Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

A new, toxic element-free Mg-based metallic glass for biomedical applications

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ARTICLE INFO

Keywords:
Metallic glasses
Biomaterials
Mg alloys
Thermal stability
Mechanical property

ABSTRACT

As part of a project to develop new and more performant types of metallic glass (MG) for use in biomedical applications, we developed a new ribbon-metallic glass with two different compositions, $Mg_{(85-x)}Ca_{(8+x)}Au_7$ (with x = 0, 2, 4) and $Mg_{(81-x)}Ca_{10}Au_7Yb_{(2+x)}$ (with x = 0, 8). The super-cooled liquid region was evaluated to be ΔT = Tx − Tg = 22 °C, where Tx is the temperature of crystallization and Tg is the glass transition temperature. The thermal stability of this material was investigated using different measurement methods. No crystallization was detected after 30 min at 120 °C, which is of major interest for sterilization processes in the medical field. Resistance to crystallization was also investigated. All the results highlight the suitability of this new metallic glass for biomedical applications.

1. Introduction

The progressive ageing of the world's population has increased the need for improved and longer-lasting materials for use in biomedical devices. The majority of current medical devices are either made of ceramics or metallic alloys composed mainly of Titanium [1,2], which is known for its reliable biocompatibility. However, the most well-known of these common titanium alloys, Ti-6Al-4V, can contain vanadium and aluminum. The latter have been identified as potentially toxic ions. The design of a new alloy that provides reliable mechanical characteristics without negative effects on the human body is a current challenge for the biomedical sector. Crystalline alloys containing biocompatible elements such as magnesium are now commonly used for orthopedic implants or substitutes for cranial bones, especially in pediatric surgery [3,4].

Metallic glass is a new kind of material that has attracted increasing interest over the past fifty years. Since the elaboration of the first metallic glass $Au_{75}Si_{25}$ by Klement et al. [5] in 1960, these materials have been used in a wide range of fields for the development of magnetic devices, microsystems and aeronautic or biomedical applications. From a general point of view, the absence of grain and grain boundaries provides mechanical strength and resistance to corrosion, making this product an ideal candidate for use as a biomaterial.

It was thus logical to develop Mg-based amorphous alloys for the biomedical field from 1988 onwards [6]. Compared to other bulk metallic glasses (BMGs), these alloys presented a low Young's modulus close to that of human bone, thus providing a stress-shielding effect and avoiding osteolysis [7], in which a high Young's modulus of the biomaterial results in the stress being carried by the biomaterial alone, leading to bone resorption. Non-desirable elements for the human body such as Ni, Cu or Be are often added to these alloys to increase the glass-forming ability, respect the empirical rules for the development of an amorphous alloy [8,9] and increase the mechanical properties of the biomedical glasses. However, a number of trials have created amorphous calcium [10,11] or magnesium [12,13] -based alloys containing different proportions of Mg and Ca. Mg and Ca are two of the main metallic elements contained in the human body. Nevertheless, the sole use of these two elements can cause brittleness, high sensitivity to oxidation and a rapid degradation of the alloy in the human body, leading to consequences such as osteolysis and stress-shielding problems. To avoid this, zinc is added to most glassy alloys as a catalyzer to slow the degradation of Mg and Ca. Zinc is one of the most abundant elements in the body, with 85% of this metal located in the muscles and bones [10]. As the glass-forming ability (GFA) increases with the number of components in the alloy, researchers attempted to add a fourth and fifth element to this initial system [14,15]. This combination of Mg, Ca and Zn breaks down in the human body without any risk of cytotoxicity and has a crucial advantage: these elements all actively stimulate the creation of bone cells [16,17]. However, the relatively rapid degradation of zinc casts doubt on a full biocompatibility of Zn, as

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https://doi.org/10.1016/j.jnoncrysol.2017.11.024
Received 14 September 2017; Received in revised form 2 November 2017; Accepted 10 November 2017

highlighted by Calin et al. [18].

This work focuses on the development of a fully biocompatible bulk metallic glass with higher stability in human body fluid and less brittleness. The first part of this work focuses on the development of reliable new compositions for Mg-based metallic glasses without toxic elements, as described by Calin and coworkers [18]: $Mg_{85-x}Ca_{8+x}Au_7$, with x = 0, 2, and 4 (at.%). This assertion will be validated with cytotoxicity tests. The second part of the study focuses on the addition of Yb to the alloy system. Au and Yb are fully biocompatible elements, and Yb is a rare-earth element used to thermally stabilize the alloy system or to increase the glass-forming ability. Two types of alloys were investigated:

- $Mg_{(85-x)}Ca_{(8+x)}Au_7$ where x = 0, 2 and 4
- $Mg_{(81-x)}Ca_{10}Au_7Yb_{(2+x)}$ where x = 0 and 8

The first investigations assessing the resistance to crystallization and thermal stability with and without Yb via differential scanning calorimetry and XRD measurements are reported here.

