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A colourimetric and microstructural study of the tarnishing of gold-based bulk metallic glasses

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ABSTRACT

The tarnishing of the Au–Ag–(Pd)–Cu–Si bulk metallic glass system is studied based on the Yellowness Index detection and on microstructural investigations during various and prolonged low-temperature exposures. Polished surfaces tarnish faster than as-cast surfaces due to the removal of the native SiO_2 film. The rate decreases with decreasing nominal Cu/Si and Si/Au ratios, with removing Pd, and with microalloying of Al. The tarnishing mechanism is controlled by the internal oxidation of the glassy matrix forming amorphous SiO_2 dendrites. This triggers the partitioning of metallic elements that enhances the rate of out-diffusion and surface oxidation of Cu.

1. Introduction

Duwez and co-workers [1] reported in 1960 that the Au–Si system can form amorphous alloys at around the eutectic composition of Au–18 at.% Si by rapid quenching. Even if the critical thickness of the amorphous sample was only 50 μm, this was the first time that crystallization of a metallic melt was avoided altogether during solidification. Since then, numerous metallic glass forming alloy systems have been explored. It was only in 2005 that the Au–Si system has been revisited by Schroers et al. who drastically enhanced the glass-forming ability by adding Pd, Ag and Cu [2]. The compositions reported by Schroers et al. have enough gold content to be considered as 18 carat gold alloys (i.e. at least 75 wt.% Au, corresponding to approximately 50 at.% Au) and are massive enough to be considered as bulk metallic glasses (hereafter called BMG), whose prerequisite is a critical thickness of at least 1 mm. Among those, the best Au-based glass-former is the $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ composition with a critical thickness of 5 mm and a glass transition temperature, T_g, of around 128 °C [2].

In 2009, Zhang and co-workers investigated the Pd-free Au–Ag–Cu–Si glass system and observed a sharp decrease in the glass transition with increasing gold content. For example the lowest reported T_g is 66 °C for the composition $Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$ BMG alloy [3]. Other researchers modified the ternary Au–Cu–Si systems by alloying with other elements such as Sn [4], Ti or Y [5], in order to improve certain properties, like the glass forming ability, or simply to reduce the costs by reducing the noble metal content.

The $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ BMG possesses a premium white gold colour [6,7], and a Vickers hardness value of 360 HV1 [2], that is approximately 1.5–2 times higher than the hardness of cold worked or age hardened conventional gold alloys (e.g. $Au_{54.9}Ag_{16.7}Cu_{28.4}$ at.%) [8]. This value is much higher than the minimum hardness value required for jewellery items, which is set to be as least 100 HV1 for reasonable wear resistance and service performance [8]. Moreover, the low melting temperature of these BMG of approximately 370 °C, minimal solidification shrinkage (i.e. less than 0.5%) [9] and a good processing ability [2] are highly desired properties for jewellery and dentistry applications. However, any significant change in the colour of a jewellery or dentistry alloy due to exposure to atmosphere or contact with skin or saliva is obviously undesirable. The body temperature of 37 °C is 90° lower than the T_g for the $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$. At this temperature, which is approximately $0.77T_g$ (in K), the glassy structure is stable against crystallization for hundreds of years according to the time-temperature-transformation diagram of Ref. [10]. During isothermal aging at 37 °C, structural relaxation processes (or α relaxation) will occur very slowly, taking decades to be completed due to its relative sluggish bulk diffusivity. At $0.7–0.8T_g$ (in K), most BMGs do not show fast oxidation or tarnishing effects. For example, Zr-based and Ni-based BMGs have extremely low parabolic oxidation rates at temperatures, which are 60–90° below T_g [11–13].

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It is intuitively reasonable to expect that an 18 carat gold alloy would not be distinctly affected by undesirable tarnishing. Nevertheless, after a few hours of exposure to a non-protective atmosphere, the $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ glassy alloy assumes dull yellowish gleams. The colour gradually deepens to become orange and later shows locally orange-brown corrosion products forming on the surface. The tarnishing is even more pronounced, as soon as the alloy is worn as jewellery and comes in contact with sweat or saliva. Therefore, recent studies have been focused on the wet corrosion behaviour of gold-based BMGs in artificial sweat or artificial saliva baths [6,7,14–16]. Some of these investigations have been performed on melt spun ribbons, which were consumed by the corrosion process [14,15]. In the present article a systematic colourimetric study of the tarnishing process is applied to the Au–Ag–(Pd) –Cu–Si BMG system. The study is based on detection of the Yellowness Index and the determination of the colour change. Various BMG compositions were cast into plates of 2 mm thickness and polished specimens were stored under different atmospheric conditions in order to detect the rate of the surface tarnishing as a function of the corresponding environmental condition. For the first time the colour change rate was quantified for any BMG system during exposure to air. A standard sulphide immersion test was also performed. Microstructural examinations of the tarnished surfaces were performed by STEM, TEM, FIB and XPS, revealing important information towards the understanding of the tarnishing mechanism.

