

## Understanding atomic-scale phase separation of liquid Fe-Cu alloy

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Received June 25, 2011; accepted July 29, 2011

Using liquid Fe<sub>60</sub>Cu<sub>40</sub> alloy as a model, the structure of liquid Fe-Cu alloy systems is investigated in the temperature range 1200–2200 K, covering a large metastable undercooled regime, to understand the phase separation of liquid Fe-Cu alloys on the atomic scale. The total pair distribution functions (PDFs) indicate that liquid Fe<sub>60</sub>Cu<sub>40</sub> alloy is ordered in the short range and disordered in the long range. If the atom types are ignored, the total atom number densities and PDFs demonstrate that the atoms are distributed homogeneously in the liquid alloy. However, the segregation of Fe and Cu atoms is very obvious with decreasing temperature. The partial PDFs and coordination numbers show that the Cu and Fe atoms are not apt to get together on the atomic scale at low temperatures; this will lead to large fluctuations and phase separation in liquid Fe-Cu alloy.

**liquid alloy, phase separation, atomic scale, Fe-Cu alloy, undercooling**

**Citation:** Wang H P, Wei B B. Understanding atomic-scale phase separation of liquid Fe-Cu alloy. Chinese Sci Bull, 2011, 56: 3416–3419, doi: 10.1007/s11434-011-4739-x

Phase separation frequently occurs in various systems, including colloids, liquid crystals, and metal alloys. This has aroused great research interest in the field of condensed-matter physics in recent years [1–6]. In metal alloy systems, liquid phase separation is always characteristic of monotectic and peritectic alloys such as Al-Pb, Fe-Sn, Fe-Cu, and Co-Cu alloys [7–9]. For this type of alloy, it is usually hard to achieve high undercooling before nucleation of secondary droplets because of the low liquid-liquid interface energy. This causes great difficulties in the study of phase separation at high undercoolings. It is also difficult to directly observe the phase separation *in situ* because of the opacity and metastability of the alloys. Although experimental observations can be achieved in some transparent solutions, the scale is always at the micrometer level. It is desirable to understand the phase separation on the atomic scale.

To date, there have been extensive investigations on the phase separation of metal alloys, and most research has focused on investigating the solidified microstructures experimentally or by simulation [10,11]. It has been shown that core-shell microstructures form within Fe-Co-Cu and

Fe-Sn alloy droplets solidified during free fall [12,13]. The phase-separation processes in Fe-Cu and Ni-Cu-Pb alloys have been simulated by field methods. It has been shown that the Cu- or Pb-rich phase always forms the outer layer because of surface segregation, whereas internal microstructural evolution is mainly controlled by Marangoni convection [14,15]. In contrast, much work remains to be done in understanding atomic-scale phase separation. The serious experimental difficulties encountered on the atomic scale have resulted in atomic-scale phase-separation mechanisms being less well understood. Changes in liquid structure are therefore of great importance for clarifying the kinetics of phase separation. Molecular dynamics (MD) calculations combined with a reasonable potential model have served as a powerful tool for studying the structures of liquid alloys [16–18].

Fe-Cu alloy is a typical peritectic alloy system, and involves repulsive interactions between Fe and Cu. Its liquid alloy always separates into two liquids when the temperature decreases below its liquidus temperature because of a metastable immiscible gap in the phase diagram. Although various studies of the phase separation of Fe-Cu alloys have already been performed, it is still an appropriate model sys-

