Intermetallics 41 (2013) 35–43

Contents lists available at SciVerse ScienceDirect

Intermetallics

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

A study on the surface structures and properties of Ni-free Zr-based bulk metallic glasses after Ar and Ca ion implantation

Haoling Jia [a], Claudiu I. Muntele [b], Lu Huang [a], Xia Li [c], Gong Li [a,c], Tao Zhang [d], Wei He [a,e], Peter K. Liaw [a,*]

[a] Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996-2200, USA
[b] Center for Irradiation Materials, Alabama A&M University, P. O. Box 1447, Normal, AL 35762, USA
[c] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
[d] School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100191, China
[e] Department of Mechanical, Aerospace and Biomedical Engineering, The University of Tennessee, Knoxville, TN 37996-2200, USA

A R T I C L E I N F O

Article history:
Received 25 October 2012
Received in revised form
8 April 2013
Accepted 14 April 2013
Available online 16 May 2013

Keywords:
B. Glasses, metallic
F. Ion-beam methods
F. Corrosion behavior

A B S T R A C T

Ca or Ar implantation was performed on a $Zr_{46}Cu_{37.636}Al_{8.364}Ag_8$ (in atomic percent) bulk metallic glass (BMG) at 10 keV with a fluence of 8×10^{15} cm^{-2}. The effects of ion implantation on the surface microstructure, nano-hardness, and corrosion behavior of the Zr-based BMG have been studied. The results showed that the BMG specimen maintained an amorphous structure after Ar or Ca ion implantation. The thermodynamic stabilities were altered by ion implantation, and the relaxation of an amorphous structure is shown. The surface nano-hardness and corrosion resistance were enhanced after ion implantation. The efficient improvement of the surface performance by ion implantation on BMGs was analyzed and discussed.

1. Introduction

Bulk metallic glasses (BMGs) are metallic alloys, which could avoid crystallization during solidification and thereby vitrify at relatively low cooling rates [1]. Their amorphous microstructure yields excellent properties, such as high strength, elasticity, corrosion resistance, and unique processing capabilities [2–5]. The unique combination of chemical properties and processing capabilities makes BMGs a potential biomaterial for versatile implant applications. As potential biomaterials, BMGs with high corrosion resistance are required in order to survive the aggressive human-body environment. Moreover, the forces generated by the skeleton system can cause the fretting and fatigue of implants [6]. Thus, as a competitive candidate of implant materials, the mechanical behavior, such as the surface wear resistance and fatigue endurance, of Zr-based BMGs in a human-body environment should satisfy the requirement of the human body. In our previous work, the bio-corrosion [4], corrosion-mechanical behavior [6], and biocompatibility [7] of the BMG alloy, $(Zr_{55}Al_{10}Cu_{30}Ni_5)_{99}Y_1$ (atomic percent, at. %), were comprehensively studied, which suggest initial biosafety. However, the Zr-based BMG alloy contains a constituent element, Ni, which is toxic to the human body, despite its good corrosion resistance, corrosion-mechanical property, and biocompatibility. Development of Ni-free Zr-based BMGs was reported to have good corrosion resistance to a human-body environment [8], which renders them as potential biomaterials.

Surface properties are of great importance for biomaterials, such as bioactivity [9]. Surface modifications, like ion implantation and coating, are very common methods to improve surface-related properties, including wear and corrosion resistance. Investigations on the ion-implanted BMGs have been reported by other researchers. Daroczi et al. [10] studied the structure and the associated changes in magnetic properties of amorphous ribbons after ion implantation. Yang et al. [11] used a high acceleratory voltage of 40 kV to conduct Co implantation, and focused on the structure and surface-wear study. However, few attempts have been made, concerning the ion-implantation effects on corrosion and surface nano-hardness of ion-implanted BMG alloys. In the present work, calcium (Ca) ions were implanted to the surface of the BMG specimens, since Ca implantation has been reported to impart good properties to biomaterials, such as biocompatibility, bioactivity, osteoconductivity, direct bonding to bone, etc. [12,13]. As a reference, argon (Ar) ions were implanted based on the similar atomic

* Corresponding author. Department of Materials Science and Engineering, The University of Tennessee, 427-B Dougherty Engineering Bldg., Knoxville, TN 37996-2200, USA. Tel.: +1 865 974 6356; fax: +1 865 974 4115.
E-mail address: pliaw@utk.edu (P.K. Liaw).

