Study on the structural relationship between the liquid and amorphous Fe$_{78}$Si$_9$B$_{13}$ alloys by ab initio molecular dynamics simulation

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The structure of the liquid and amorphous Fe$_{78}$Si$_9$B$_{13}$ alloys is investigated by ab initio molecular dynamics simulation. The amorphous structure bears a strong resemblance to the liquid structure on both the atomic and electronic levels. Chemical short-range order is evidenced by higher Fe coordinating proportion than the nominal one around both Si and B atoms in both the liquid and amorphous states. The atomic distances and the local densities of states show that Fe–Si bonding is stronger than Fe–B bonding and Si and B tend to repulse each other. © 2007 American Institute of Physics. [DOI: 10.1063/1.2737937]

The structural relationship between the liquid and the solid states is a long-standing question.\(^1,2\) Recent progresses on the bulk metallic glass\(^3\) strengthen the importance of the liquid-amorphous structural relationship in multielement systems. However, very few works have been done to clarify this problem.

The existing studies on Fe–Si–B alloys have mainly focused on the crystallization process, and the thermal and magnetic properties.\(^4,5\) In situ x-ray diffraction\(^6\) and neutron scattering experiments\(^7\) have been carried out to investigate the crystallization process, particularly in the early stage. As demonstrated in these experiments, a crucial factor for the design of the good magnetic properties in Fe–Si–B alloys is that the DO$_3$-type $\alpha$-Fe(Si) solid solution must be precipitated in the first instance. The precursor of the precipitation is phase separation whose physical nature based on the amorphous structure is not well understood in the amorphous Fe–Si–B alloys.

Cluster models are often adopted to understand the nucleation process in both the liquid and amorphous states. The cluster models are generally on the medium-range scale\(^8\) and need a rational basis in the atomic and electronic levels. Chemical short-range order and finding out the physical foundation to the structural evolution in Fe–Si–B amorphous alloys.

The AIMD simulations were carried out using the most recent version of the Vienna ab initio simulation package\(^11\) by implementing the projector augmented wave method.\(^12,13\) The plane-wave basis set contained components with energies up to 319.0 eV. Exchange and correlation effects were described by the energy functional parametrized according to Perdew and Zunger\(^14\) and adding generalized gradient corrections.\(^15\) Only the $\Gamma$ point was used to sample the supercell Brillouin zone.

All the dynamical simulations were carried out in the canonical ensemble ($nvt$) through a Nosé\(^16\) thermostat to control temperature. A cubic cell containing 77 atoms with periodic boundary condition was used to simulate the liquid or amorphous system. The initial configuration was a well-equilibrated liquid Fe system by random substitution of some Fe atoms with Si and B atoms. Due to the lack of experimental density of the liquid Fe$_{78}$Si$_9$B$_{13}$ alloy, we employed the same density, 91/nm$^3$, for both the liquid and quenched alloys. For the liquid alloy, the system was equilibrated at $T=1473$ K for 6 ps with 2000 configurations being collected for structural analysis. Six liquid configurations, separated by 1 ps each, were independently quenched to 300 K at a cooling rate of $3.33 \times 10^{14}$ K/s. Afterward, the six configurations were simulated for 6 ps to produce structural functions. Then, the arithmetical mean of each structural function is evaluated.

The total pair distribution function (PDF) is derived from the PDFs according to Eq. (1):

$$g_{total}(r) = 1 + \sum_{a,b=1}^{n} \frac{c_{af}c_{bf}^{\ast}}{\langle f \rangle^2} [g_{ab}(r) - 1],$$

where $n$ is the number of elements, and $c_a$ and $f_a$ are the concentration and atomic scattering factor of the $a$th element in the alloy, respectively. $\langle f \rangle$ is the average atomic scattering factor which is defined by the equation

$$\langle f \rangle = c_1f_1 + c_2f_2 + \cdots + c_nf_n.$$  

The total pair distribution functions of the Fe$_{78}$Si$_9$B$_{13}$ alloy by simulation labeled as $l$-calc for the liquid alloy and $a$-calc (with standard deviation) for the quenched alloy are shown in Fig. 1. For comparison, the experimental curve ($a$-expt) on the amorphous ribbon is also plotted. The experimental setups and the data processing program can be referred for Ref. 17. Our simulations may overestimate the bonding between transition-metal atoms. Therefore, the first peak position of $a$-calc is shorter by about 0.1 Å than that of $a$-expt. Moreover, the quenched configurations may be more ordered than the amorphous ribbon, so that the first peak of $a$-calc is higher and narrower than that of $a$-expt.

