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An in-depth investigation of Mg-Zn-Ca metallic glasses: A first principles study

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ABSTRACT

The atomic structures, glass forming evolutions, mechanical properties and high pressure behavior of $Mg_{75}Zn_{20}Ca_5$ and $Mg_{60}Zn_{35}Ca_5$ bulk metallic glasses, which are promising candidates for biomedical implants, have been examined by using ab initio molecular dynamics simulations. The pair-distribution function and coordination number analyses show that increasing Zn content in the alloy results in a decrease in several bond distances and an increase in the total coordination number of each species due to the atomic size difference between Mg and Zn atoms. According to the Voronoi tessellation, bond pair and bond angle distribution analyzes, the fivefold geometrical arrangements (pentagonal-bipyramid) are the most predominant in the first coordination shell, indicating the stability of the amorphous states and their dense atomic packing. The most striking result emerged from the calculations of mechanical properties is that an increase of Zn ($\geq$30%) content in the alloy yields embrittlement in the alloys. Under uniaxial compressions, both compositions undergo structural failure between 6 and 8 GPa. Under hydrostatic pressure, a diminishing in fcc/hcp ordering and an enlargement of the ideal icosahedral ordering may indicate a more disordered structure. In our view, these results represent a good step toward understanding the atomic structures Mg-Zn-Ca bulk metallic glasses.

1. Introduction

Bulk metallic glasses (BMGs) have been attracting widespread interests due to their outstanding mechanical, physical and chemical properties [1–3]. A beneficial feature of BMGs is their amorphous structure, which offers several important characteristics, for instance higher mechanical strengths in the absence of dislocation defects and tunable macroscopic properties by a wide range of chemical compositions [3,4]. Mg-Zn-Ca BMGs have many unique properties as compared to other metallic glasses. Firstly, Mg, Zn and Ca are biocompatible elements because they are normally found in human body and are therefore suitable for biomedical applications. These types of BMGs also have very low Young's and shear moduli, making them a promising candidate for implants in orthopedic applications. While most metal prostheses used as implants require removal by a second operation from the body, Mg-Zn-Ca BMGs degrade/corrode in the body by the effects of body fluids and thus no additional operation is needed. In addition, since the elemental metals forming these BMGs are also found in the bone, they also contribute to the healing process [5–14]. Yet there are several challenges that are still needed to overcome for their practical applications. One of them is the rapid corrosion of these BMGs, which weakens the mechanical strength of implants before the complete recovery. Another problem, perhaps the most important, is that when Mg corrodes under the body fluids, hydrogen gas, which is very harmful for tissues and organs, is released (Corrosion reaction of Mg: $Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2$) [7,12,13]). Recently, Zyberg et al. [7] have shown in their groundbreaking study that releasing of hydrogen gas can be reduced and even completely eliminated by the formation of Zn-rich and O-rich passivating layer on alloy surfaces. Thus, the slower degradation of BMGs can be achievable, and plus their mechanical properties can be preservable during the healing. The formation of this passivating layer does indeed depend on the amount of Zn (at least 28%) and the short-range order of the glasses [7]. Therefore, understanding the short-range order of these amorphous materials is mandatory to control and adjust many macroscopic properties such as corrosion rate, mechanical properties etc.

Although Mg-Zn-Ca glasses are very promising materials and have attracted substantial interests, there are very few publications on theoretical modeling and investigations of their structure at the atomistic level. Preliminary investigations focused on mainly binary alloys such as Mg-Zn [15], Mg-Ca [16], and it was showed that their local structure was dominated by icosahedral motifs. In the first study on Mg-Zn-Ca ternary alloys, their structural properties were investigated using an empirical tight-binding potential [17]. In another study, Gulenko et al.

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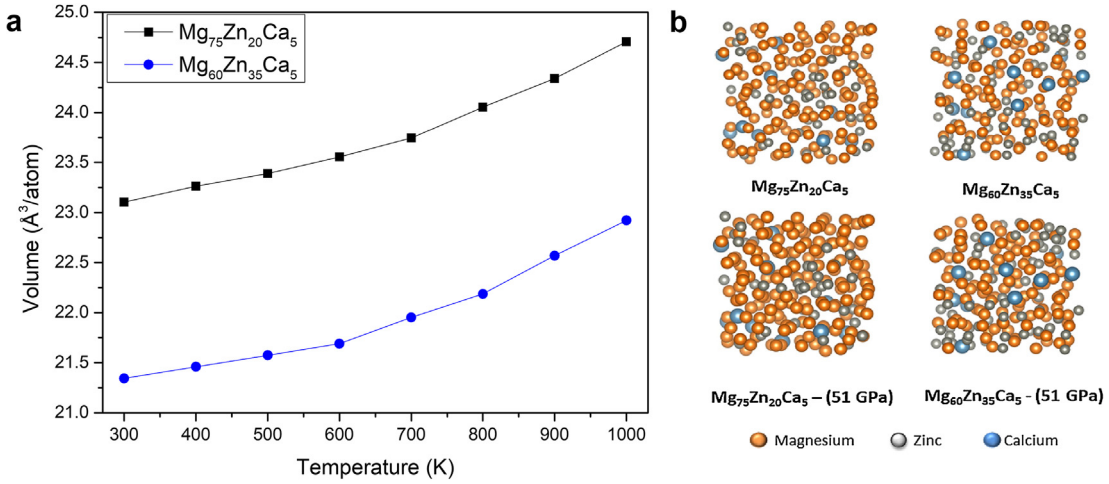

Fig. 1. (a) Variation of volume per atom as a function of temperature during the quenching processes (b) The view of simulated systems.

