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Origin of enhanced glass-forming ability of Ce-containing Al–Fe alloy: *Ab initio* molecular dynamics study

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ABSTRACT

Using *ab initio* molecular dynamics simulation, glass-forming abilities of $Al_{90}Fe_{10}$ and $Al_{90}Fe_5Ce_5$ alloys have been investigated successfully correlated with the atomic structure and composition. The origin of enhanced glass-forming ability for $Al_{90}Fe_5Ce_5$ alloy is interpreted by taking advantage of the calculated information. It is found that the enhanced glass-forming ability with the addition of Ce into $Al_{90}Fe_{10}$ alloy, in contrast to the transitional metallic glass, has nothing to do with the kinetic factor and stability of local atomic packing, but the atomic environment and medium-range order in the supercooled liquid state. A comparison of structure and composition between the supercooled liquid and potential crystalline phases demonstrates that the precipitation of the solid solution and compounds from the amorphous matrix for $Al_{90}Fe_{10}$ alloy becomes much more difficult with the addition of Ce. After glass transition, the resultant glassy state for $Al_{90}Fe_5Ce_5$ alloy is further stabilized by stable local atomic packings.

1. Introduction

The formation mechanism of multi-component bulk metallic glasses (BMGs) has been one of the most outstanding issues in solid-state physics and materials science [1–3]. In addition to these multi-component glass-forming alloys, several binary glassy alloys have been successfully synthesized [4]. However, these binary glassy alloys exhibit low glass-forming ability (GFA), evidenced by their relatively high critical cooling rates and smaller critical sizes compared with the multiple-component BMGs. An interesting phenomenon in BMGs is that the selective minor additions can dramatically improve the GFA of binary alloys [5,6]. In this way, new BMGs with much greater GFA can be fabricated through suitable alloying based on the binary alloys.

By alloying rare earth (RE) elements, a series of BMGs with high GFA based on Mg, Zr, Fe, Cu, Ti, Pd metals have been successfully developed, whereas no Al-based BMGs prepared by copper mold casting has been reported [7,8]. As early as 1988, He et al. [9,10] found that the addition of Ce can significantly improve the GFA of Al–Fe alloy. The recent study showed that the optimum glass-forming zone includes four glassy alloys with compositions of $Al_{90}Fe_5Ce_5$, $Al_{90}Fe_6Ce_4$, $Al_{89}Fe_5Ce_6$ and $Al_{89}Fe_6Ce_5$ [11]. Although great efforts have been made to improve the GFA of Al-rich ternary alloy, at present, only the ribbon and powder forms can be synthesized [12–15]. It has been realized that Al-based glassy alloys are very different from most of the known BMG-formers. For example, the compositions of Al-based glasses greatly deviate from the eutectic region [9,16], from which the liquidus temperature rises steeply. Thus, it becomes difficult to design the Al-based BMG-forming alloys guided by the conventional rules. To uncover the origin of this extraordinary nature, a number of experimental works were carried out to characterize the internal structure of Al-based glassy alloys [17–20]. Sheng [17] pointed out that the solute-centered quasi-equivalent clusters are prevalent in the Al-based glassy alloys and they play an important role in the GFA. By using X-ray absorption fine structure, Mansour [18] found the micro-inhomogeneous feature in the $Al_{90}Fe_xCe_{10-x}$ ($x = 3$, 5, and 7) glassy alloys. Zhang [19] observed that there is a prepeak in the structure factor for $Al_{90}Fe_5Ce_5$ glassy alloy. These experiments have provided useful information to understand the structure of Al-

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based glasses. However, the detailed atomic structure is still unclear. To circumvent this problem, rational theoretical structure modeling is highly imperious.

Recently, *ab initio* molecular dynamics (AIMD) simulations have been used to investigate the structure and dynamic property for some Al-based alloys. For example, based on the AIMD simulation, Bian et al. [21,22] pointed out that the bonding between transition metal (TM) and Al atoms plays a critical role in the GFA of Al–Fe alloy. Wang et al. [23] predicted the diffusion coefficient and viscosity of Al–Zr alloys *via* the Einstein and Darken equations by AIMD simulation. They found that the addition of Zr can drastically reduce the self-diffusion coefficient of Al. A recent study has characterized the atomic packing of $Al_{89}La_6Ni_5$ glassy alloy *via* computer simulations employing effective pair-potentials derived from AIMD simulation data using the inverse Monte Carlo method [17]. Although several encouraging discoveries of internal structural feature are achieved [17,21–24], the origin of enhanced GFA caused by the small addition of Ce into Al–Fe alloy has not been well understood. The aim of this work is to investigate the kinetic property and atomic structure as a function of temperature for the $Al_{90}Fe_{10}$ and $Al_{90}Fe_5Ce_5$ alloys (the optimized Al–Fe–Ce glass-forming alloys contain 5–6 at.% Ce [11]), and more importantly, reveal the origin of enhanced GFA of $Al_{90}Fe_5Ce_5$ alloy.

