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Correlation between structure and glass-forming ability in $Al_{86}Ni_{14-x}La_x$(x = 3,5,9) alloys: An *ab initio* molecular dynamics study

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ABSTRACT

The correlation of atomic and electronic structures with glass-forming ability (GFA) in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9 at.%) alloys were systematically investigated via *ab initio* molecular dynamics simulations for understanding the mechanism of GFA in Al-based alloys. The obtained glass transition temperatures indicate that GFA is better in $Al_{86}Ni_9La_5$ alloy, consistent with experimental measurements. In contrast to most other alloy systems where topological order and atomic packing efficiency are key to GFA, in Al-based alloys the chemical short-range order around Al atoms play more important role in GFA. It is revealed that chemically random distribution of Al atoms favors GFA. Meanwhile, Ni and La atoms are more chemically repulsed and preferred to Al atoms, respectively. Moreover, the electronic structure calculations demonstrate that the Al-3p and Ni-3d electrons are strongly hybridized, which is found to be critical in determining Fermi surfaces and GFA in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) alloys. Taken the hybridization effect into account, the coincidence between good GFA and the local minimum of the electronic density of states at the Fermi level is obtained and verified for the first time by *ab initio* calculations. This finding provides new physical understanding for designing better Al-based bulk MGs.

1. Introduction

Aluminum-based metallic glasses (MGs) have attracted much attention during the past three decades [1–24]. A group of Al-TM-RE (TM = transition metal, RE = rare earth) MGs with remarkably high Al content (>80 at.%) has been discovered, exhibiting high strength in combination with good ductility and corrosion, which makes them suitable for application as advanced engineering materials [3–7]. Unfortunately, glass-forming ability (GFA) of Al-based glass-forming alloys is very poor. For example, $Al_{86}Ni_9La_5$ alloy is one of the best glass-forming ternary Al-based alloys, but its maximum critical thickness is only 780 μm [20,22], barely reaching the borderline that qualifies them as bulk MGs. Thus, it is desirable to figure out the key factors affecting GFA of Al-based alloy for fabricating Al-based bulk MGs.

So far, some structural models have been proposed for understanding the underlying structure basis of GFA in binary and ternary alloys. Miracle et al. proposed the efficient cluster packing (ECP) model [25–28] and found that GFA in such alloys may be correlated to the efficiently packed solute-centered atom clusters. However, this model is found not to be applicable to Al-based alloys, mainly because the chemical effect was not taken into account in this model [21]. On the other hand, it is found that local environments around TM and RE elements in Al-TM-RE alloys are different, so that GFA in Al-based alloys was attributed to the distinct topological orders of solute atoms [29–31]. *ab initio* calculations also show that the topological short-range order correlates directly with the Al-solute bond length in $Al_{89}La_6Ni_5$ MGs [8]. In addition, a prepeak reflecting medium-range order (MRO) was observed in $Al_{86}Ni_{14-x}Y_x$ (x = 2–9 at.%) MGs by X-ray diffraction, based on which a MRO structure formed by 13 atomic clusters with icosahedral packing theme was proposed to correlate to good GFA in $Al_{86}Ni_{14-x}Y_x$ (x = 2–9 at.%) systems [16,17]. Yang et al. used a cluster packing and cluster line model to design the optimum glass-forming compositions in Al-TM-RE alloys and found that GFA is highly sensitive to composition [13,23]. Although plenty of studies have been devoted to understanding GFA in Al-based glass-forming alloys, it is still not clear how the local atomic structures affect GFA in these systems. The effect of composition change on atomic structures has not been systematically characterized for understanding the mechanism of GFA, either. For example, how do

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atomic structures change with adjusting La or Ni content in Al-Ni-La MGs, and how does composition change influence GFA in Al-based MGs? Furthermore, what roles do chemical short-range order and electronic structures play in GFA in Al-based alloys, which have not been explored, either. Thus, it is critical to elucidate the above important issues for designing better Al-based BMGs.

In this work, *ab initio* molecular dynamics (MD) simulations were employed to study the atomic structures, chemical short-range order, electronic structures and their variation with composition change in model systems of $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) glass-forming alloys. Glass transition temperature in $Al_{86}Ni_9La_5$ alloy is found to be higher than the other two systems, indicating better GFA of $Al_{86}Ni_9La_5$ alloy, consistent with experimental measurement. The structural analysis reveals that atomic structures in nearest neighbor shells in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) alloys progressively change with La or Ni content change, indicating direct correlation between atomic structure and GFA. However, the population of icosahedral clusters is very low and very weak correlation was found between icosahedral clusters and GFA in these systems. Furthermore, CSRO around Al atoms exhibit strong correlation with GFA in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) alloys. Chemically random distribution of Al atoms favors better GFA. The electronic calculations show that GFA in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) alloys can be also evaluated in terms of the local minimum at Fermi level in electronic density of states. However, p-d hybridization of Al and TM atoms plays a key role in determining the Fermi surfaces in Al-based alloys and has to be incorporated into nearly-free-electron model. The above findings provide new and comprehensive insight into the underlying mechanism of GFA in Al-TM-RE glass-forming alloys.

The remaining paper is organized as follows: In Sec. 2, the detail of simulation is described. In Sec. 3, the atomic structure properties in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) are analyzed. The electronic structure calculations in three alloys were presented in Sec. 4. Finally, a conclusion is given in Sec. 5.