2. Experimental methods

Bulk metallic glass specimens of compositions listed in Table 1 were produced starting from the pure elements by using a Topcast TCE10 centrifugal casting device. The pure elements, with purity greater than 99.995%, were inductively heated in a quartz crucible coated with zirconia and the melt was cast into a split copper mould with plate geometry. The dimension of the mould cavity was 2 × 12 × 47 mm. The copper mould was not water cooled and the temperature of the mould in the vicinity of the cavity was monitored during the casting procedure. The Cu mould was massive and only a slight increase of the temperature of 3–5 °C has been detected during each casting. Each sample was mechanically ground with SiC papers down to 1200 grits and polished with suspensions of diamond particles with size from 6, down to 3, and to 1 μm. This procedure is hereafter called the standard polishing procedure. Prior to all experiments, the specimens were shown to be x-ray amorphous by X-ray diffraction (XRD). The onset temperature of the glass transition, T_g, was detected using small specimens representing the tips of the plates by differential scanning calorimetry (DSC) by scanning from 0 °C at a heating rate of 20 °C/min with a Perkin Elmer Hyper DSC 8500. Standard polished specimens of approximately 1 cm^2 surface area of different compositions were stored together under controlled and stable storage conditions of temperature and air atmosphere. The controlled room temperature (RT) condition was 23 °C ± 2 °C with 50% ± 5% humidity. The storage of specimens at 37 °C ± 1 °C and 75 °C ± 1 °C was performed in furnaces at laboratory atmosphere (not air-conditioned). Additionally, for the $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ composition, one specimen was stored at 75 °C ± 1 °C under constant Ar flux, one in vacuum at RT, one in a desiccator at RT filled with laboratory air, and one specimen in a freezer at −18 °C ± 1 °C.

The standard sulphide immersion testing was performed with specimens with surface areas of approximately 1 cm^2 and followed the standard test procedure: DIN EN ISO 1562:2004. Prior to the immersion test, the specimens were embedded in an epoxy resin material and standard polished as described above. After an initial colour detection, the samples were installed together in a testing device that automatically immersed the surface of the specimens in the solution every 60 s for a period of 13 ± 2 s of submersion time. The testing solution was a sodium sulphide aqueous solution of 0.1 mol/l of Na_2S. The solution was prepared by dissolving 22.3 g of sodium sulphide hydrate, $Na_2S \times H_2O$ (about 35 wt.% Na_2S) in twice deionized water until a final volume of 1000 ± 3 ml was achieved. During the first 72 h of testing, the test was interrupted every 24 h, the solution was renewed and the samples were removed and cleaned with ethanol and subjected to the colourimetric detection. The time out of the immersion testing apparatus was minimized and the samples were promptly re-installed in the automatic device for further immersion testing. After 72 h the immersion was automatically cycled every 60 s as described above for an additional 96 h without exchanging the solution, and the colourimetric detection was performed only at the end, after an overall testing time of 168 h (7 days).

The colourimetric analyses were performed on 1 cm^2 surface areas using 10 × 10 × 2 mm specimens. The initial colour was detected shortly after the top surface was standard polished and, afterwards, the colour change was detected regularly during the storage in controlled and stable conditions and during the sulphide immersion testing. The change in colour was determined according to the standard DIN 6174. Applying the standard DIN 5033-3, the colour is represented by three coordinates: L^* for luminescence, a^* for colours in the range from red to green, and b^* for colours in the range from yellow to blue. Using these colour coordinates, the colour change ΔE was calculated as:

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2} \tag{1}$$

The Yellowness Index (YI) was calculated according to the standard ASTM D1925. This is a numerical grading system to categorize the whiteness of white gold alloys [17,18]. The YI index is used to describe the aberration from a perfect white towards a yellowish colour, and quantifies the quality of commercial white gold alloys, as white gold tends to have a yellow component in its colour. A YI value between 0 and 19 is attributed to a premium white colour which is most desirable, while a YI between 19 and 24.5 describes a standard white. Off-white colours possess a YI value of 24.5–32 and colours with a YI exceeding 32 are called non-white. The upper

Table 1

Studied bulk metallic glass compositions with corresponding glass transition temperatures, T_g, and Cu/Si and Au/Si nominal atomic ratio and Yellowness Index values, YI. The T_g are the onset temperatures of the calorimetric glass transition signals during up-scans with 20 °C/min. The YI characterizes the whiteness of white gold alloys and are detected in this work soon after grinding and polishing the surfaces of freshly cast materials. A value of Yellowness Index below 19 is considered a premium white gold colour.

BMG composition in at.%	$T_{g(onset)}$ in (°C)	Atomic ratio Cu/Si	Atomic ratio Au/Si	Yellowness Index after polishing
$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$	128	1.65	3.01	17.80
$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{25.9}Si_{16.3}Al_1$	120	1.59	3.01	15.01
$Au_{50}Ag_{7.5}Cu_{25.5}Si_{17}$	104	1.50	2.94	14.74
$Au_{60}Ag_{7.5}Cu_{15.5}Si_{17}$	86	0.91	3.53	16.09
$Au_{60}Ag_{5.5}Pd_2Cu_{15.5}Si_{17}$	95	0.91	3.53	17.28
$Au_{65}Ag_{7.5}Cu_{10.5}Si_{17}$	69	0.62	3.82	18.01

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