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Role of nanosize icosahedral quasicrystal of Mg-Al and Mg-Ca alloys in avoiding crystallization of liquid Mg: Ab initio molecular dynamics study

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ABSTRACT

We have used highly accurate first-principles molecular dynamics simulations to explore the structural (both topological and chemical ordering) evolution during solidification of $Mg_{90}Ca_{10}$ and $Mg_{90}Al_{10}$ liquids upon cooling. Using various structural analysis methods, we find that local atomic structure of both amorphous alloys are characterized by major distorted and perfect icosahedral symmetry. The fraction of fivefold icosahedra around Mg atoms in Mg-Ca alloy is higher than in Mg-Al alloy. Eutectic $Mg_{90}Ca_{10}$ alloy shows strong chemical short range order, which further increases upon cooling. In contrast, $Mg_{90}Al_{10}$ shows weak chemical short range ordering which seems to show weak temperature dependency behavior. The fraction of fivefold icosahedral symmetry, which is responsible for geometrical frustration, and the atomic size are responsible for the dynamic slowdown and causing glassy formation.

1. Introduction

The study of glass formation has attracted many attentions in recent years due to the fact that amorphous materials, such as metallic glasses, have unique mechanical properties [1–4]. Metallic glasses can be obtained by rapid quenching of pure liquid metals [5–11], and alloying [12–15]. The glass forming ability (GFA) could even be increased by alloying with three or more elements to produce bulk metallic glasses (BMGs), of which the size in thickness or diameter is larger than 1 mm. Understanding of local atomic structure of metallic glasses is one of the most challenging problems of condensed matter. Glass transition usually involves complex processes accompanied by structural, thermodynamic and dynamic transitions. The complexity even gets worse by alloying with multi-components or even with changing the concentration of impurities [16–18]. It is often believed that the local icosahedral short range order (ISRO) dominates in the metallic melts and BMGs [19–23]. This explanation even becomes more complicated for liquid alloys as alloying, and size effects lead to local chemical short range order (CSRO) that may enhance or disfavor ISRO [24]. Recently, the understanding of dynamics during glass transition extends from the local short-range order (SRO) to medium-range order (MRO). The frustration between this SRO and MRO is responsible for dynamic heterogeneity and slow dynamics; controlling the GFA and fragility in metallic liquids [25–27].

In recent years, Mg-based alloys have attracted many attentions due to their unique properties [28–31] as biodegradable materials for implants [32–34]. Alloying with elements such as Ca and Al could greatly improve the mechanical properties of Mg-based alloys [35]. Mg-Ca alloys are a special type of metallic glass since both Mg and Ca are simple metals, while other metallic glasses are mostly transition-metal based, with lightweight and low-density making them a potential candidate for a variety of useful applications. First-principles molecular dyna calculations demonstrate the domination of ISRO with some degree of arrangement leading to the nanoscale icosahedral quasicrystalline phase of amorphous $Mg_{90}Ca_{10}$ [36].

The knowledge of local structure evolution of these alloys is essential for technological and fundamental sciences point of views. Despite the technological and fundamental importance of these systems, much attention is rather given to the study of transition metal based metallic glasses. In this work, using ab initio molecular dynamics simulations (AMDs), the short-range structures in liquids and amorphous $Mg_{90}Ca_{10}$ and $Mg_{90}Al_{10}$ have been extensively studied. AMDs are free from a priori established assumptions of interatomic interaction, but due to the high computational time the calculation is restricted to a few hundred atoms. Alternatively, one may use the recently constructed interatomic potential for Al-Mg-Ca alloys to explore the entire phase diagram and amorphous state domain [37]. Both Al and Ca are FCC metals with different chemical properties, e.g., atomic size of Ca is