2. Methodology

ab initio MD simulation with a canonical NVT (*constant atom number*, *volume*, and *temperature*) ensemble was performed by the Vienna *ab initio* simulation package [32]. A projected augmented wave method [33] and generalized gradient approximation [34] were used to describe the electron-ion interactions. The *ab initio* MD simulations were carried out only at Γ point, while the electronic structure calculation was performed with 1 × 1 × 1 k-point mesh. The initial configuration containing 200 atoms in a cubic box with periodic boundary conditions applied in three directions was constructed for $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9), respectively, and equilibrated in high temperature at 1500 K for 2000 MD time steps (each time step is 3 fs). Temperature was controlled by the Nose-Hoover thermostat. The samples were then cooled down to 300 K with a cooling rate of $3.33*10^{13}$ K/s. In cooling process, the atomic configurations at different temperatures were extracted. Before isothermal relaxation at each temperature of interest, the densities of these configurations were adjusted to have zero pressure. After that, they were further relaxed isothermally for 20,000 time steps (60 ps) for the structure analysis.

3. Structure properties in $Al_{86}Ni_{14-x}La_x$(x = 3,5,9) liquids and glasses

Fig. 1 shows atomic volume (V_a) change with decreasing temperature (T) in three systems, respectively. It can be seen that there is a kink in each curve, which indicates glass transition in three systems in cooling process. Thus, the glass transition temperature T_g can be identified by fitting the data below and above kink, and marked with arrows, respectively, as shown in Fig. 1. It is found that T_g in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) glass-forming alloys are about 550 K, 630 K and 580 K, respectively. According to the parameter of $T_{rg} = T_g/T_m$ [35] and assuming similar melting temperature T_m in three alloys, T_{rg} is larger in $Al_{86}Ni_9La_5$ alloy, indicating better GFA in $Al_{86}Ni_9La_5$ alloy. According to the experimental measurements, T_m is indeed almost the same in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) alloys [23]. Therefore, our *ab initio* MD simulations obtain consistent results with the existing experiments on GFA in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) alloys [17].

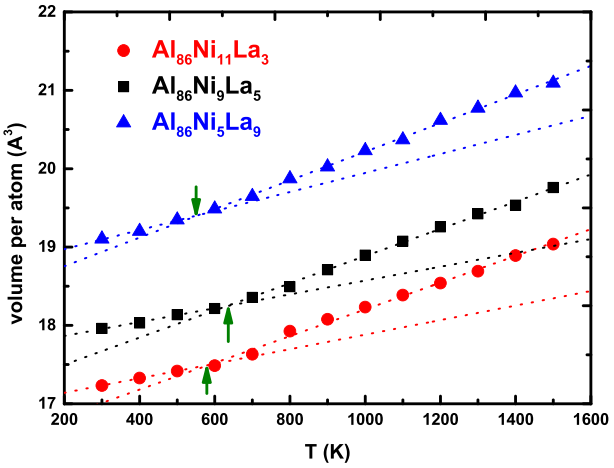

Fig. 1. Atomic volume change with decreasing temperature in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) metallic alloys in quenching process, respectively. The scattered curves represent simulation data and dashed lines are fitting to the simulation data for determining glass transition temperature.

To understand the underlying structural basis of GFA in $Al_{86}Ni_{14-x}La_x$ (x = 3,5,9) alloys, we first analyzed the structural properties and their temperature evolution in three metallic alloys. Fig. 2 shows the total pair correlation functions (PCFs) at various temperatures in three metallic alloys, respectively. With decreasing temperature, the first peaks of PCFs in three metallic alloys become sharper and the second peaks gradually split into two small peaks (r_{21}, r_{22}). This indicates that the short-range order becomes stronger and the medium-range order is also developing in three systems in glass formation. It is worth noting that the shoulders in the first peaks are emerging at low temperature region. While the shoulder is on the left side of the first peak in $Al_{86}Ni_{11}La_3$ MG, the shoulder is on the right side in $Al_{86}Ni_5La_9$ MG. For $Al_{86}Ni_9La_5$ MG, however, there are two shoulders on both sides of the first peak. Therefore, the atomic structures in nearest neighbor shells are progressively changed with La or Ni content change. With increasing La content, a shoulder on the right side of the first peak is developing in $Al_{86}Ni_9La_5$, and further enhanced as La content is further increased in $Al_{86}Ni_5La_9$. Meanwhile, the shoulder on the left side is disappearing with increasing La content. This implies that the left shoulder on the first peak in $Al_{86}Ni_{11}La_3$ and $Al_{86}Ni_9La_5$ is mainly contributed by Ni atoms, while the right shoulder on the first peak in $Al_{86}Ni_9La_5$ and $Al_{86}Ni_5La_9$ mainly results from La atoms. Fig. 3 shows the partial PCFs in $Al_{86}Ni_9La_5$ MG at 300 K. It is clearly seen that both Ni-Ni and Ni-Al pairs make contributions to the left shoulder of the first peak, while both La-Ni and La-Al pairs are related to the right shoulder of the first peak. Therefore, with systematic increase of La or decrease of Ni in $Al_{86}Ni_{14-X}La_x$ (x = 3,5,9), the left shoulder is disappearing, while the right shoulder is emerging. As shown above, $Al_{86}Ni_9La_5$ alloy exhibits