A5Ti alloy is basically constituted by the same phases as the A5 as confirmed by the respective diffraction patterns where there is ample correspondence of reflections (Fig.2 a, b). The Indium apparently modifies the eutectic microstructure.

Rapidly quenched ribbons are fully amorphous (Fig. 2, patterns a1, b1, and c1). Their DSC traces and thermophysical data are given in Fig. 3 (a, b and c) and Table 1. The \( T_g \) and \( T_x \) of A5 are a few degrees lower than those given in [3]. The eutectic temperature, \( T_m \), is very close and the liquidus (\( T_L \)) is 630 K. The heat of fusion, \( \Delta H_f \), is comparable, whereas the heat of crystallization, \( \Delta H_x \), is much lower. Our value corresponds to 52\% of \( \Delta H_f \), rather close to previous findings [8], contrary to 76\% of ref. [3]. The reason for this discrepancy is not known, being all materials fully amorphous. Data reported in Table 1 show that additions of Ti and In increase \( T_l \) due to a slight departure from the eutectic.

In DSC experiments, ribbons show an exothermic broad signal at low temperature due to relaxation phenomena followed by the glass transition and then crystallization. \( T_g \) values were determined precisely after relaxing samples at 373 K for 120 minutes. The main crystallization peak of A5 starts more progressively than those of the other two samples. This suggests the growth of quenched-in nuclei embedded in the amorphous matrix [9]. With the addition of Ti, besides the shift at higher temperature of \( T_g \) and \( T_x \), a sharper peak is obtained. In the case of A5In \( T_g \) and \( T_x \) shift to lower temperature. In Fig. 3 are also reported DSC traces of A5Ti (b2h) and A5 (a2h) samples annealed for 2 hours at 408 K in order to check for stability against crystallization of the undercooled liquid. While \( T_g \) remains manifest, the peaks are shifted to low temperatures because of partial crystallization, as demonstrated by XRD analysis, with marked change in the shape of the traces. For A5, the second exothermal peak becomes more prominent, and for A5Ti the single crystallization peak is even sharper. XRD of the annealed samples suggest the formation of a limited number of equilibrium phases which implies a shift in composition of the remaining amorphous matrix and, possibly, a modified crystallization behaviour [10]. The stability of

![Figure 3](image-url)
the alloys in the undercooled regime where superplastic forming can be performed, was checked with isochronal DSC experiments at 408 K for 5 hours on as-cast ribbons. After 112 minutes A5 ribbons start to crystallize. Ti addition increase the resistance against crystallization since no exothermic crystallization signal appear up to 5 hours annealing. Addition of In decreases such resistance to 46 minutes.

Bulk amorphous samples were obtained in all cases. The maximum diameter of the cone which resulted fully amorphous is 3 mm for A5, 2.1 mm for A5Ti and 2.3 mm for A5In (Fig.2).

The colour of alloys is reported in Table 1 as indicated by comparative visual inspection of the as-quenched ribbons. It remains unchanged for storage times of several months, however, if the samples are handled their surfaces are subject to tarnishing rather quickly.

The Vickers hardness, values, Hv are similar for all alloys and confirm those reported earlier [3].

Table 1. Thermal data (collected at 0.33 K/s), colour, and hardness of A5, A5Ti and A5In ribbons.

| Alloy | T_g K | T_x K | −ΔH_x J/g | T_m K | T_l K | ΔH_f J/g | Colour | Hv HVN |
|-------|-------|-------|-----------|-------|-------|----------|--------|-------|
| A5    | 396   | 453   | 21.6      | 617   | 630   | 41.4     | White with yellow nuance | 364 ± 7 |
| A5Ti  | 396   | 459   | 22.4      | 618   | 652   | 38.4     | White with yellow-red nuance | 368 ± 4 |
| A5In  | 391   | 447   | 21.9      | 617   | 653   | 43.1     | Silvery white | 365 ± 14 |

4. Conclusions
The thermal stability of the Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3} alloy is improved by the addition of 1% at. Ti and decreased by that of 1% at. In.

On continuous heating the crystallization occurs some 50-60 degrees above T_g. Such temperature window can be wide enough for giving the alloy a suitable shape [11]. Above T_g (408 K) it occurs in times of minutes or hours according to the alloy composition. Bulk samples were produced as cones with maximum size of 3.0 mm (A5), 2.3 mm (A5In) and 2.1 mm (A5Ti).

The amorphous alloys can be classified among white golds. However, they are subject to tarnishing after handling. The hardness is definitely higher compared to conventional golds.

Further improvement can be envisaged by tuning the composition closer to eutectics and by alloy modifications to suppress the tendency to tarnishing.

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