Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

General structural and dynamic characteristics beneficial to glass-forming ability of Fe-based glass-forming liquids

Nannan Ren[a], Baoshuang Shang[b], Pengfei Guan[b,*], Lina Hu[a,*]

[a] Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jingshi Road, 17923 Jinan, Shandong Province, PR China

[b] Beijing Computational Science Research Center, ZPark II, No.10 West Dongbeiwang Road, Haidian District, Beijing, PR China

ARTICLE INFO

Keywords:
Fe-based glass-forming liquid
Glass-forming ability
Structural evolution
Dynamic heterogeneity

ABSTRACT

It is known that the relatively poor glass-forming ability (GFA) is a big problem for the development of Fe-based metallic glasses (MGs) and thus understanding the GFA-related structural and dynamic characteristics is significant. Using classical molecular dynamics (MD) simulations, the present work aims to discover the general GFA-related features in Fe-based liquids by the addition of large metallic (Ni) and small non-metallic (P) elements, respectively, into pure Fe melts. Simulation results demonstrate the better GFA of both the $Fe_{80}Ni_{20}$ and $Fe_{20}P_{20}$ liquids than that of pure Fe. Compared with pure Fe liquid, in both $Fe_{80}Ni_{20}$ and $Fe_{20}P_{20}$ glass-forming liquids, more ⟨0, 0, 12, 0⟩, ⟨0, 1, 10, 3⟩ and ⟨0, 1, 10, 2⟩ icosahedron-like clusters with slow dynamics form rapidly during cooling, accompanied with depressing ⟨0, 3, 6, 4⟩, ⟨0, 3, 6, 5⟩, ⟨0, 2, 8, 4⟩ and ⟨0, 4, 4, 6⟩ bcc-like clusters with faster dynamics. Also, the dynamic heterogeneity of $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ liquids experiences a more dramatic increase before glass transition. These findings reveal the general structural and dynamic characteristics in Fe-based glass-forming liquids beneficial to GFA and shed light on how to enhance GFA from the structural and dynamic origin.

1. Introduction

Fe-based metallic glasses (MGs) have been attracting more and more attention because of the good mechanical and magnetic properties with low cost [1–4]. However, the relatively poor glass-forming ability (GFA) is a big obstacle in the way of its further development and wider application. Therefore, it is necessary to gain an insight into GFA and to realize the general features related to it [5–7].

Due to the limitation of experimental measurements (i.e., the difficulty in obtaining high temperature or direct quantification of cluster, energy and dynamics), molecular dynamics (MD) simulations have become a widely used method to investigate the structures and dynamics of MGs so as to understand the GFA-related characteristics [7–12]. For example, many works for Cu-Zr alloys have demonstrated that icosahedral clusters contribute to slow dynamic behaviors and thus influence the GFA [10–12]. A lot of efforts have also been devoted to revealing the GFA of some Fe-based alloys through simulations [13–18]: Zhou et al. found that more bcc-like clusters have a close relationship with the poor GFA of $Fe_{80}Si_{10}B_{10}$, whereas the prism-like clusters improve the GFA [14]. Pan et al. demonstrated that different GFA can be attributed to the complexity degree of molten structure caused by introducing different elements [15]. Jiang et al. investigated the atomic packing of three MGs, finding that Y and Nb atoms can promote the formation of icosahedron-like clusters and their connectivity with large polyhedra, therefore enhancing GFA [18]. It is well known that MGs are usually processed by quenching the melt, spanning a wide temperature range. Therefore, figuring out the evolution of structural and dynamic features in the temperature range from high-temperature melts down to the glass transition is very necessary [8,19,20]. Jiang et al. studied the structure evolution and dynamic properties of Al-Ag [21], Al-Cu [22–24], Ag-Ge [25] and Ga [26] liquids in this wide temperature range, where distinct differences exist among systems with different GFA. However, the detailed common characteristics of the Fe-based liquids with enhanced GFA remain mystery in this respect.