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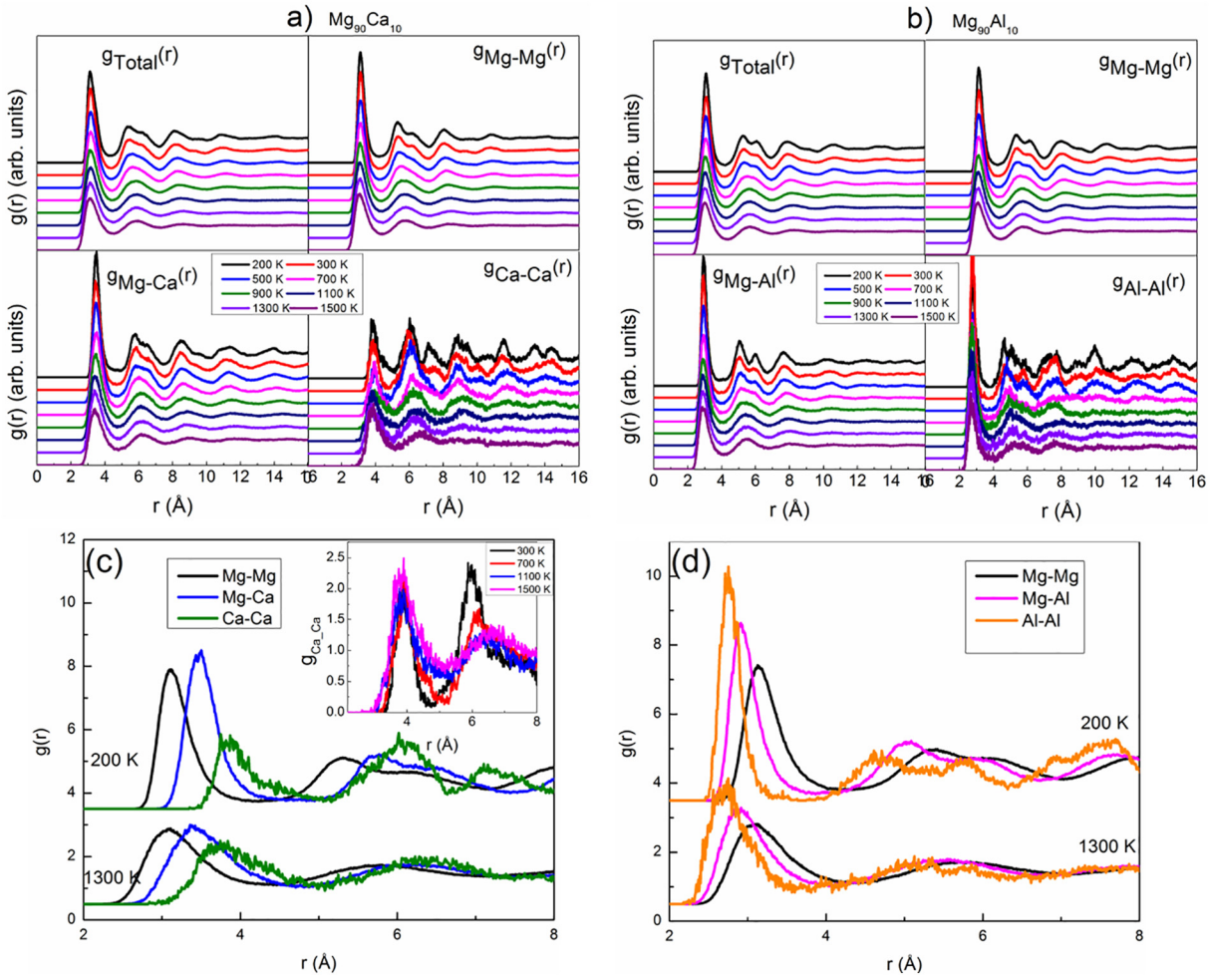

Fig. 1. Variation of total and partial correlation functions of a) $Mg_{90}Ca_{10}$ and b) $Mg_{90}Al_{10}$ alloys as a function of temperature. The curves are shifted upward for clarity. (c) and (d) are the comparison of peak position at representative temperatures.

larger than that of Mg atom, an atomic size of Al is smaller than that of Mg atom. It would, therefore, be very interesting to look at the effect of alloying on the solidification processes of liquid Mg in both cases, which has not been reported yet.

2. Computational details

We perform the first-principles calculation using the Vienna ab initio simulation package (VASP) [38,39]. Projected augmented plane waves [40] (PAW) with the local-density approximation (LDA) have been adopted. Both $Mg_{90}Ca_{10}$ and $Mg_{90}Al_{10}$ alloys consist of 200 atoms with 180 Mg atoms and 10 Ca, and 10 Al atoms, respectively, in a cubic supercell based on standard periodic boundary conditions. The calculations are performed using a canonical ensemble (NVT) by means of a Nosé thermostat to control the temperature [41]. The equation of motion is solved via the velocity Verlet algorithm with a time step of 3 fs. Only the Γ point is used to sample the Brillouin zone of the supercell. The same cooling protocol adopted for both systems. The liquid samples were first prepared and well equilibrated at 1700 K. Then the rapid quenching is performed by cooling the liquid down to the desired temperatures with a cooling rate of 3.33×10^{13} K/s. After quenching,

Table 1
The evolution of interatomic distances (r_{i-j}*in Å*), the partial coordination number, Z_{i-j}, the CSRO parameter, η_{i-j} of $Mg_{90}Ca_{10}$ and $Mg_{90}Al_{10}$ alloys. Our calculations show a good agreement with the experimental values in parenthesis taken from ref. [48].

T (K)	1500	1100	700	300
$Mg_{90}Ca_{10}$				
r_{Mg-Mg}	3.10	3.10	3.13	3.13 (3.2)
r_{Mg-Ca}	3.43	3.43	3.49	3.49 (3.6)
r_{Ca-Ca}	3.80	3.84	3.94	3.90
Z_{Mg-Mg}	10.55	10.79	11.00	11.07
Z_{Mg-Ca}	1.29	1.41	1.57	1.64
Z_{Ca-Ca}	1.30	1.09	0.99	0.88
η_{Mg-Ca}	0.01	0.04	0.06	0.07
$Mg_{90}Al_{10}$				
r_{Mg-Mg}	3.10	3.11	3.14	3.14
r_{Mg-Al}	2.92	2.92	2.94	2.92
r_{Al-Al}	2.70	2.71	2.76	2.76
Z_{Mg-Mg}	10.73	11.24	11.66	11.98
Z_{Mg-Al}	1.13	1.15	1.18	1.15
Z_{Al-Al}	0.92	1.01	0.85	0.91
η_{Mg-Al}	0.01	0.001	0.01	0.004