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Development of novel 18-karat, premium-white gold bulk metallic glasses with improved tarnishing resistance

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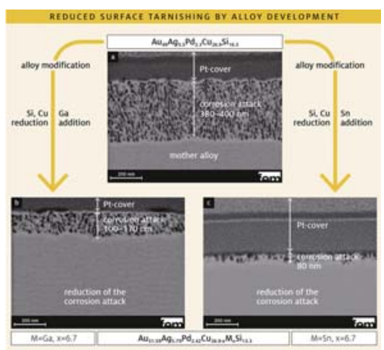
HIGHLIGHTS

- Partial substitution of Cu by Sn and Ga enabled a shift of the glass-forming region towards a lower Si content.
- The variation of the glass-forming ability is attributed to changes in the reduced glass transition temperature and in the driving force for crystallization.
- The novel compositions exhibit improved tarnishing resistance.
- The corrosion improvement goes beyond a simple reduction of out-diffusion due to the reduction of Cu and Si.

GRAPHICAL ABSTRACT



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ABSTRACT

The 18kt gold-based bulk glass-forming composition $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ is modified in order to reduce its fast surface tarnishing caused by internal oxidation of Si, partitioning and fast out-diffusion of Cu and Au. By partially substituting Cu by the species Ga or Sn, the formation of Si as primary crystalline phase is facilitated and a distinct increase of the liquidus temperature is observed. It is found that a reduction of the Si content recovers the glass-forming ability of the novel Ga/Sn-containing alloys, reflected by an increasing reduced glass transition temperature, T_{rg}, and a decreasing driving force for crystallization. This strategy is used to reduce the amount of Cu and Si, which are responsible for the fast surface tarnishing. Corrosion studies of the novel alloys reveal that the Cu release into an artificial saliva test solution is up to eight times lower than that of the mother alloy and the corrosion depth in artificial saliva is drastically lowered by 50% for the Ga-bearing alloys and by 80% for the Sn-bearing alloys.

1. Introduction

The eutectic Au-Si system was the first metallic system to be obtained as a glass from the liquid phase [1]. The amorphous flakes, obtained by splat quenching, showed poor glass-forming ability (GFA) and were unstable, resulting in certain decomposition and the occurrence of crystalline phases after 24 h at room temperature. The partial replacement of Si by Ge resulted in an increase of the thermal stability upon heating from the glassy state [2]. More recently, Pd, Ag and Cu were added to the binary Au-Si eutectic system and a number of Au-based bulk metallic glass (BMG) compositions with high GFA and high thermal stability were developed [3]. Among these, the most promising 18-karat BMG composition for jewelry and watch making applications is the

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$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ alloy, hereafter termed 'mother' alloy composition.

This alloy has a critical casting thickness, d_c, of 5 mm and a hardness of ~350–360 HV1 [3,4] (the Vickers hardness under a load of 1000 N), which is significantly higher than the hardness of conventional 18-karat crystalline gold alloys [5,6]. In addition, it exhibits a premium white gold color [7], which is highly desirable for jewelry items. With time, the premium-white color turns, regrettably, into an unattractive yellowish brown [7,8], making the alloy inappropriate for jewelry or dentistry applications. The surface tarnishing is abnormally fast, even at room temperature and it worsens in contact with saliva or sweat [4, 6–9]. The fast color change is induced by the partitioning of Au and Cu and the formation of Cu_2O or Cu_2S products on the surface. The Cu corrosion products are observed to dissolve into liquid test solutions and the amount of Cu dissolution is evaluated as a measure for corrosion attack. This process is connected to the inwards growth of amorphous SiO_2 in dense branching morphology, which results from the internal oxidation of the amorphous metallic matrix [7]. A reduction of the Cu content slows the rate of the color change down and transforms the paralinear tarnishing rate of the mother alloy into a pure logarithmic rate behavior, characteristic for passivating oxidation [7]. Furthermore, it was proposed that the tarnishing of Au-based BMGs could be brought to acceptable rates if the Cu/Si and/or the Au/Si ratios are changed significantly [7].

The corrosion/oxidation resistance and the GFA of a BMG composition are two decoupled material properties, making the development of bulk glass-forming alloys, exhibiting a high performance in both fields, challenging. In general, the addition of elements that act to reduce the environmental interaction [6,10–12] do not necessarily act to increase or maintain the GFA of the mother alloy, and in many cases the GFA is reduced [6,10]. To improve the tarnishing resistance of Au-based BMGs, Cr, Co and Ni are not the elements of choice due to the occurrence of skin irritations and allergic responses [13].

