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Influence of crystallinity on thermo-process ability and mechanical properties in a Au-based bulk metallic glass

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ABSTRACT

The present investigation addresses the impact of crystallinity on the mechanical properties: hardness (HV) and toughness (K_{IC}) in an $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ BMG which appears especially attractive for applications in jewelry and watch making industries. Thermal stability is first determined using differential scanning calorimetry (DSC), X-ray diffraction and thermo-mechanical analysis (TMA). Then the conditions (time, temperature) in which crystallization is observed (during annealing above the glass transition temperature) and the kinetics are determined. Results show an increase of hardness proportional to the volume fraction of the crystalline phase (ϕ) (from about 350 HV up to about 480 HV), and a drastic reduction in fracture toughness from about 20 MPa$\sqrt{m}$ down to 1.5 MPa$\sqrt{m}$ for fully crystalline structure. Finally the conditions required achieving a good compromise between hardness and toughness are established.

1. Introduction

Bulk metallic glasses (BMGs) are very attractive new materials since they combine a high mechanical strength and a high toughness [1–5]. Indeed for instance in many Zr-based BMGs the elastic limit is typically 2 GPa, with a toughness as high as 100 MPa$\sqrt{m}$. Recently BMG based on precious metals have been developed, especially based on gold [6–18]. The gold alloys are used in jewelry and watchmaking industry for their esthetic appearance and inertia to the environment. For these applications, a hardness superior to 300 HV is desirable to facilitate the final machining and reduce the wear of the final product. The maximum hardness that can be obtained with the standard crystalline 18 karats gold (Au_{75}-$Ag_{12.5}$-$Cu_{12.5}$ (wt%)) through a combination of heat treatment and cold working is about 290 HV [19–24]. Gold-based bulk metallic glasses (BMGs) are an alternative as they present unique properties in comparison with crystalline counterparts, especially easy thermoplastic processing combined with a high hardness. Various compositions have been reported in the literature [7–13]. One of the most attractive one is that developed by Schroers et al. [7,8]. For this BMG, various physical and mechanical properties have been investigated in the literature. For instance, the fully amorphous structure exhibits a hardness of 350 HV and a toughness of about 20–25 MPa$\sqrt{m}$ [25].

However, these BMGs, like all other amorphous materials, are in an out of equilibrium state, due to the rapid solidification process used for their fabrication. Consequently a transformation as a function of time is expected, especially during annealing at fairly high temperature. This evolution can induce the crystallization phenomenon. Formation of crystalline particles may have a positive impact on some mechanical properties, like hardness or elastic modulus, but result in a drastic reduction in fracture toughness (1–2 MPa$\sqrt{m}$) comparable with silica glass. This influence has been reported in various BMGs, e.g. Zr-based [26,27] or La-based BMGs [28].

Nevertheless, some authors proposed the introduction of controlled crystallization phases as one of the methods to induce significant global plasticity. Usually BMGs fail catastrophically by the formation of localized extensive plastic deformation regions known as shear bands. Rapid propagation to failure of few shear bands is the main reason for the poor ductility. The ductility can be improved by initiation of a large number of shear bands promoted by crystalline phases. Raghavan et al. [29] have shown that an optimal amount of devitrification may also yield a BMG-matrix composite with desirable strength and ductility. Hays et al. [30] obtained an in situ ductile crystalline phase/BMG matrix composite in the Zr-Ti-Cu-Ni-Be system. This interesting microstructure leads to an increase in the plastic strain to failure, impact resistance and toughness of the metallic glass.

In the gold based BMG, a lot of studies concerning

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thermoplastic deformation in the supercooled liquid region have been reported, as well as concerning thermal stability [13–18].

However the influence of thermal treatment (and hence the influence of crystallinity) on the mechanical properties has not been precisely investigated. Therefore the present paper addresses this influence, mainly on hardness and toughness, two properties which are usually in "conflict".

2. Experimental procedures

2.1. Materials

The Au-based BMG specimens were produced applying pure elements and employing a Topcast TCE10 centrifugal casting device. The pure elements, with purity of at least 99.995%, were inductively melted in a quartz crucible coated with zirconia and the melt was cast into a massive split copper mould with a plate shaped cavity of 2*12*47 mm. The copper mould was not cooled during the casting process and the temperature of the mould in the vicinity of the cavity was monitored during the casting procedure. Only a slight increase of the temperature of 3–5 °C was detected during each casting. The composition has been controlled by EDX (Table 1), amounts are in atomic and in weight percent, i.e. this alloy can be hallmarked as 18 karats.

2.2. Experimental techniques

Density has been measured by Archimedes's technique. To follow the thermal stability of the alloy, three methods have been used: DSC, X-ray diffraction (XRD) and thermo-mechanical analysis (TMA).