In order to verify whether the quenched configurations by AIMD simulation are amorphous or not, we performed Voronoi analysis on the configurations and employed a signature to represent shapes of the polyhedron: $(n_5, n_4, n_5, n_6)$.
The PDFs of both the liquid and amorphous Fe78Si9B13 alloys, namely, $g_{\text{FeFe}}(r)$, $g_{\text{FeSi}}(r)$, $g_{\text{FeB}}(r)$, $g_{\text{SiSi}}(r)$, $g_{\text{SiB}}(r)$, and $g_{\text{BB}}(r)$ are shown in Fig. 2. In the liquid state, the split of the second peak is distinguishable in the three curves of $g_{\text{FeFe}}(r)$, $g_{\text{FeSi}}(r)$, and $g_{\text{BB}}(r)$. After being quenched into the amorphous state, the entire six PDFs exhibit pronounced split in the second peak. However, in liquid Fe–Si binary alloys,9 there are no splitting up of the second peak, while in liquid Fe–B binary alloys,17 an asymmetry is visible in the total interference functions in the region of the second peak. We speculate that this phenomenon may be related to the larger glass forming ability of the Fe78Si9B13 and Fe–B alloys than the partially crystallized state.

All the three PDFs related to Fe have pronounced first peaks and minor second peaks; in contrast, the second peaks play a more important role in $g_{\text{BB}}(r)$, $g_{\text{SiB}}(r)$, and $g_{\text{SiSi}}(r)$. Especially in $g_{\text{SiB}}(r)$, the second peak becomes dominant over the first peak. These features in the PDFs suggest that (1) covalent bonding exists in Fe–B and Fe–Si pairs, (2) B and Si likely repulse each other, and (3) B and Si tend to have similar atom next-nearest neighbors.

As determined from Fig. 2, the first peak position $r_{\text{FeSi}}$ of $g_{\text{FeSi}}(r)$ is 5.4% shorter than the arithmetical mean of $r_{\text{FeFe}}$ and $r_{\text{SiSi}}$ in the liquid state, and 7.4% shorter than that in the amorphous state. On the other hand, the $r_{\text{FeB}}$ is 1.5% shorter than the arithmetical mean of $r_{\text{FeFe}}$ and $r_{\text{BB}}$ in the liquid state, and 2.9% shorter than that in the amorphous state. These again imply that Fe–Si and Fe–B bonding exist in both states, and that the Fe–Si bonding is stronger than that of Fe–B. However, no bonding may exist between Si and B, since $r_{\text{SiB}}$ is 2.8% and 6.0% larger than the arithmetical mean of $r_{\text{SiSi}}$ and $r_{\text{BB}}$ in both states, respectively.

The amorphous $g_{\text{SiSi}}(r)$ has a second peak located around 4.0 Å. Moreover, the value of $r_{\text{FeSi}}$ is 2.40 Å. We then deduce that such behavior resembles the distribution of Si atoms in the DO3-type α-Fe(Si) solid solution in which a Si atom is coordinated by eight atoms of Fe at 2.448 Å with the shortest Si–Si distance of 3.9975 Å.20

We further analyzed the constitutional proportion of the three elements in the partial coordination numbers (estimated from the area of the first peak of each PDF). It is found that around a Fe atom, the constitutional proportions of the three elements resemble their nominal proportions, especially in the liquid state. Such data for the Si and B atoms are com-