This study aims at the development of an Au-BMG with improved tarnishing resistance by reducing the content of disadvantageous elements (Cu, Si). As the major field for applications of this alloy family lies in the decorative applications, certain Au contents are favored, meeting the hallmarking conventions in the jewelry and watch market. Hence, the gold content should not be below a certain weight percentage. Specifically, a weight percentage of 75% gold, resembling an 18-karat composition (solid, red line in Fig. 1), was considered as target composition in this case.

For the Au-Cu-Si system, the glass-forming region (GFR) is found along the narrow compositional region along the eutectic trough at almost constant Si concentration [15,16] and is schematically marked in the liquidus projection in Fig. 1 [14]. The GFR is a compositional region with low nucleation temperatures for crystallization upon solidification [17]. The degree of undercooling of a liquid and the corresponding GFA directly depend on the driving force for nucleation, the intrinsic diffusivity, and the interfacial energy between the primary precipitating phase and the liquid [18,19]. The lowest nucleation temperatures were found at the transition point from the fcc primary Au-phase to the diamond cubic primary Si-phase [17]. It has to be noticed that along this narrow GFR, the alloys with a low Cu and high Au content, on the one hand exhibit an enhanced corrosion resistance [7], on the other hand their glass transition temperature is located far below 373 K (100 °C) [15], limiting their potential for commercialization.

Based on the above considerations, we have successfully developed several 18-karat premium white gold BMG compositions with improved tarnishing resistance by shifting the GFR towards a lower Si concentration through substituting Cu. Here, we report on the criteria that were applied to develop the novel compositions as well as on their processability for jewelry and dentistry applications.

2. Experimental

The samples were produced by melting the pure elements inductively (purity >99.95%) in an Al_2O_3 crucible in a high purity argon atmosphere (vacuum of ~5×10^{-3} mbar prior filling with Ar containing ~0.5 ppm oxygen) and pouring them into a water-cooled Cu mold

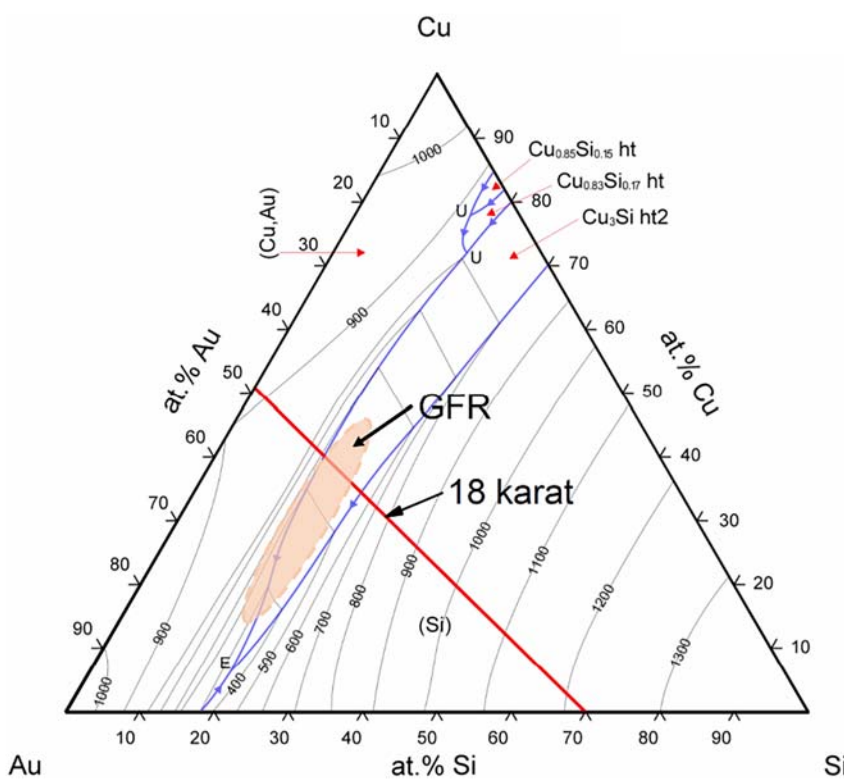

Fig. 1. Liquidus projection of the Au-Cu-Si phase diagram [14]. The GFR spreads along the Au-Cu axis at an almost constant Si content. The solid, red line represents the 18-karat border, below which the alloys possess a Au content of at least 75 wt%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)