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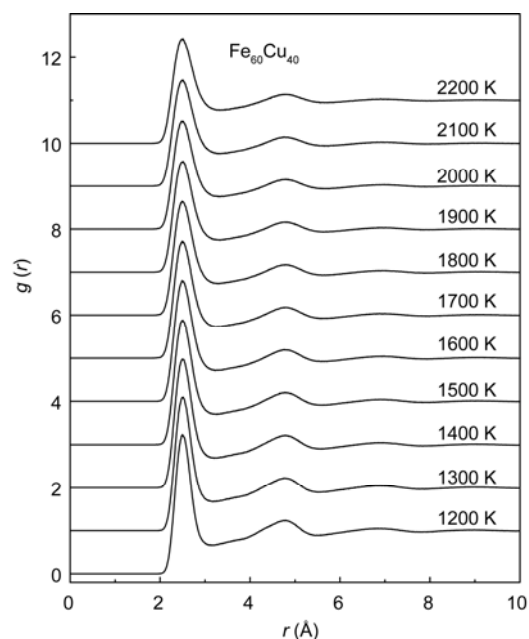
tem for exploring atomic-scale phase separation. Using  $\text{Fe}_{60}\text{Cu}_{40}$  alloy as the research subject, the purpose of this work is to reveal the atomic distribution in liquid Fe-Cu alloys, using MD calculations, to further understand atomic-scale phase-separation mechanisms.

MD calculations were performed to study the liquid structure of Fe-Cu alloys. The MEAM model was used because it is valid for both fcc and bcc alloys [19,20]; this is described in more detail by Baskes [21]. In the model, 19200 Fe atoms and 12800 Cu atoms are arranged in a cubic box under a constant-pressure and constant-temperature (NPT) ensemble; the ensemble is subject to periodic boundary conditions. The temperature is adjusted every 50 steps. The pressure is set to 1 bar to simulate real conditions. The time step is 1 fs. To obtain the equilibrium liquid state, the calculation starts at 3000 K, and is kept constant for 200000 steps. A cooling process with a  $10^{13}$  K/s cooling rate is performed for calculations at 100 K temperature intervals. At each temperature, 100000 steps are carried out to obtain equilibrium. The last 50000 steps are used to calculate the final results. All codes (LAMMPS) are run in a Lenovo 1800 Cluster system.

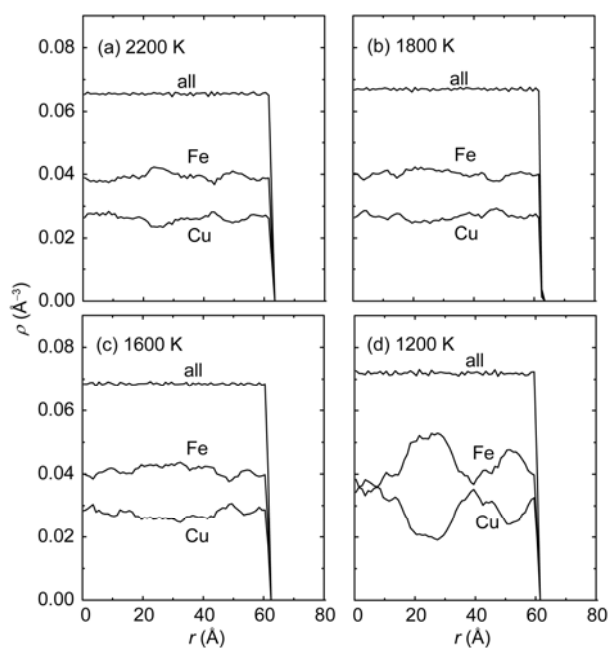
To examine the state of the calculated cell at every calculated temperature, the pair distribution function (PDF) is computed by the expression  $g(r) = V\langle n_i(r, r + \Delta r) \rangle / (4\pi r^2 \Delta r N)$ , where  $V$  is the calculated cell volume,  $n_i(r, r + \Delta r)$  is the atom number around the  $i$ th atom in a spherical shell between  $r$  and  $r + \Delta r$ ,  $\langle \dots \rangle$  is the average symbol, and  $N$  is the atom number. The temperature range for the liquid structure is 1200–2200 K, including both a superheating range and a large metastable undercooled regime. Figure 1 presents the PDF results for  $\text{Fe}_{60}\text{Cu}_{40}$  alloy; these results suggest that the atomic structure is ordered in the short range and disordered in the long range, even at the lowest temperature of 1200 K. By combining with the mean-square displacement versus time, it can be concluded that  $\text{Fe}_{60}\text{Cu}_{40}$  alloy is a highly metastable liquid below its liquidus temperature of 1706 K, rather than a solid.