### Table 1. Constitutional proportion (%) of elements in partial coordination numbers of Si and B atoms.

<table>
<thead>
<tr>
<th>Terms</th>
<th>$N_{\text{SiFe}}$</th>
<th>$N_{\text{SiSi}}$</th>
<th>$N_{\text{SiB}}$</th>
<th>$N_{\text{BFe}}$</th>
<th>$N_{\text{BSi}}$</th>
<th>$N_{\text{BB}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal</td>
<td>78.0</td>
<td>9.0</td>
<td>13.0</td>
<td>78.0</td>
<td>9.0</td>
<td>13.0</td>
</tr>
<tr>
<td>$l$-calc</td>
<td>82.0</td>
<td>11.9</td>
<td>6.1</td>
<td>87.9</td>
<td>5.3</td>
<td>6.8</td>
</tr>
<tr>
<td>$a$-calc</td>
<td>90.7</td>
<td>7.3</td>
<td>2.0</td>
<td>92.6</td>
<td>1.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>
have the bonding state at about −8.0 eV with the
both states of Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} alloy.
smaller than their nominal values in both states. These results
the Si and B atoms are surrounded by only Fe atoms
smaller than their nominal values in both states. These results
form cluster units. These units extend in the three dimensions
to form larger clusters where the correlations of Si–Si, Si–B,
and B–B are likely bridged by Fe atoms. Since the Fe–Si
bonding is stronger than the Fe–B bonding, the DO\textsubscript{3}-type
\alpha-Fe(Si) solid-solution-like structure should nucleate more
easily from the amorphous alloy matrix. This lays the physical
foundation for the experimental result that DO\textsubscript{3}-type
\alpha-Fe(Si) solid solution acts as the primary precipitate during
the crystallization process of the amorphous Fe–Si–B-based alloys.
In summary, in both the liquid and amorphous
Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} alloys, the chemical short-range order is evi-
denced by the partial coordination number analysis. The atomic distances and the LDOSs show that Fe–Si bonding is
stronger than Fe–B bonding and that Si and B tend to repulse
each other. The feature of the PDFs of Fe–Si and Si–Si
makes it rational to construct cluster models based on the
DO\textsubscript{3}-type \alpha-Fe(Si) solid solution to study the nucleation pro-
cess in the amorphous Fe–Si–B-based alloys.

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University for reading this letter.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{(Color online) Local densities of states of the Fe, Si, and B atoms of the
amorphous alloy.}
\end{figure}

piled in Table I, where \( N_{\alpha\beta} \) is the proportion of the population of element \( \beta \) in the partial coordination number of element \( \alpha \). In the liquid state (l-calc), Fe atoms tend to
concentrate around Si and B atoms, while in the amorphous
state (a-calc) this tendency even enhances. In the amorphous
state, among the nearest neighbors of Si and B, the constitu-
tional proportions of Fe atoms are 90.7\% and 92.6\%, which
are markedly higher than their nominal values. In cases of
Si–B and B–Si coordination, \( N_{\text{SiB}} \) and \( N_{\text{BSi}} \) are noticeably
smaller than their nominal values in both states. These results
demonstrate that similar chemical short-range order exists in
both states of Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} alloy.

For the understanding of the covalent bonding on the
electronic level, local densities of states (LDOSs) have been
calculated for both alloys. Since the LDOSs of the amor-
phous alloy are similar to those of the liquid alloy, only the
LDOSs of the amorphous alloy are plotted in Fig. 3.

From Fig. 3, we observe that the \( p \) electrons of Fe atoms
have the bonding state at about −8.0 eV with the \( s \) electrons of Fe, Si, and B atoms. Moreover, the Fe–Si bonding is
stronger than the Fe–B bonding. The \( p \) electrons of both Si
and B atoms have bonding states around −3.6 eV with the \( s \)
electrons of Fe atoms. However, by taking into consideration
the shape of \( g_{\text{SiB}}(r) \) in Fig. 2, we speculate that no bonding
state exists in Si–B pairs.

Based on the above analysis, one can imagine a cluster
model for amorphous Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} alloy, in which nearly all
the Si and B atoms are surrounded by only Fe atoms (ex-
plitly ten Fe atoms for Si, eight Fe atoms for B in this alloy) to
form cluster units. These units extend in the three dimensions
to form larger clusters where the correlations of Si–Si, Si–B,