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# Sluggish mobility and strong icosahedral ordering in Mg–Zn–Ca liquid and glassy alloys

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**Abstract**

The dynamic properties and atomic configuration of Mg, Mg–Zn, Mg–Zn–Ca and Mg–Zn–Ca–Cu liquid and solid systems were comprehensively studied using ab initio molecular dynamics calculation. The viscosities of an Mg–Zn–Ca alloy were measured from 700 K to 960 K. It was found that Zn and Ca in Mg liquid induce remarkable slowing down of atoms, but Cu acted as a stimulus to the diffusion. Icosahedral short-range orders are most dominant in Mg–Zn–Ca alloys in view of the existence of a majority of 1551 type of bond pairs, $\langle 0,0,12,0\rangle$ type of Voronoi polyhedra. Icosahedral medium-range orders can be formed in Mg–Zn–Ca alloys by the perfect icosahedra via the linkage of vertex-, edge-, face- and intercross-shared atoms. It is suggested that the high glass forming ability of Mg–Zn–Ca alloys is essentially related to the sluggish mobility and strong icosahedral short- and medium-range ordering in the undercooled liquid.


*Keywords:* Mg–Zn–Ca; Dynamic properties; Atomic structure; Ab initio molecular dynamics; Icosahedral medium-range orders

## 1. Introduction

Bio-absorbable implants have been widely employed in orthopedic surgery and have become an important materials field today. Of the miscellaneous metallic implants developed, Mg-enriched crystalline material showed a Young's modulus similar to that of bone ($E = 3$–$20$ GPa), favorable compatibility with bone cell and tissue growth, and antibacterial properties [1–3]. However, their wide application has been limited by their rapid corrosion rate accompanied by hydrogen evolution in vivo [2]. In recent years, Mg-based bulk metallic glasses (BMG) have attracted significant attention as potential bio-absorbable implant materials, owing to their higher strength and better corrosion resistance than traditional magnesium crystalline materials.

The earliest BMG were developed in 1988 in the Mg–TM–RE (TM, transition metal; RE, rare-earth element) system [4]. This type of BMG exhibits a wide supercooled liquid region, high glass-forming ability (GFA) and high tensile strength. Based on this ternary system, many multi-component Mg-based BMG have been prepared [5–9]. Unfortunately, RE-containing Mg-based BMG exhibit bad biocompatibility for biomedical materials. Recently, great progress has been achieved in the synthesis and properties of RE-free Mg-based BMG by adding a few per cent of Ca element to the Mg–Zn binary system. New Mg–Zn–Ca BMG with a critical diameter of 4 mm were prepared using conventional casting techniques [10–14]. Their feasibility as biodegradable metallic materials was evaluated by investigating their mechanical, corrosion and cytotoxicity properties. The experimental results show that these BMG are of higher cell viability than that of as-rolled pure Mg. Through animal experiments, Zberg et al. [10] revealed that the Mg–Zn–Ca BMG exhibit a great reduction in hydrogen evolution, as the content of Zn is below a threshold value of 28 at.%, and the same good tissue compatibility as observed in crystalline Mg implants. Wang et al. [11] synthesized Fe particle reinforced $Mg_{69}Zn_{27}Ca_4$ BMG

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composites by copper mold injection casting with industrial raw materials. It was shown that the corrosion resistance of this type of BMG-based composite has been remarkably improved in 3.5 wt.% NaCl solution compared with that of AZ31 and pure Mg. The reliability of the compressive fracture strength of $Mg_{96-x}Zn_xCa_4$ ($x = 30$, 25) BMG has also been investigated [12]. It was found that the compressive fracture strength of Mg–Zn–Ca BMG exhibit surprisingly high uniformity. In the present work, as shown in Supplementary Fig. 1, it was found that the addition of Cu increases the corrosion potential and decreases the corrosion current density of Mg–Zn–Ca metallic glasses in PBS solution, thus delaying the biodegradability of this type of metallic glass alloy. The compressive fracture strength of Mg–Zn–Ca BMG is enhanced by addition of Cu. However, it was also found that the glass-forming ability of Mg–Zn–Ca BMG is reduced by the appropriate addition of Cu. Crystalline phases are precipitated, as the content of Cu is >3 at.%. The large GFA, good biocompatibility, low cost and easy recycling ability of Mg–Zn–Ca BMG make them promising for structural engineering or biomedical application.