2. Experimental procedure

2.1. Sample preparation

The base materials were prepared using Mg (99, 9%), Ca (99, 9%), Au (99, 9%) and Yb (99, 9%). The components were weighed using a high precision balance. A higher Mg content was added to the alloy melt to counterbalance potential loss due to the evaporation of Mg. Preliminary tests revealed a difference of 2 to 3 at.% between the nominal composition and the EDX data. The master melt ingot was produced in a carbon crucible under high purity argon, using the induction melting technic. The ribbon samples were prepared using a custom-made melt spinning device under argon atmosphere by induction melting of the master alloy. When the ingot had melted, was a bright orange colour and showed a liquid-like behavior, it was ejected onto a single copper roller at a speed of at 2500 rpm. The composition containing 10% Yb was amorphous but was highly brittle and thus unusable. The compositions were checked by EDX for the $Mg_{85}Ca_8Au_7$ alloy.

The samples were approximately 5 mm wide with a thickness of 20–40 µm. These ribbons (Fig. 1) were cut into small squares measuring approximately 5 × 5 mm. The thickness of samples was checked by blocking the ribbon in a support under a microscope, and the width was measured using a caliper. Ribbons were used as samples because this composition does not present a sufficient glass-forming ability to allow bulk production.

2.2. Experimental methods

The amorphous character and the different steps of crystallization were examined via X-Ray diffraction conducted at room temperature. The small square samples were placed on a *Si*-support and exposed to Cu Kα radiation in a D8 Bruker device. The working conditions were 40 kV and 40 mA for the X-ray tube, with an angular range between 20° and 70°. Diffraction patterns were analyzed using EVA software [19].

The parameters, Tg, Tx and the range of the super-cooled liquid region of this new metallic glass were then determined by differential scanning calorimetry. Two devices were used for this purpose. A standard commercial device, the Netzsch DSC 204 F1, was used to carry out isothermal measurements under argon atmosphere. The heating rate before the isothermal step was set to 80 K/min and a slower rate, 10 K/min, was used for the last ten degrees to prevent the occurrence of an overshoot. The temperature was then maintained for 30 min. A Perkin Elmer DSC was used under high purity dry nitrogen at a flow rate of 20 ml/min for non-isothermal characterizations. For all tests, each sample was sealed in an aluminum can and an empty can was used as a control. To obtain optimal accuracy of the results during the experiments, all the samples have the same mass, 14 mg, with the exception of samples tested for the influence of the heating rate, where the sample weights about 20 mg.

Nano-indentation tests were also conducted to evaluate the Young Modulus and thus obtain information about the mechanical properties about the new glassy alloy. Indentations were performed using a Nano Indenter G200 (Agilent Technologies) with a Berkovich tip using the CSM Thin Film Method, with a depth limit of 500 nm and a surface approach velocity of 10 nm/s. The ribbon sample was fixed to a resin substrate with a thin layer of conductive silver paint.

3. Results

3.1. XRD analysis

XRD diffractograms of the metallic glasses are presented in Fig. 2. The observed shape is typically representative of an amorphous structure. The absence of a sharp crystalline diffraction peak confirms the amorphous nature of the newly developed glasses, with and without Yb in the alloy.

The diffractogram of the first experiment shows no trace of peaks, and all four samples are fully amorphous. However, the addition of Yb is clearly revealed to produce a more stable, non-crystalline alloy. After determining the amorphous character of the alloy, the different properties of the glass (Tg, Tx, etc.) were determined.

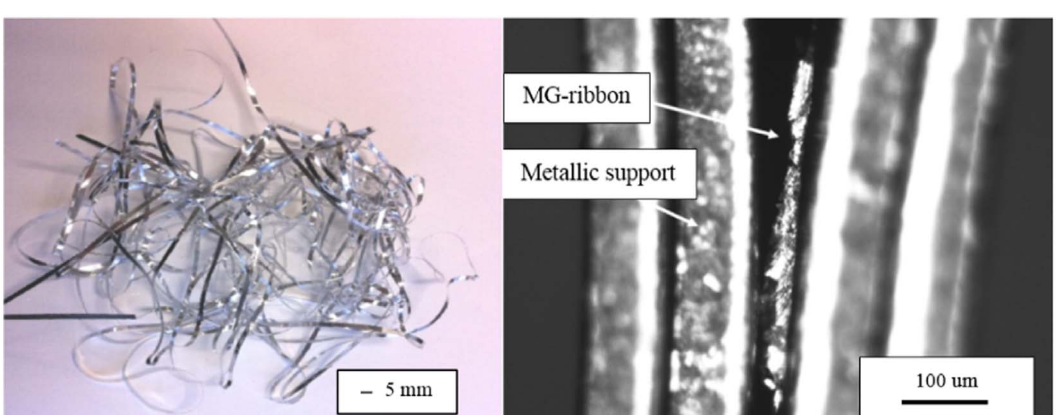

Fig. 1. Picture of the newly developed BMG.