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SPECIAL TOPIC — 80th Anniversary of Northwestern Polytechnical University (NPU)

Ab initio molecular dynamics simulations of nano-crystallization of Fe-based amorphous alloys with early transition metals*

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The addition of early transition metals (ETMs) into Fe-based amorphous alloys is practically found to be effective in reducing the α-Fe grain size in crystallization process. In this paper, by using *ab initio* molecular dynamics simulations, the mechanism of the effect of two typical ETMs (Nb and W) on nano-crystallization is studied. It is found that the diffusion ability in amorphous alloy is mainly determined by the bonding energy of the atom rather than the size or weight of the atom. The alloying of B dramatically reduces the diffusion ability of the ETM atoms, which prevents the supply of Fe near the grain surface and consequently suppresses the growth of α-Fe grains. Moreover, the difference in grain refining effectiveness between Nb and W could be attributed to the larger bonding energy between Nb and B than that between W and B.

Keywords: *ab initio* molecular dynamics, Fe-based amorphous alloys, nano-crystallization, atomic diffusion

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1. Introduction

In order to improve the performance in the electronic system and enhance energy saving in the electric power grid, Fe-based nano-crystalline alloys with excellent soft magnetic properties were invented to reduce the power loss in the electric-magnetic transforming process. Due to their potential in energy saving, Fe-based amorphous/nano-crystalline alloys have increasingly received the attention of researchers in recent years.[1–5]

Ever since the successfully development of the FINEMET® alloy with the typical composition of $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$,[6–13] it has been well recognized that the addition of heavy transition metals such as Nb not only helps increase the ability to form amorphous state in the initial solidification process, but also plays a crucial role in the nano-crystallization process such as annealing the amorphous alloy. It has been reported that the Nb atoms could suppress α-Fe grain growth by inhibiting atomic diffusion, which is due reasonably to the large atomic size of Nb.[6,13,14] Therefore it was expected that the atoms with larger size can exhibit more significant effect of reducing the grain size. However, the addition of W into the Fe-based alloys did not lead to better nano-crystallization result after being annealed,[14,15] suggesting that the atomic size is not the reason for the grain refining effect.

Therefore, the true mechanism for the early transition metals (ETM) to influence the grain refinement is yet to be discovered, which causes the bewilderment in designing new compositions with better productivity and magnetic properties.

In this article, *ab initio* molecular dynamics simulations are performed to investigate the diffusion behavior of Fe, Si, B, Cu and two typical transition metals Nb and W in amorphous structures, so that the grain refinement mechanism of the early transition metals could be better revealed. This work could contribute to better understanding of nano-crystallization process and the development of nano-crystalline soft magnetic alloys.

2. Simulation configuration

Vienna *ab-initio* simulation package (VASP) was used to perform the simulation based on the density functional theory. The interaction between particles (ions and electrons) was described with projector augmented-wave pseudo-potential on the Perdew–Burke–Ernzerhof-type generalized gradient approximation basis. Canonical ensemble was applied as the number of atoms, the sampling volume, and the temperature

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were configured. The Γ-point was used to sample the Brillion zone in the simulation of amorphous structure. The temperatures were controlled by Nosé thermostat.[16] Electron spins have been taken into account throughout the simulation.

The compositions are configured as $Fe_{70}(B/Cu/Si)_{15}(Nb/W)_{15}$ based on the following considerations. (i) Fe should be the main component. (ii) The commonly used elements such as B, Cu, and Si are included to reveal any possible interactions with ETMs. (iii) Nb and W are chosen as typical ETMs since they have large atomic sizes but different experimental effectiveness during crystallization.

The time interval for simulation was set to be 2 fs for each MD step. There were 200 atoms involved in the simulation of the amorphous structure. Since most of the alloy compositions in this study can hardly be made into amorphous phase experimentally, the sizes of the various simulated supercells were theoretically determined by adjusting the isotropic internal stress to less than 0.5 kbar (50 MPa).

