Intermetallics 63 (2015) 73–79

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Bulk metallic glasses based on precious metals: Thermal treatments and mechanical properties

S. Cardinal [a, b], J. Qiao [a, b], J.M. Pelletier [a, b, *], H. Kato [c]

[a] Université de Lyon, CNRS, France
[b] INSA-Lyon, MATEIS UMR5510, F-69621 Villeurbanne, France
[c] Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan

ARTICLE INFO

Article history:
Received 15 December 2014
Received in revised form
9 March 2015
Accepted 4 April 2015
Available online 29 April 2015

Keywords:
A: Metallic glasses
B: Fracture toughness
B: Thermal stability
B: Glass transition and crystallization
B: Mechanical properties

ABSTRACT

The thermomechanical behavior of precious based metallic glasses has been investigated. Their compositions are free of nickel for biocompatibility. The gold-based BMG has a gold content resulting in 18 Karats alloy, a supercooled liquid region of 43 °C and a casting diameter up to 5 mm in rod. The compositions of platinum and palladium based BMGs are interesting as they can be formed into bulk glassy rods with diameter up to 15 and 30 mm respectively. The platinum-based BMG has a platinum content resulting in 850 Pt grade with a supercooling region reaching 58 °C. The palladium-based BMG is principally composed of 40 wt.% palladium and 32 wt.% platinum, with a large supercooling region reaching 73 °C.

The thermoplastic deformation of these BMG has been examined using thermomechanical analyser (TMA) and the results show that the alloys can be easily processed in the supercooled liquid region. During thermal processing, crystallization must be controlled since it improves hardness and elastic modulus, but embrittles the alloys and stops the deformation. The high hardness of Au-, Pt- and Pd- base BMGs (respectively 340, 420, 460 HV) twice the value of conventional precious metals, coupled with good properties for superplastic forming in the supercooled liquid region made them promising materials for watch making and jewelry applications.

1. Introduction

Precious metals and their alloys are used for many applications, especially in jewelry, due to their aesthetic appearance and inertia to the environment. One of the most important mechanical properties for material used in jewelry is its hardness [1–3]. For instance, in the watch industry, in addition to good processability, a hardness superior to 300 HV is desirable to facilitate the final machining watch cases and reduce wear and scratching of the final product. A good toughness is also required so as to limit the brittleness. Unfortunately, pure gold, pure platinum or pure palladium are rather soft and thereby vulnerable to wear and scratching. Alloys based on these pure metals have been developed. Their mechanical properties have been improved but they remain not excellent, and this limited improvement is achieved only after complex thermo-mechanical treatments [4–6].

In recent years, a number of new bulk metallic glasses (BMG) forming alloys have been developed. These alloys show an extraordinary ability to resist crystallization and may solidify as a glass when cooled at sufficient rates [7–15]. They exhibit attractive mechanical properties and an excellent processability at a moderate temperature, as illustrated for instance by Kumar et al. [16–18], who investigated molding and usage in electrochemical applications. A lot of different alloys have been proposed in the literature, e.g. Zr-, Cu-, Ti- or Mg- based metallic glasses, but also based on precious metals, like Au [19–28], Pt [29–31] or Pd [32–38]. In the as-cast state they exhibit a high hardness, a very high yield stress and a good elastic modulus. However, during the thermo-processing operation these materials have to be heated and since they are in an out of equilibrium state, modifications of their atomic arrangement may occur. Crystallization may be observed during this processing operation and this structural modification has a lot of consequences on the mechanical properties of BMGs [39–42]. This influence is fairly well documented in many BMGs (like Zr-

* Corresponding author. Université de Lyon, CNRS, France.
E-mail addresses: sandrine.cardinal@insa-lyon.fr (S. Cardinal), jichao.qiao@insa-lyon.fr (J. Qiao), jean-marc.pelletier@insa-lyon.fr (J.M. Pelletier), hikato@imr.tohoku.ac.jp (H. Kato).

http://dx.doi.org/10.1016/j.intermet.2015.04.003
0966-9795/

based metallic glasses). Unfortunately, information related to influence of thermal treatments on mechanical properties in precious-based BMGs is still limited so far. Data related to the thermal stability of alloys can be determined using conventional methods, like differential scanning calorimetry (DSC), X-ray diffraction (XRD) or electron microscopy. However since the mechanical properties of BMGs are very sensitive to the microstructure, thermo-mechanical analysis may be also a very suited method to follow in situ the microstructural state evolution [43,44].

Thus, the current work explores the influence of thermo-mechanical treatments on the crystallization of Au-, Pt- and Pd-based BMGs and the consequence on their mechanical properties. Various heat treatments have been performed to modify the structural state.

2. Experimental methods

2.1. Materials

BMGs have been elaborated in the Institute for Materials Research, at the Tohoku University, in Sendai (Japan). Au-based BMG was produced in melting equipment under argon atmosphere. Samples were made using copper-mold casting method. Pd- and Pt-based BMGs, which contain phosphorus, were prepared by melting the elements in a quartz tube under B_2O_3 flux and water quenched. Rods with 5 mm in diameter and 25 mm in length were obtained.

