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On the abnormal room temperature tarnishing of an 18 karat gold bulk metallic glass alloy

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ABSTRACT

The amorphous 18 K white gold alloy of the composition $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ at% possesses a premium white-gold color and a Vickers hardness value 1.5 times that of conventional white gold alloys. These properties, together with the low melting temperature of ca. 370 °C and its good processability are highly desired for jewelry applications. Nevertheless, the premium white color of this alloy is unstable and turns into a yellowish brown color after some time. The intense tarnishing of the $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ at% bulk metallic glass alloy under various different environmental conditions has been investigated by SEM, STEM, TEM, and Auger spectroscopy (AES) and linked to a chemical interaction between the copper and the silicon of the alloy. A mechanism behind the tarnishing is discussed in detail and suggestions are made for future alloy development towards a tarnish resistant 18 K amorphous white gold alloy.

1. Introduction

The amorphous white gold alloy $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ at% was first introduced in 2005 [1] and is considered an interesting alloy for jewelry production, as it has a gold content of 76 wt% (18 K), an attractive color [2], and a comparatively high hardness of about 360 HV1, which exceeds typical hardness values of conventional white gold alloys 1.5 times (about 220 HV1). As precious metal alloys are usually very soft and therefore prone to be scratched or even deformed, achieving such a high hardness is of great interest for jewelry applications. For decorative applications, the color of an alloy is also important. The "whiteness" of a white gold is usually quantified by the so called yellowness index YI [3] and was previously reported to be 25.3 [4] for $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ (at%), which corresponds to a "standard-white" or "off-white" category [3]. Recent studies [5] have shown that the alloy even has a "premium white" color with an average YI of 17.7 when it is measured on a freshly polished sample surface. Nevertheless, the white color is not stable and assumes yellow-like colors rather quickly, after just a few hours of exposure, and it forms corrosion-like products on the surface after being worn as a jewelry item [2,5]. This tarnishing is detrimental to decorative applications and turns out to be the major obstacle for applications in the jewelry sector. This study investigates the tarnishing behavior of $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ with regards to possible decorative applications and gives recommendations for its improvement.

2. Experimental

Amorphous granules with the composition $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ (at%) in spherical shape were produced by melting the pure elements (purity $\geqslant$ 99.99 at%) in a modified Indutherm VC500 casting device equipped with a graphite crucible with a small nozzle at the bottom. The melt was forced through the nozzle by applying a high argon pressure on the melt surface. Melt droplets then first fell through air into a water/ethanol mixture at room temperature inside a quenching tank, which provided the sufficient cooling rate to bypass crystallization and to form a glass. Later the free fall distance was fluxed with Ar to reduce oxidation. The majority of the spheres had a diameter ranging from 0.7 to 2 mm, and these were used in this study. The carbon contamination from the graphite crucible in the final product was measured by GDOES spectroscopy to be below the detection limit (0.005 wt%).

Sample 1 is a fully amorphous plate of $2 \times 10 \times 30$ mm. It was produced by applying copper mold casting in an Indutherm MC15 according to the casting routine described in [4]. One side of the sample was polished prior to storage to remove the original cast surface. This sample was not kept under controlled environmental conditions, but was handled with bare hands for various different investigations and then stored in a plastic sample bag for about 30 months. During the handling, the sample probably faced different forms of pollution and grades of humidity in its environment including sweat from touching the sample with bare hands.

Samples 2–5 were cast fully amorphous in plate geometry ($2 \times 12 \times 47$ mm) applying copper mold casting in a Topcast TCE10 centrifugal casting device.

The pure elements were melted in an yttria coated quartz crucible and directly cast into a Cu mold with a plate geometry.

The tarnishing layers on the samples surfaces were investigated by preparing thin lamellas cut normal to the tarnished surface with a focused ion beam and analyzing the lamellas in STEM modus (30 kV). A semi-quantified analysis of the chemical composition was carried out with an Oxford EDX system. The TEM investigation was carried out with a Jeol JEM 2010.

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The tarnish tests were carried out for 7 days at 37 °C in simulated body fluids (artificial sweat and saliva), according to the test standards DIN EN ISO 10271 and DIN EN 1811. The sample surfaces were grinded prior to testing in order to remove possible oxide residues of the casting process. Two samples were separately tested for each test solution (samples 2–5).

3. Results

At the beginning of this study the granules fell freely in air into the quenching tank and were found to be covered with an oxide layer of up to 100 nm thickness on the surface, which was detected by SEM/EDS analysis to be SiO_2. An etching treatment with hydrofluoric acid (HF) removed this SiO_2 layer from the granules. The surface oxidation was later reduced by minimizing the distance between crucible and the surface of the quenching liquid and by fluxing the atmosphere with argon gas. The majority of the granules produced under Ar flux showed a very smooth surface and the oxide film was too thin to be detected.

In sharp contrast to polished samples, as-cast granules (not etched or otherwise treated) were kept several months at room temperature in air without showing signs of the tarnishing related color change. To investigate the tarnishing behavior of the granules, one badge of granules was subjected to HF etching to remove the cast SiO_2 and subsequently aged at 75 °C in air. Fig. 1 shows the granules as-cast and after aging at room temperature and at 75 °C. Already after 7 days, a distinct change in the color could be observed in the HF-treated badge (see Ref. [2]), whereas the untreated granules remained white. After 37 days at 75 °C in air, the HF-etched granules assumed an overall dark yellow color; the untreated aged granules gradually began to tarnish as well. Storing the granules in air at room temperature for two years had almost no effect on the granules colors. The corresponding XRD spectra (not shown here) did not show signs for the formation of crystals caused by the heat treatment.