0966-9795/$ – see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.intermet.2013.04.010

radius and weight between Ar and Ca atoms. A Ni-free metallic glass with the composition of $Zr_{46}Cu_{37.636}Al_{8.364}Ag_8$ was chosen to conduct the ion-implantation experiment, owing to its good glass-forming ability and excellent mechanical behavior at room temperature [14].

The critical issues of the present work are (1) to investigate the structure and thermal stabilities of the $Zr_{46}Cu_{37.636}Al_{8.364}Ag_8$ BMG before and after Ar or Ca (Ar/Ca) ion implantation; (2) to study the effects of Ar/Ca ion implantation on the surface nano-hardness of BMG specimens; and (3) to probe the effects and underlying mechanisms of ion implantation on corrosion behavior of as-cast and as-implanted BMGs in a simulated body fluid.

2. Experimental methods

Alloy ingots with a nominal composition of $Zr_{46}Cu_{37.636}Al_{8.364}Ag_8$ (at. %) were prepared by arc-melting the mixture of pure elements in an argon atmosphere. Rectangular plates (1 mm × 10 mm × 50 mm) were fabricated by copper-mold casting, which would be cut into small pieces with a size of 1 mm × 5 mm × 5 mm for ion implantation. The end of each specimen was polished to a 1200-grit surface finish to diminish the effect of surface roughness, and ultrasonically cleaned in distilled water.

Ar or Ca ions were implanted to BMG substrates at 10 keV, with a fluence of 8×10^{15} ions/cm^2, using an Eaton NV-200 implanter, which is a low-energy ion implantation. Therefore, the power input to the sample by ion bombardment is modest, and the substrate mean temperature rise is small (the substrate is clamped to a heavy metal holder with high thermal conductivity). An expected mean temperature increase of the BMG specimens is about 10–15 °C in the ion-implantation experiments, which would not bring major effects to the following analysis [15].

The amorphous microstructure was confirmed by the lab X-ray diffraction (XRD) within the resolution limit, using a Philips X-ray Generator 3100 operated at 45 kV and 40 mA with CuK$_\alpha$ radiation. Differential-scanning calorimetry (DSC, Perkin–Elmer DSC7) was used to characterize their thermal properties at a heating rate of 20 °C/min in an argon atmosphere. The specimens for DSC measurements were cut from the implanted samples composed of both the unimplanted substrate and implanted surface [as shown in the inset of Fig. 2]. DSC scanning was run twice for each specimen from 50 to 600 °C.

The damage to the ion-implanted samples was simulated by the Stopping and Range of Ions in Solids (SRIM) code [16,17], which is a collection of software packages that calculate many features of the transport of ions in matters, including the ion-implantation surface treatment. For the experimental fluence of 8×10^{15} ions/cm^2, the depth profile in displacements per atom (dpa) and the ion concentration induced by irradiation to the BMG substrates were calculated under full-cascade, using a theoretical density of 7.318 g/cm^3 and a threshold displacement energy of 40 eV. The SRIM-predicted damage profile is determined from the sum of the predicted vacancy concentration of Ar/Ca and the replacement collisions.