Although the total atomic distribution of the  $\text{Fe}_{60}\text{Cu}_{40}$  alloy can be deduced from Figure 1, the distribution of Fe and Cu atoms is not clear. Whether phase separation occurs is therefore unknown, and the distribution of the atom number density is calculated to clarify this point. The simulated cell is divided into slabs of thickness 1 Å, and the atom number is statistically averaged in each slab, as shown in Figure 2. In each part of the figure there are three curves: the atom number density for Fe atoms, for Cu atoms, and for all the atoms. For all four temperatures studied, the atom number densities for all the atoms are almost flat; this shows that the atoms distribute homogeneously in the liquid alloy if the atom types are not discriminated.

Figure 2 also displays the distribution of different atoms at various temperatures. For the cases of 2200 K (Figure 2(a)) and 1800 K (Figure 2(b)), the atom number densities of Fe and Cu atoms fluctuate slightly around their average



**Figure 1** Pair distribution functions of liquid  $\text{Fe}_{60}\text{Cu}_{40}$  alloy. These indicate that Fe-Cu alloys are ordered in the short range and disordered in the long range.

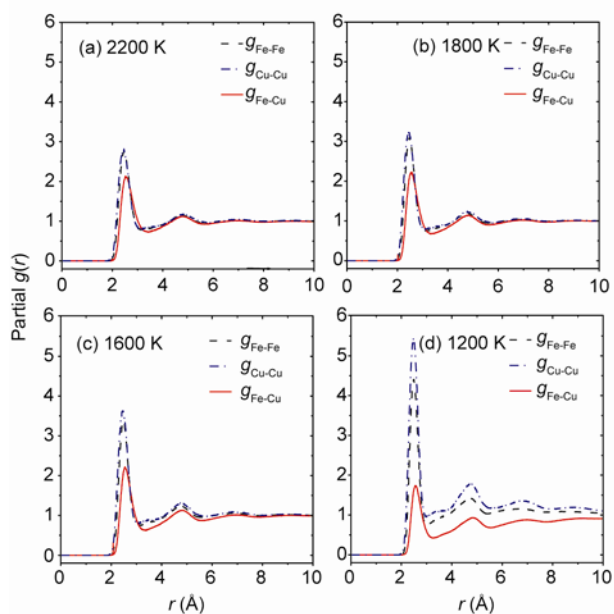


**Figure 2** Atom number density profiles along the  $x$ -axis of liquid  $\text{Fe}_{60}\text{Cu}_{40}$  alloy at 2200 K (a), 1800 K (b), 1600 K (c), and 1200 K (d).

values at different positions. This means that no phase separation occurs in liquid  $\text{Fe}_{60}\text{Cu}_{40}$  alloy because these temperatures are higher than the liquidus temperature of 1706 K. The binodal line in the experiment is about 100 K lower than this temperature, i.e. around 1600 K. For the case below the binodal line at 1600 K (Figure 2(c)), the fluctuations of the atom number densities of Fe and Cu become

larger than those at 2200 K (Figure 2(a)) and 1800 K (Figure 2(b)). When the temperature falls to 1200 K (Figure 2(d)), the fluctuations are extremely serious. For Fe atoms, the atom number density at the 30 Å position is about 25% larger than its average value. For Cu atoms, the atom number density at the 30 Å position is about 30% lower than its average value. The width of this serious fluctuation is about 20 Å. A similar situation occurs in the 45–55 Å range. Although complete phase separation does not occur, i.e. some Cu atoms are still in the Fe-rich zone and some Fe atoms are still in the Cu-rich zone, the segregation of Fe and Cu atoms is significant. The above results were calculated along the  $x$ -axis. We also examined the results along the  $y$ -axis and the  $z$ -axis, and the situations were similar. Accordingly, we can speculate that the same types of atom begin to segregate when the temperature is below a critical value. In particular, the segregation becomes increasingly pronounced with decreasing temperature.