2. Computational methods

AIMD simulations are conducted on the basis of the density functional theory, and implemented by using the Vienna *ab initio* simulation package (VASP) [25]. The Perdew–Burke–Ernzerhof (PBE) exchange correlation functional [26] is employed with projector augmented wave (PAW) pseudopotentials [27]. All the simulations are performed in a canonical ensemble (NVT) by means of a velocity scaling to control the temperature. The pressure-volume curve is adopted to make the average pressure being zero at each temperature. The equation of motion is solved *via* the velocity Verlet algorithm [28] with a time step of 5 fs (1 fs = 10^{-15} s). Cubic cells containing 200 atoms with periodic boundary condition are used to simulate the alloys. Only the Γ-point is used to sample the supercell Brillouin zone. The initial structures are equilibrated at 2000 K, which is well above the melting temperature of the alloy. After sufficiently relaxed for 4000 steps, the alloys are cooled down from 1600 K to 298 K at the rate of 10^{12} K/s to produce amorphous solids. At each temperature, the last 3000 configurations are used for analysis.

The self-diffusion coefficient D_i for i species is calculated using the long-time evolution of the mean square displacement (MSD) by the following equation:

$$D_i = \frac{\left\langle \left| \vec{r}_{ai}(t+t_0) - \vec{r}_{ai}(t_0) \right|^2 \right\rangle,}{6tN_i} \tag{1}$$

where $\vec{r}_{ai}$: the coordinates of atom a of i species; t_0: the arbitrary origin of time. The summation goes all over the atomic number N_i of i species and the diffusion coefficient is averaged over all possible t_0.

Considering a homogeneous repartition of the atoms in the alloy, the pair correlation function (PCF) represents the probability to find an atom in the shell dr at the distance r of another atom. By distinguishing the chemical species it is possible to compute the partial PCF, $g_{ij}(r)$:

$$g_{ij}(r) = \frac{dn_{ij}(r)}{4\pi r^2 dr \rho_i} \quad \text{with } \rho_i = \frac{V}{N_i} = \frac{V}{N \times c_i} \tag{2}$$

where $dn_{ij}(r)$: the number of i atom at the space between r and $r + dr$ of a given j atom; N: the total number of particles; ρ_i: the partial number density; c_i: the concentration of i species. By using $g_{ij}(r)$, the partial CN, Z_{ij}, can be calculated by

$$Z_{ij} = \int_0^{r_{\min}} 4\pi r^2 \rho_{ij} g_{ij}(r), dr \tag{3}$$

where $r_{\min}$: the bond length cutoff, which is set as the first minimum in partial PCF. The Z_{ij} gives the average number of j-type neighbour for an i-type atom within the first coordination shell in $g_{ij}(r)$.

The generalized PCF, $G(r)$, is accessed by

$$G(r) = 4\pi\rho_0[g(r) - 1]. \tag{4}$$

The partial static structure factor $S_{ij}(q)$ is defined through a Fourier transformation of $g_{ij}(r)$ as

$$S_{ij}(q) = 1 + 4\pi\rho_{ij} \int_0^{\infty} r^2 \frac{\sin qr}{qr} \left(g_{ij}(r) - 1 \right) dr \tag{5}$$

The detailed structures are analyzed using the Voronoi tessellation method [29]. The Voronoi index, $<n_3,n_4,n_5,n_6>$, is used to designate and differentiate the polyhedron type, where n_i denotes the number of i-edged face of the Voronoi polyhedron and $\sum n_i$ is equal to the total CN with centered atom.

The voids (free volume) are estimated by choosing the limit between zones filled with particles and void zones. It is assumed that a maximal distance above which a point would be far enough from the particles. This zone is then considered as a void. The distance defining voids is given by Le Roux and Jund [30]:

$$d_{\text{voids}}(\max) = R_{\text{moy}} + \frac{R_{\text{cov}}(\min)}{2.0} \quad \text{with } R_{\text{moy}} = \frac{\sum_{i=1}^{N_a} R_{\text{cov}}(i)}{N_a} \tag{6}$$

where $R_{\text{cov}}(i)$: the covalent radius of i species; $R_{\text{cov}}(\min)$: the smallest covalent radius of the different species.

3. Results and discussion

3.1. Transport properties

Fig. 1 shows the temperature dependence of MSD for the $Al_{90}Fe_{10}$ and $Al_{90}Fe_5Ce_5$ liquids and supercooled liquids from 1600 K to 400 K. It is seen that the MSD curves exhibit threefold in the temperature range from 1000 to 400 K: (1) for short times (less than 0.05 ps), MSD increases proportionally to t^2 because of the free ballistic motion of atoms; (2) for long times (more than 1 ps), the atomic motion becomes diffusive and the MSD shows a linear dependence on time; (3) for intermediate times (from 0.05 to 1 ps), a plateau appears and becomes more and more remarkable with the decrease of temperature. The microscopic reason for the appearance of the plateau is the so-called 'cage effect' for a tagged particle [31]. When the temperature is below 800 K, no long-range diffusion of atoms is perceptible on the time scale for $Al_{90}Fe_{10}$ alloy, whereas this temperature is slightly lower for $Al_{90}Fe_5Ce_5$ alloy, as shown in Fig. 1(a) and (b). If the glass transition is assumed to take place when the atoms are