In order to obtain amorphous structure, an isothermal annealing was first performed at 1800 K to remove any artificial factors in the initial structures. The dimensions of the supercell during the isothermal annealing started with 1.1 times the normal size to ensure the initial mobility of the atoms, and then shrank to 1.08, 1.06, 1.04, 1.02, and 1 times the normal size after 2000 MD steps, which accounted for 12000 MD steps in all. In order to obtain room-temperature structures, cooling process from 1800 K to 1000 K was adopted with 5000 MD steps in steps of 200 K, corresponding to the cooling rates of 2×10^{13} K/s. Finally, the diffusion ability of the alloys was studied with an isothermal MD simulation of 1000 steps at 1000 K to ensure the continuous migration of the atoms.

3. Simulation results

3.1. Atomic distribution properties of simulated structure

After the stabilization of the $Fe_{70}(Nb,W)_{15}(B,Si,Cu)_{15}$ structure, the partial pair correlation functions (PPCFs) are calculated and shown in Fig. 1. It can be easily found that the neighboring distances of the atoms exhibit a wide distribution, indicating the absence of structural ordering that is correlated to any crystalline phases.

Generally, these PPCF curves have two different types. Most of the curves have their first peak significantly larger than the others, especially when the primary element Fe is involved; whereas some of the other curves do not have their first peak significantly larger than the other peaks, such as the PPCF curves of B–B and Si–Si pairs. Such a feature is well consistent with some of the former results[17,18] claiming that the metalloid atoms in the amorphous alloys prefer to be separated by metal atoms for better chemical stability since the bond energies between metalloids and metals are usually larger than those among metalloid atoms.

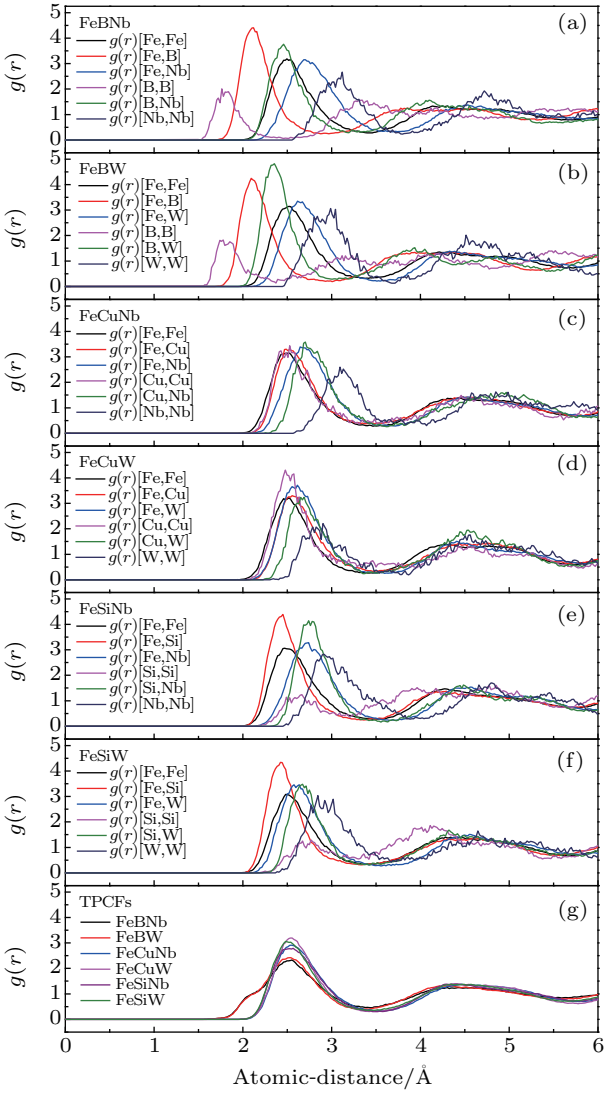


Fig. 1. (color online) Partial pair correlation functions of simulated amorphous alloys: (a) FeBNb, (b) FeBW, (c) FeCuNb, (d) FeCuW, (e) FeSiNb, (f) FeSiW. (g) Total pair correlation functions.

3.2. Local compositions of the simulated amorphous alloys

In order to have better overview on the atomic bonding preference, the total pair correlation functions (TPCFs) are calculated by combining the corresponding PPCFs (Fig. 1), and the atomic neighboring criterions that are used for calculating the local compositions are determined at the first minimum of the TPCFs. Accordingly, the neighboring compositions of different atoms are calculated and the results are shown in Fig. 2.