To make the most of the advantage of BMG, it is essential to thoroughly understand their dynamics properties and structural mechanism. In recent years, experimental investigations and theoretical modeling have been performed on Zr-, Pd-, Mg- and La-based BMG alloys using X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), anomalous X-ray scattering and neutron diffraction, molecular dynamics (MD) and ab initio molecular dynamics (AIMD). Theoretically, cluster dense packing [15] and quasi-equivalent cluster models [16] have been developed besides the structural theories, such as dense random packing of the hard sphere [17], the trigonal prism model [18] and the chemical twinning model [19]. To understand the ultrahigh strength of Co–Fe–Ta–B BMG, Inoue et al. [20] investigated the precipitates from the BMG and deduced that the ultrahigh strength of Co-based BMG results from the formation of local atomic ordering. Hui et al. [21] proved that the short-range order in Co–Fe–Ta–B BMG is of a $(Co, Fe)_2B$-like but not $(Co, Fe)_{23}B_6$-like crystallographic structure. Yao et al. [22] found that the high strength in Fe–Nb–B BMG is associated with the formation of a network-like structure. Gerold et al. [23] conducted EXAFS studies on the nature of atomic correlations of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (vit1) BMG alloy in the as-quenched state, and found that the atoms tend to form a dense packing. Using the AIMD calculation, Hui et al. [24] revealed that the icosahedral short- and medium-range orders (ISRO and IMRO) are most dominant in vit1 BMG in view of the presence of a majority of bond pairs (BP) and Voronoi polyhedral (VP). Short-range ordering (SRO) was found by Mattern et al. [25] in Zr–Ti–Al–Cu–Ni BMG in terms of the pair correlation function (PCF). A high degree of dense random packed structures has also been confirmed from the XRD profiles in ternary La–Al–Ni [16,26] and Mg–Cu–La [17,27] BMG alloys. Cheng et al. [28,29] investigated the influence of local structure on the dynamics in the Cu–Zr and $Cu_{46}Zr_{47}Al_7$ systems by MD simulation using EAM potentials, and found that the local icosahedral clusters are responsible for the viscosity of the supercooled liquid. Jiang et al. [30] measured the general PCF and structure factor (SF) of the $Cu_{46}Zr_{46}Al_8$ glass alloy using synchrotron radiation XRD. ISRO, of which Al atoms are caged in the center of icosahedra with Cu and Zr atoms are the vertices, have been evidenced in the $Cu_{46}Zr_{46}Al_8$ BMG by AIMD simulation [31].

In spite of such great progress in the structural characterization of BMG, the dynamic properties and structural characterization of Mg–Zn–Ca glassy alloys during the glass formation process are still less understood. In particular, the mobility and short-to-medium-range order in the atomic packing of this type of BMG have not been reported. In the present work, a comprehensive study of the evolution of the dynamic properties and atomic configuration of Mg, Mg–Zn, Mg–Zn–Ca and Mg–Zn–Ca–Cu alloys from liquid to solid state was performed using AIMD calculation. The mean square displacement (MSD), PCF, SF, BP, coordination numbers (CN) and VP were analyzed for these metals and alloys with different components. The short-to-medium-range ordering was investigated in these metallic glasses. Based on these results, the nature of glass transition and the relation of GFA to the atomic structure for this type of MG are discussed. This work has implication for providing guideline for the optimization of the composition and properties of BMG alloys, especially for the alkaline–earth metal base BMG.

## 2. Methodology and experiments

### 2.1. Methodology

Mg, $Mg_{70}Zn_{30}$, $Mg_{66.25}Zn_{28.75}Ca_5$, $Mg_{65}Zn_{27.5}Ca_{7.5}$ and $(Mg_{66.25}Zn_{28.75}Ca_5)_{97}Cu_3$ were chosen for this work (for convenience, these four subjects are named Mg, MZ, MZC5, MZC7 and MZCC in the following context). The reason for investigating MZC5 and MZC7 is that these two BMG exhibit relatively large GFA, with critical diameters of 5 and 2 mm, respectively. And with the addition of Cu atoms, the GFA of the alloy is decreased compared with those of MZC5 and MZC7, as shown in Supplementary Fig. 1.

The AIMD calculation was implemented by employing the Vienna ab initio simulation package. The electron–ion interactions and the exchange and correlation function of electrons are described by the ultra-soft pseudopotential and the generalized gradient approximation, respectively [32,33]. A canonical NVT (constant number, volume and temperature) ensemble was used. The sampling of $k$-mesh is on Γ point only. The time step used in the AIMD simulation is equal to 5 fs. The AIMD calculations were performed with a cubic supercell containing 240 atoms. These four types of atoms were distributed randomly in the supercell with the initial density obtained by the average atomic volume.