The composition of these BMGs were selected as they are free of biotoxic elements [45], especially nickel and close to those of classical alloys used in jewellery (Table 1). Composition of gold corresponds to 18 karats and that of the Pt-based BMG to 850 Pt grade.

Density has been measured by Archimede's technique and dense materials are obtained. Values are as follows: 11.1 g/cm^3, 15.5 g/cm^3, 13.5 g/cm^3, for Pd-, Pt- and Au-based BMGs, respectively.

2.2. Experimental techniques

Thermal stability has been investigated by DSC and in-situ XRD and thermo processability has been studied by thermo-mechanical analysis (TMA).

The thermal properties of the BMGs were determined using DSC, which was conducted at a heating rate of 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. To ensure the reliability of the data, a temperature calibration was performed before conducting the experiments with indium and zinc standard specimens, giving an accuracy of ±0.2 K and ±0.02 mW, respectively. 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 ($\Delta T_x = T_x - T_g$).

The amorphous nature of the BMGs was characterized by XRD at room temperature. The XRD equipment was a θ–θ Bruker D8 Advance system (Germany) using Cu K_α radiation ($\lambda = 0.1540$ nm). The working voltage of the instrument was 40 kV and the current was 40 mA. The intensity data were collected by a linear detector (LynxEye).

Kinetics of crystallization were studied by high temperature X-ray diffractometry (HTXRD). The in-situ experiments were performed using an Anton Paar HTK 1200 oven chamber, under a high vacuum. The initial heating was carried out with a heating rate of 20 K/min. The sample was kept at constant temperature and the X-ray measurements were started after a holding time of 10 s, in the 2θ region of 28°–52°. Spectra are registered either during continuous heating each 5 °C or during isothermal annealing at various temperatures.

Microstructure and deformation morphologies were observed by optical microscopy (OM, AXIOCam, Zeiss).

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 disk with a thickness of 2.6 mm, was heated with a heating rate of 5 K/min and the penetration depth (ΔL) was recorded as a function of temperature or time during isothermal annealing.

Young's modulus was determined by measuring the resonance frequency (Grindosonic apparatus). Vickers hardness tests were performed on mirror polished samples using two different apparatus: a Buehler Micromet 5104 for loads lower than 1 kgf and a Testwell durometer for loads up to 30 kgf (see Table 1).

3. Experimental results

3.1. Structure and thermal stability

All the investigated metallic glasses were examined by X-ray diffraction. No Bragg peak was detected in the as-cast specimen, indicating the amorphous nature of these states. Fig. 1 shows the DSC curve obtained for the Au-based BMG with a heating rate of 20 K/min. Similar curves are observed in all the alloys. Characteristics values are gathered in Table 2: T_g, T_x and ΔT_x.

The low glass transition temperature for the Au-based BMG has to be noted, compared with that of Pd- and Pt- based BMGs. This low value favorites the processability of the alloy at a low temperature. However, ΔT_x is an important parameter as it determines the domain in which the BMG is thermo-processable. In the case of the Au-based BMG, the domain is not wide (only 43 °C) and processability will be probably more critical. In addition to the value of T_g and T_x, some authors have also taken into account the liquidus temperature value (T_l) and introduced some parameters combining T_g, T_x and T_l [46–48]. It is a refinement on the glass forming ability of metallic alloys and a more precise indicator. However, the value of ΔT_x is a first and simple indicator.

The thermal stability has also been investigated using in situ XRD experiments. Two tests have been performed: Continuous heating to evaluate the effect of temperature on crystallization and isothermal annealing at a temperature between glass transition and crystallization temperatures to evaluate the effect of time.

Fig. 2(a) and (b) show the results obtained for the palladium composition. The scans in Fig. 2(a) are given from room temperature to 400 °C. The alloy is initially fully amorphous (only a very broad hump is observed). At 315 °C, peaks appear and grow until complete crystallization. Crystallization appears earlier in XRD compared to values expected from DSC experiments (350 °C). This can be explained by a low heating rate. Indeed the heating rate during DSC is 20 K/min. Taking into consideration the duration required for any XRD spectrum (typically 5 min), obtained each 5 K,

Table 1
Composition (in at.% and wt.%) of the investigated BMGs.

Composition	at.%. / wt.%	at.%. / wt.%	at.% / wt.%	at.% / wt.%
AuCuAgSi	50 at.% Au (77.2 wt.%)	25.5 at.% Cu (12.7 wt.%)	7.5 at.% Ag (6.3 wt.%)	17 at.% Si (3.8 wt.%)
PtCuCoP	60 at.% Pt (85.3 wt.%)	16 at.% Cu (9.3 wt.%)	2 at.% Co (0.9 wt.%)	22 at.% P (4.5 wt.%)
PdPtCuP	35 at.% Pd (40.5 wt.%)	15 at.% Pt (32.0 wt.%)	30 at.% Cu (20.7 wt.%)	20 at.% P (6.8 wt.%)