It can be found that the compositions surrounding Fe atoms are slightly Nb/W rich compared with the nominal compositions. Moreover, when Si is added, the Si atoms have strong preference to be surrounded by Fe rather than neighbor with other Si atoms, which indicates that Si could be well dissolved in Fe-rich environments like α-Fe grains as commonly recognized in metallurgy.

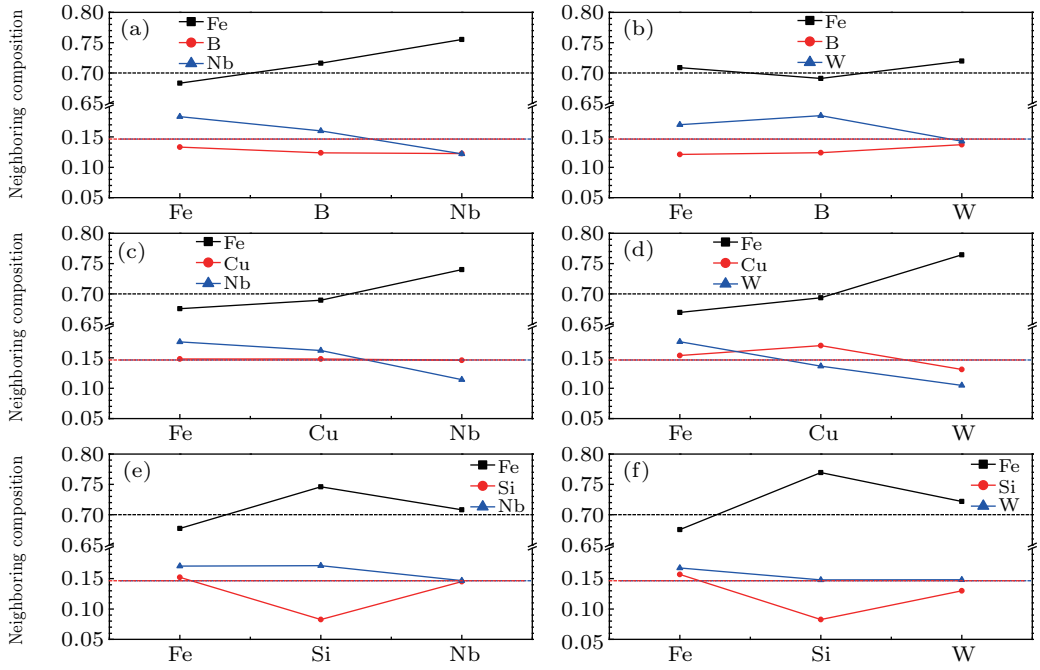


Fig. 2. (color online) Neighboring compositions of atoms in simulated amorphous alloys: (a) FeBNb, (b) FeBW, (c) FeCuNb, (d) FeCuW, (e) FeSiNb, (f) FeSiW.

3.3. Atomic migration activities in simulated amorphous alloys

The key to the formation of the soft magnetic nanocrystalline structure lies in the hetero-crystallization process of the amorphous alloys, which requires the sufficient volume fraction of α-Fe formation with strictly confined grain growth. The growth of the hetero-grains depends heavily on the atomic diffusion to feed the growing grains with necessary atoms. Thus the diffusion behavior of the atoms is crucial to the nano-crystallization process.

In the *ab initio* molecular dynamics (AIMD) simulation, atomic diffusion ability could be calculated from the mean square displacements (MSDs) of the atoms based on the Einstein equation

$$\mathrm{MSD}(t)_\alpha \to 6D_\alpha t + B_\alpha,$$

where $\mathrm{MSD}(t)_\alpha$ is the time dependent MSD of the element α, D_α is the diffusion coefficient of the element α, and B_α represents the fluctuation, which is negligible when the diffusion time becomes sufficiently large.