Differential Scanning Calorimetry (DSC) was conducted at a heating rate of 5 and 20 K/min using a standard commercial instrument (Pekin Elmer, DSC-7) under high purity dry nitrogen at a flow rate of 20 ml/min. Then the characteristic temperatures can be obtained: the glass transition temperature (T_g), the temperature corresponding to the onset of the crystallization (T_x) and then the supercooled liquid temperature region ($\Delta T = T_x - T_g$).

The as cast alloy was structurally characterized by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer, which produces the Cu Kα radiation The kinetics of crystallization was studied during isothermal annealing at various temperatures (130, 150 and 170 °C). After different annealing times, X-ray diffraction was performed at room temperature, to determine the percentage of crystallinity of the specimen. In-situ experiments were also carried out.

Thermo-mechanical analysis (TMA) experiments were performed using a classical dilatometer (Setaram TMA 92-1750), with a purified argon gas to avoid oxidation of the samples. In this test, a constant load of 0.05 N was applied on the sample through a tip with a diameter of 4 mm. The sample, a plate with a thickness of 2.6 mm, was heated and the penetration depth (ΔL) was recorded as a function of temperature or time during isothermal annealing. TMA is employed to examine the thermal expansion but it has been shown by Qiao et al. [31] and Kato et al. [32] that viscosity can be deduced too. The knowledge of this property is required to determine the process ability and the best conditions to perform this processing.

Young's modulus (E) and Poisson ratio (ν) have been obtained using the classical ultrasonic pulse echo technique. Vickers hardness of the as-cast and annealed alloys was performed at room temperature on mirror polished samples using a load of 300 g.

Fracture toughness measurements (K_{IC}) of the as-cast and annealed alloys were conducted on single edge notched beam. For this test, specimens of dimensions 30*3*2 mm were cut from the plates using electric-discharge machining. Large notches have been first manufactured using a 0.3 mm thick diamond disk and then a finer notch was created (with a root radius of 40 μm) using a razor blade manually covered with a 3 μm diamond paste, up to the final depth of a/w = 0.4–0.5 where a is the crack size and w the sample width (Fig. 1). To ensure a plane-strain condition, ASTM E 399 specifies that both specimen thickness (B) and crack length (a) must meet a minimum size requirement [33]. The following conditions $B > 2.5^*(K_{IC}/\sigma_y)^2$ and $a > 2.5^*(K_{IC}/\sigma_y)^2$ must be met in order to obtain consistent K_{IC} values. If we consider the values of literature [25] $K_{IC=}20$ MPa and $\sigma_y = 1$ GPa, the criteria are met.

The specimens were loaded in four-point bending on a Schenk Trebel 5kN compressive device operating at a constant displacement rate of 0.5 mm/min. The mechanical behavior can be quantified in terms of the energy of fracture G_{IC}, $G_{IC} = K_{IC}{}^2 1 - v^2$.

Fracture surfaces of the tested specimens were analyzed using a Zeiss Supra 55VP scanning electron microscope. The fracture toughness was also estimated using the method introduced by Xi et al. [34]. The scale of vein patterns (s) on the fracture surface of a glass is related to the fracture toughness (K_c) and the yield strength (σ_y) through Eq. (1).

$$s = 0.025.\left(\frac{K_{IC}}{\sigma_y}\right)^2 \tag{1}$$

3. Experimental results

3.1. Characterization of the as cast state

The XRD pattern, shown in Fig. 2, does not reveal any significant peak for the as-quenched material, indicating that it is fully amorphous.

Values of density (ρ), hardness (HV), Young modulus (E) and Poisson ratio (ν) are given in Table 2. Values reported in the literature are also indicated. Results obtained in the present work are in agreement with those reported in the literature. Hardness is very high for a 18 karat gold alloy. Indeed, a value of maximum 250 HV is generally obtained for classical crystalline gold alloys. The value of the Poisson ratio (ν) is high. It has been shown by various authors [3,25,26,35] that plasticity in bulk metallic glasses is favored by a high value of this ratio (typically higher that 0.4), this result is a good indicator for the existence of a possible plasticity.

3.2. Thermal stability

Thermal stability was investigated by three methods (DSC, TMA, XRD) and compared. During continuous heating and isothermal annealing, the influence of the heating rate and the influence of the temperature have been studied.

3.2.1. Continuous heating

The DSC curves of the as-quenched state are shown in Fig. 3. Two different heating rates have been used, 5 and 20 K/min. The amorphous material exhibits a glass transition temperature, T_g, followed by a wide supercooled region with a temperature

Table 1
Chemical composition of the bulk metallic glass.

	Au	Cu	Si	Ag	Pd
At%	49	26.9	16.3	5.5	2.3
Wt%	76.5	13.5	3.6	4.7	1.9