As we know, Fe-based MGs, especially bulk metallic glasses (BMGs) synthesized so far, usually contains no less than four types of elements [3], leading to complex liquid structure which is difficult to probe into. However, despite the variety of the elements, the addition into Fe-based MGs can be divided into two types: large metallic elements such as Ni, Co, Cr, Mo, Nb, Y [3,5,27] and small metalloid elements like C, B, Si, P [2,3,28]. The metal-metalloid type Fe-based MG is typically composed

* Corresponding author.
E-mail addresses: pguan@csrc.ac.cn (P. Guan), hulina0850@sina.com (L. Hu).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.10.029
Received 15 August 2017; Received in revised form 10 October 2017; Accepted 14 October 2017

of 80% metal and 20% metalloid elements, while the metal-metal glass has no strict composition requirements [3]. Literatures have shown that both of the types could improve the GFA [2,3,5,27,28]. Uncovering the common characteristics of structures or dynamics between the two types of additions helps to uncover the general GFA-beneficial features in Fe-based liquids. Consequently, we chose two simplified binary alloy models, $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ as the glass-forming samples and pure Fe as a comparison in this work. Using classical MD simulations to the whole solidification process of high temperature liquids, we obtained glassy $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ as well as crystalline Fe respectively, which indicates the better GFA of $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$. The structural information was investigated mainly by using pair distribution function and voronoi polyhedron analysis. The mean square displacement, diffusion coefficient and especially non-Gaussian parameter characterizing dynamic heterogeneity were used to study dynamic features. Our results reveal that there indeed are common GFA-beneficial structural and dynamic characteristics in Fe-based alloys, although the two addition elements (Ni and P) are so different.

2. Simulation details

In this work, classical molecular dynamics (MD) simulations were carried out for Fe, $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ liquids employing the LAMMPS package [29]. The embedded-atom method (EAM) potential for Fe [30], Fe-Ni [31] and Fe-P [32] were used. Each sample model contains 16,000 atoms with periodic boundary conditions and was equilibrated at high temperatures at least 600 K above the liquidius temperature (Fe and $Fe_{80}Ni_{20}$ at 2500 K and $Fe_{80}P_{20}$ at 2000 K) for 2 ns. Then the samples were quenched to 300 K under a cooling rate of 1 K/ps and independent configurations at different temperatures were selected for further adequate relaxation. The system was first equilibrated at each selected temperature for at least 0.5 ns. After reaching the equilibrium, the system was hold for another at least 0.5 ns and > 500 configurations during this time were collected for further structural and dynamic analysis. Cooling rate influences structural features in metastable liquids [33,34], but in this work, we only discussed the structural and dynamic properties in the equilibrium state, where the effect of cooling rate is not our concern. The timestep was set as 1 fs. The *NPT* resemble was used with Nose-Hoover thermostat [35] and barostat [36] under zero external pressure.

3. Results and discussion

3.1. Pair distribution function

Pair distribution function (PDF) g(r) represents the probability of finding an atom at distance r from an average center atom. Fig. 1(a)–(c) shows the g(r) of pure Fe, $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ at different temperatures. We compared g(r) at 1850 K from our MD simulation work with that from other works which were obtained by X-ray diffraction data (1843 K) [37], neutron diffraction data (1873 K) [38] and AIMD (ab initio molecular dynamics) simulation (1873 K) [39] in the inset of Fig. 1(a). Our calculated g(r) is in good agreement with the experimental data and the AIMD calculations, further demonstrating the reliability of our simulated atomic configurations. The g(r) at 300 K is displayed using dash lines. It can be seen clearly that pure Fe solid is crystalline with sharp peaks, while $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ are amorphous with broad peaks and splitting second peaks. These results suggest the better GFA of $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ than pure Fe. According to the calculated enthalpy-temperature (H-T) relation (not shown here), the crystallization temperature of the Fe liquid is about 1000 K and the T_g of $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ liquids are about 950 K and 850 K respectively at the cooling rate of 1 K/ps.