The MSDs of the elements in the simulated alloy compositions are calculated and the results are shown in Fig. 3. Taking the MSD curves of Fe as reference, it can be clearly found that within the composition variation of B/Cu/Si, B and Cu each exhibit a significantly larger diffusion rate, and Si has its diffusion activity close to that of Fe.

On the other hand, the diffusion activities of Nb and W are similar to each other. It can be found that except for the compositions with B addition, neither Nb nor W exhibits low diffusion ability in spite of their large atom size. Among the simulated compositions, their diffusion rate decreases only when coexisting with B.

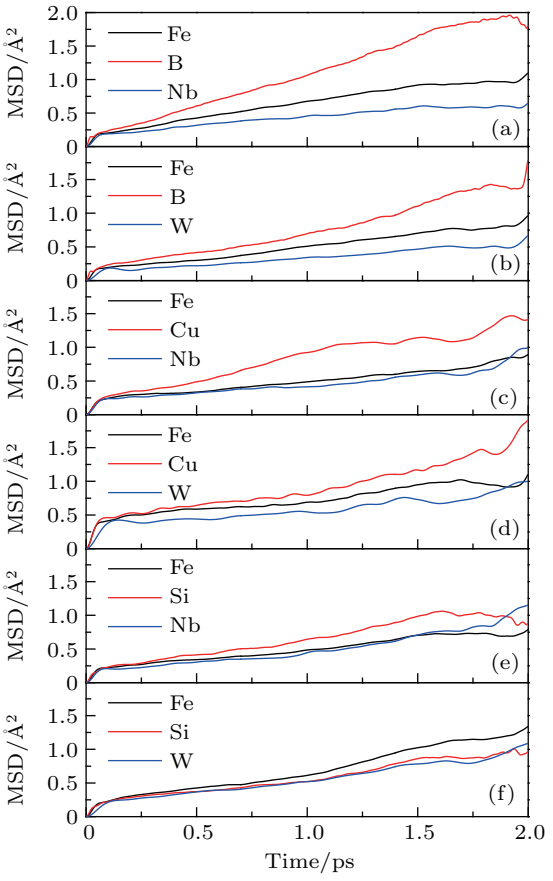


Fig. 3. (color online) Plots of MSD of the element versus simulation time in the amorphous alloys: (a) FeBNb, (b) FeBW, (c) FeCuNb, (d) FeCuW, (e) FeSiNb, (f) FeSiW.

4. Discussion

4.1. Fundamental nano-crystallization mechanism

Generally, the crystallization process consists of nucleation and grain growth process. The nucleation process is caused by the local rearranging of the atoms, which could be triggered by the fluctuation of the local composition and energy. Although short range migration of the atoms is involved for rearranging, this process does not require the compositions to redistribute on a large scale, thus it is not significantly dependent on the diffusion ability of the atoms.

On the other hand, the grain growth in the nano-crystallization process of the Fe-based amorphous alloys exhibits a large scale redistribution of the compositions, which depends heavily on the diffusion ability of the atoms. Specifically, as schematically shown in Fig. 4, Fe and those α-Fe dissolvable elements (such as Si) must be locally concentrated to build the α-Fe grains, consequently making the surrounding diffusion layer lacking in α-Fe forming elements and rich in other elements. Long range diffusion starts to play its role in feeding these regions with α-Fe forming elements from the amorphous matrix and diffusing the enriched other elements into the amorphous matrix, so that the growth of α-Fe progresses.

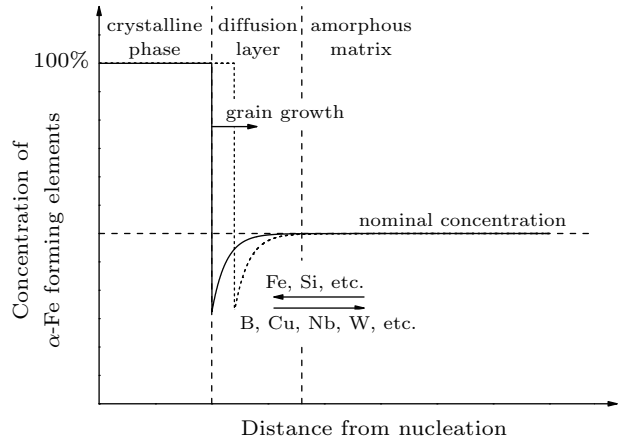


Fig. 4. Relation between grain growth and diffusion in nano-crystallization process.