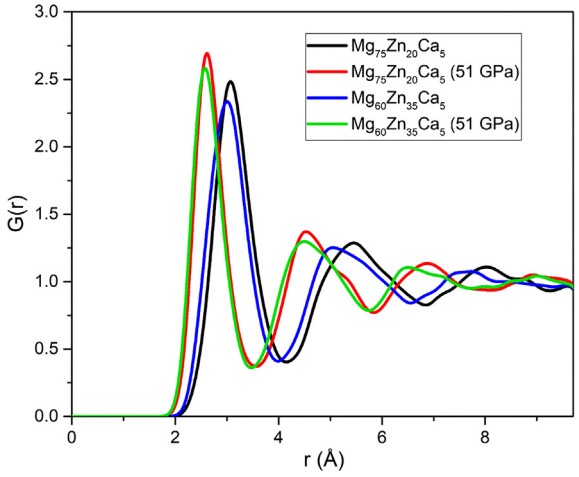

Fig. 2. Total pair distribution functions (PDFs) of the glasses.

[18] simulated Mg-Zn-Ca alloys having different compositions using a classical molecular dynamics (MD) technique. Although these simulation techniques allow working on large systems with too many atoms, their results are highly dependent on the force field used. Additionally many quantum mechanical phenomena (such as bonding, charge transfer) are ignored during these calculations. In contrast, quantum mechanical simulations based ab initio molecular dynamics (AIMD) techniques yield more accurate results, though it lets modeling of fewer atoms [19]. To the best of our knowledge, there are four detailed reports on AIMD simulations of Mg-Zn-Ca ternary alloys in the literature. Zhao et al. [20] calculated the viscosities of alloys in liquid form and correlated the well glass forming ability (GFA) of these alloys with sluggish mobility of atoms. Mahjoub et al. [21] examined the electronic and elastic properties of Mg-Zn-Ca alloys with different compositions. Li et al. [22] reported that a percolated Zn-Zn networks could form with an increase in Zn content, which also affected the corrosion performance of these glasses. Christie studied Mg-Zn-Ca BMGs with two different compositions and observed a moderate avoidance of Zn-Zn bonding [11].

In this study, the structural and mechanical properties of Mg-Zn-Ca alloys in two different compositions, one of which had been simulated previously [11], was investigated by using an AIMD simulation. For both compositions, pair distribution functions (PDFs), the Voronoi polyhedrons (VPs), coordination number (CN) and bond pair (BP) analyses were performed. In the light of obtained results, the short-range order (SRO) and glass forming ability (GFA) of the glasses were explored. Additionally, the structural changes in both compositions under hydrostatic and uniaxial stresses and their elastic properties were investigated. We believe that our results may improve our knowledge about Mg-based BMGs and be a good guide for optimizing the composition and mechanical properties of glasses for desired applications.

2. Methodology

The alloys with $Mg_{75}Zn_{20}Ca_5$ and $Mg_{60}Zn_{35}Ca_5$ compositions were chosen for this work. The AIMD calculations were performed by using the SIESTA ab initio simulation code [23]. The Troulier-Martins pseudopotentials [24] for definition of the ion-electron interactions and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation were used for the calculation of exchange-correlation energy [25]. The double-ζ polarized orbitals were preferred for the calculations. The mesh cut-off was set to 150 Ry and only Γ-point sampling of k-mesh was used. The time step in the AIMD simulations was chosen as 1 fs (fs). Each simulation box consisted of 200 atoms with periodic boundary conditions. The initial configuration of the simulation boxes was randomly built using a hard-sphere model. The starting structures were held at 1000 K for 80 picoseconds to obtain well equilibrated liquid states, and then the liquid-states were gradually quenched to 300 K with 100 K temperature step in wholly 140 ps. All of these simulations were carried out within the NPT (constant number of atoms, constant pressure, and constant temperature) ensemble. After that, the structures at 300 K were relaxed by using a conjugate gradient (CG) approach and a variable cell optimization method in which the simulation box's shape and size and the atomic coordinates were permitted to adjust with 0.01 eV/Å force and 0.25 GPa stress tolerances. All structural and mechanical calculations were performed by using these optimized configurations unless otherwise stated. The high-pressurized forms of both alloys were achieved by using the variable cell optimization method with a gradual increase of pressure up to 51 GPa. A uniaxial stress was employed along one direction while the other stress components were firstly set to zero, and the simulation vectors were allowed to amend to the applied stress. This process was repeated for all three directions. For both hydrostatic and uniaxial stress applications, to have a continuous stress path, the initial lattice parameters and atomic coordinates at each stress step were gotten from the optimized lattice parameters and coordinates of prior step. The VESTA program for visualization of the