3.2. Voronoi polyhedron

The Voronoi tessellation is usually used to describe the arrangement and symmetry of the nearest-neighbor atoms around the center atom and each Voronoi polyhedron (VP) is labeled by the Voronoi index $\langle i_3, i_4, i_5, i_6\rangle$ [8,12], where i_j represents the number of faces with j edges. We monitored the evolution of major VPs in $Fe_{80}Ni_{20}$, $Fe_{80}P_{20}$ and Fe as temperature decreases until solidification, among which seven representative VP types are displayed in Fig. 2(a)–(c). It is clear that the fractions of ⟨0, 0, 12, 0⟩ and ⟨0, 1, 10, 3⟩ are as few as 1% at high temperatures in all the three systems. Then they start to increase at faster rates when the temperature decreases to some degree, as shown by the shadow in Fig. 2(a)–(c). In pure Fe liquid, despite the relatively rapid increase from 1800 K, the percentage of ⟨0, 0, 12, 0⟩ and ⟨0, 1, 10, 3⟩ remains small and ⟨0, 0, 12, 0⟩ accounting for 3% near crystallization is always the least one among all the seven VP types (see Fig. 2(a)). However, things are different in $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ glass-forming liquids. As highlighted by the shadow area, it is ⟨0, 0, 12, 0⟩ that increases much sharply and finally becomes one of the top three VPs in glassy solids. Similarly, ⟨0, 1, 10, 3⟩ also experiences a sharp rise in this temperature range. After a quick increase, the fractions of ⟨0, 0, 12, 0⟩ and ⟨0, 1, 10, 3⟩ reach 8% and 6%, respectively, in $Fe_{80}Ni_{20}$. In $Fe_{80}P_{20}$, they are 5% and 3%, respectively. Both of them have grown to be dominant in $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ liquids. In addition, the top three VPs are ⟨0, 2, 8, 4⟩, ⟨0, 1, 10, 2⟩ and ⟨0, 3, 6, 4⟩ with similar fractions in pure Fe liquid before solidification. But in the $Fe_{80}Ni_{20}$ and $Fe_{80}P_{20}$ glass-forming liquids, ⟨0, 1, 10, 2⟩ VPs take the first place, 2% more than ⟨0, 2, 8, 4⟩. The VP ⟨0, 0, 12, 0⟩ is generally called full icosahedron, the center atom of which has 12 neighbor atoms and all the 12 bonds are fivefold [8,12] as shown in Fig. 2(d). ⟨0, 1, 10, 3⟩ and ⟨0, 1, 10, 2⟩ are regarded as deformed icosahedra based on the previous publications [8,12,16]. Therefore, ⟨0, 0, 12, 0⟩ and its deformation ⟨0,

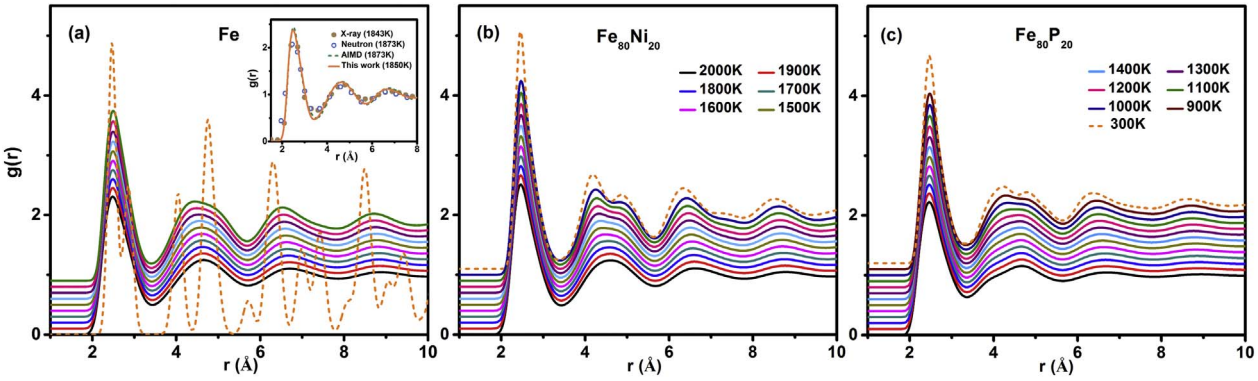

Fig. 1. The pair distribution function (PDF) of (a) pure Fe, (b) $Fe_{80}Ni_{20}$ and (c) $Fe_{80}P_{20}$ at different temperatures. The inset in (a) is the comparison of the g(r) at 1850 K in this MD simulation with the previously reported data obtained by X-ray experiments at T = 1843 K (Ref. 37), neutron scattering experiments at 1873 K (Ref. 38) and the ab initio molecular dynamics (AIMD) simulations at 1873 K (Ref. 39). The legends in (b) and (c) are for the three systems.