Therefore, the grain growth along with the control of grain size in the nano-crystallization process depends on not only the diffusion ability of the α-Fe forming elements but also that of the other elements. This is because Fe could also be prevented from supplying if those excess elements fail to be efficiently removed from the diffusion layer.

4.2. Atomic interactions during diffusion

By summarizing the curves in Fig. 3, the MSDs of the elements within 2 ps are listed in Table 1 for quantitative analysis. It can be found that without adding B, heavy metals such as Nb and W possess similar diffusion ability to Fe in the Fe-based amorphous alloys, indicating that the atom size is no longer the dominant factor to the diffusion ability of the elements.

Table 1. MSDs of the elements in 2 ps simulation.

Composition	Fe/Å^2	B/Cu/Si/Å^2	Ratio to Fe	Nb/W/Å^2	Ratio to Fe
$Fe_{70}B_{15}Nb_{15}$	1.09	1.81	1.66	0.65	0.60
$Fe_{70}B_{15}W_{15}$	0.96	1.78	1.85	0.67	0.70
$Fe_{70}Cu_{15}Nb_{15}$	0.89	1.41	1.58	0.99	1.11
$Fe_{70}Cu_{15}W_{15}$	1.10	1.90	1.73	1.00	0.91
$Fe_{70}Si_{15}Nb_{15}$	0.78	0.88	1.13	1.15	1.47
$Fe_{70}Si_{15}W_{15}$	1.07	0.97	0.91	1.09	1.02

The migration of the atoms as well as the diffusion process is controlled by two factors, i.e., the energetic activation from the bonded structure and the formation of the migration path respectively. Unlike the crystalline alloys with the atoms well aligned and firmly bonded, amorphous alloys usually have a relatively small density, thus it could be much easier to form migration paths for large atoms such as Nb and W, making them possible to exhibit similar diffusion ability to the relatively smaller Fe atoms. In fact, without adding B, W exhibits slightly smaller MSD value than Nb, indicating that the size and weight of the atom still have minor effect on the diffusion. However, when B is added into the alloy composition, the diffusion ability of Nb and W decrease dramatically. Dropping from ~ 1 Å^2 to ~ 0.65 Å^2, the decrement of Nb/W MSD brought by adding B significantly overwhelms that by the other factors, indicating the existence of strong interactions among B, Nb, and W.

In fact, it is reported that the heat of mixing between B/Nb and B/W atoms is -51 kJ/mol and -31 kJ/mol, respectively.[19] Such high values indicate the formation of strong chemical bonds between the different atoms, which could make these atoms difficult to be activated for migration, consequently reducing the diffusion ability. Since both W and Nb must be expelled from the diffusion layer to keep the grain growth progressing, the reduction of their diffusion ability should bring the effect of grain growth prevention in the crystallization process, which conduces to the formation of nano-crystalline structure.

Moreover, the heat of mixing between B and Nb is much stronger than that between B and W, and the MSD ratio between Nb and Fe appears to be lower than the ratio between W and Fe, suggesting that the diffusion reduction effect of B addition on W is weaker than that on Nb. Therefore, the addition of Nb into Fe-based and B-containing amorphous alloys could significantly promote the nano-crystallization, which is consistent with the phenomena observed in experiment, but the addition of W exhibits much less effect on reducing the grain size.

5. Conclusion

By using the AIMD simulation of $Fe_{70}(B/Cu/Si)_{15}(Nb/W)_{15}$ amorphous alloys, it is found that the diffusion abilities of the elements in the Fe-based amorphous alloys are determined by the bonding energy between the atoms and the other alloying ones, rather than the weight or size of the atoms.

It is also found that the addition of B could be firmly bonded with Nb and W, consequently leading to the dramatical reduction of the diffusion ability and the α-Fe grain refining. Moreover, experimentally observed Nb possesses better α-Fe grain refining ability than W, which could be attributed to the larger bond energy between B and Nb than that between B and W.

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