The polished surfaces of bulk specimens tarnished more rapidly than the granules in as-cast conditions. They behaved similarly to the etched granules. The tarnishing effect was noticeable even at room temperature after few hours. The effect was worse if the material was in contact with body fluids such as sweat.

Fig. 2 shows the investigation performed on sample 1 thirty months after its production. The plate was polished on one side, handled with bare hands, and used for various experiments which include XRD, color detection, cutting with cooling fluids, etc., then stored in the laboratory in a plastic bag without careful cleaning. The surface of this plate was affected by severe tarnishing, more distinctively on the polished side. The tarnishing layer on the polished side was analyzed in a FIB cut cross section by STEM (Fig. 2a) and by Auger spectroscopy (Fig. 2b). The external layer labeled with (1) is about 20 nm thick and enriched in Cu and S, with a ratio Cu:S of 2:1. Underneath this layer, the sub-surface corrosion layer (2) is enriched in Si and oxygen. The metallic matrix (3) has approximately the overall alloy composition of $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ (at%), this was determined by an EDX analysis in region 3 of Fig. 2a.

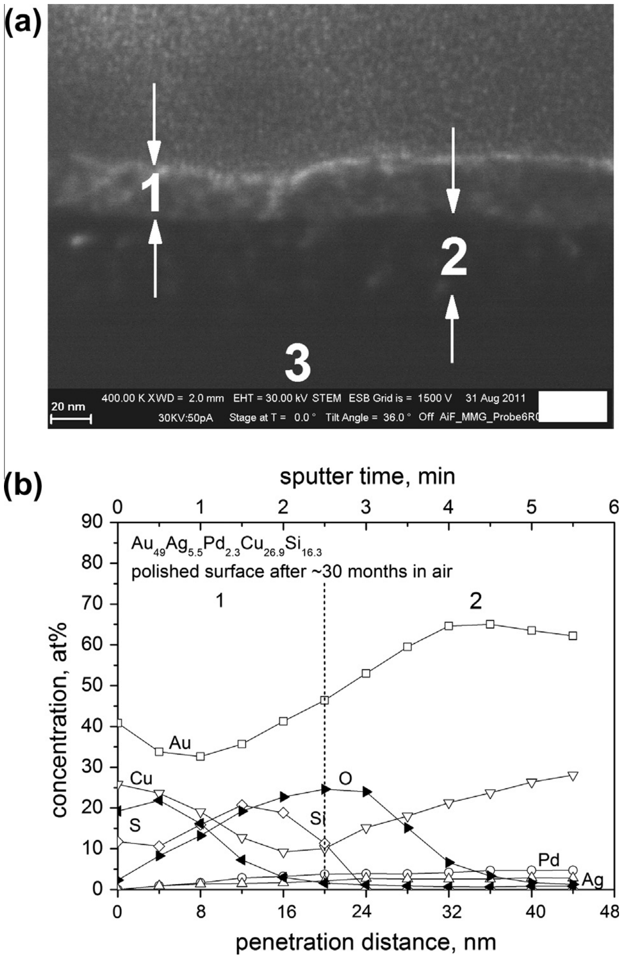

Fig. 2. (a) Cross section STEM photomicrograph of sample 1 (2 × 10 × 30 mm) of $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ after storage of 30 months in laboratory air and room temperature. (b) Auger electron spectroscopy (AES) concentration profile performed on a highly corroded location on the surface of the plate. A 20 nm surface corrosion scale of copper sulfide was detected. More internally silicon oxide was found to a maximum depth of 24 nm. No silicon is found in the matrix underneath the corrosion scale from 24 to 44 nm and apparently the Si depletion area is enriched in Au and Pd and depleted in Ag.

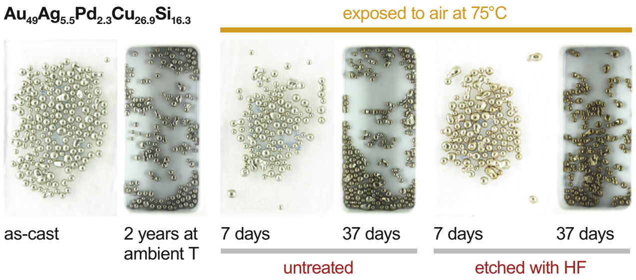

Fig. 1. Granules in as cast condition and aged at room temperature and at 75 °C in air with and without an etching treatment with HF, the apparent darker color in the later photos is an issue of the light conditions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Samples 2–5 were grinded and subsequently subjected to simulated body fluids. Some residual pores from the casting were present on the surface due to air pockets in the copper mold. In these locations, the plates were not grinded, leaving the original casting surface intact. After the test, the grinded surface areas showed a reddish color indicating a severe tarnishing, while the pore surfaces retained their initial white color (see also [2]). Only in locations where the pore surfaces were randomly scratched during the grinding procedure, the samples showed a red tarnishing as well. The metal release into the test solution per cm^2 sample surface was analyzed after the test, showing a copper concentration of 0.017 and 0.026 mg/cm^2 in artificial sweat (samples 2 and 3) and 0.058 and 0.062 mg/cm^2, respectively, in artificial saliva (samples 4 and 5). Only a comparatively small amount of Si was found in both test solutions, ranging between 0.0012 and 0.0024 mg/cm^2. The noble elements concentration in the test solution was below the detection limit.