Nanoindentation measurements were carried out on the polished ends of the implanted/controlled specimens, over a square area of 40 × 40 μm^2 for the samples using a nanoindenter Hysitron TriboIndenter with a diamond Berkovich tip, which can be described as a sphere with a radius of 260 nm. For the implanted samples, the nanoindentation experiment is conducted on the implanted end of the BMG's specimen, without any more treatment on the implanted surface, since it is still smooth enough for the nanoindentation test. The applied loading/unloading rate is 200 μN/s. The measurement was repeated 6 times to obtain

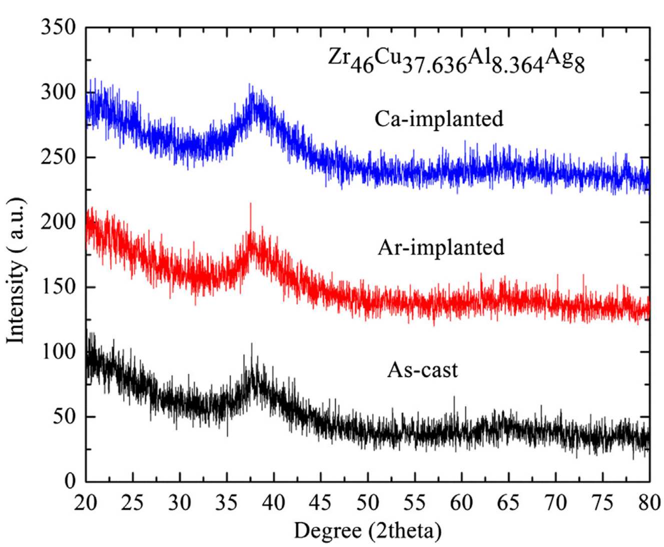

Fig. 1. The XRD patterns of BMGs $Zr_{46}Cu_{37.636}Al_{8.364}Ag_8$ before and after the Ar and Ca ion implantation, obtained from the top surface of the rectangular-plate BMG specimens.

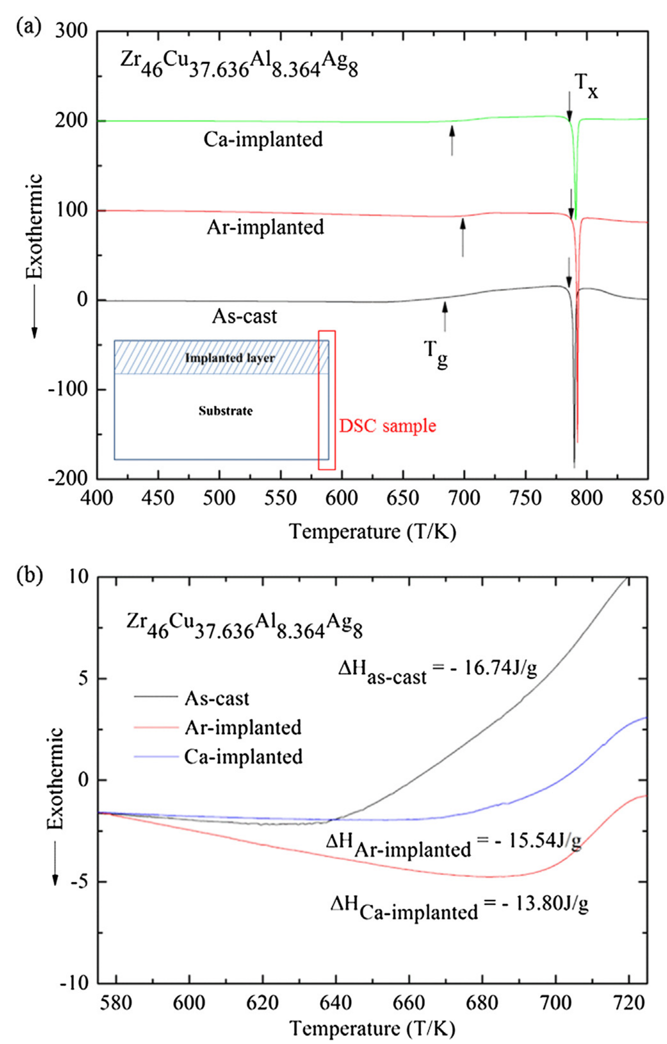

Fig. 2. (a) DSC traces of as-cast and as-implanted $Zr_{46}Cu_{37.636}Al_{8.364}Ag_8$ BMGs, and (b) an enlarged view of the glass-transition regime.