To further understand this phenomenon on the atomic scale, partial PDFs are calculated to illustrate the atomic short-range degree of order for Fe and Cu atoms, as shown in Figure 3. The  $g_{\text{Fe-Fe}}$  represents the results by calculating the PDF and ignoring the existence of Cu atoms;  $g_{\text{Cu-Cu}}$  represents the results by calculating the PDF and ignoring the existence of Fe atoms. Setting a random Fe or Cu atom as the center,  $g_{\text{Fe-Cu}}$  is obtained by calculating the PDF of only Cu atoms around this Fe atom, or only Fe atoms around this Cu atom. For the partial PDFs of  $g_{\text{Fe-Fe}}$  and  $g_{\text{Cu-Cu}}$ , the curves at 2200 K (Figure 3(a)) and 1800 K (Figure 3(b)) almost overlap. If the temperature is lower than 1800 K,  $g_{\text{Cu-Cu}}$  is larger than  $g_{\text{Fe-Fe}}$  when  $r < 10$  Å. This is particularly noticeable at the lowest temperature of 1200 K (Figure 3(d)).



**Figure 3** Partial pair distribution functions of liquid  $\text{Fe}_{60}\text{Cu}_{40}$  alloys at 2200 K (a), 1800 K (b), 1600 K (c), and 1200 K (d).

With decreasing temperature, the heights of the first peaks increase; these peaks represent the short-range degree of order at the first-neighbor distance. The first-peak value of  $g_{\text{Cu-Cu}}$  is 2.8 at 2200 K, and it increases to 5.5 when the temperature drops to 1200 K, i.e. the value at 1200 K is almost twice that at 2200 K. Moreover, the first-peak value of the total PDF of this alloy is only 3.2 at 1200 K. The order degree of the Cu atoms is much larger than the average value. The value of  $g_{\text{Fe-Cu}}$  is always smaller than  $g_{\text{Cu-Cu}}$  and  $g_{\text{Fe-Fe}}$ , and is also smaller than the average PDF of this alloy. With decreasing temperature, this effect becomes increasingly serious. When the temperature is higher than 1600 K,  $g_{\text{Fe-Cu}}$  does not fluctuate around 1 until  $r$  exceeds 6 Å. Once the temperature has decreased to 1200 K,  $g_{\text{Fe-Cu}}$  is always smaller than 1 until  $r$  increases to 10 Å. Moreover, the first-peak value of  $g_{\text{Fe-Cu}}$  decreases with decreasing temperature, suggesting that the order degree between Fe and Cu atoms decreases at much lower temperatures.

According to the above analysis, it can be inferred that Cu atoms “like” to be the neighbors of Cu atoms and Fe atoms “like” to be the neighbors of Fe atoms. Fe atoms are not “willing” to be the neighbors of Cu atoms. This leads to the main difference in the partial PDFs. To further confirm this point, the coordination numbers of Fe and Cu are statistically obtained, and they are listed in Table 1. At a high temperature, the coordination number  $N$  between Fe and Cu atoms is similar to that for normal mixing. For instance, the  $N$  of Cu surrounded by Fe atoms (Cu atoms are not counted) is 5.24 at 2200 K, which is close to the value of 4.06 for  $N_{\text{Cu-Cu}}$ . In the case of a low temperature, both  $N_{\text{Fe-Cu}}$  and  $N_{\text{Cu-Fe}}$  decrease noticeably. At 1200 K, the values of  $N_{\text{Fe-Cu}}$  and  $N_{\text{Cu-Fe}}$  are 2.20 and 3.30; these are much smaller than the values of 7.05 and 6.14 for  $N_{\text{Fe-Fe}}$  and  $N_{\text{Cu-Cu}}$ . From the coordination number perspective, the Cu atom number around a Cu atom and the Fe atom number around a Fe atom are larger than those for coordination of atoms of different types. This also indicates that the segregation of Fe and Cu atoms leads to large fluctuations in the atom number densities, although they do not separate completely because the coordination numbers are still larger than zero.

In summary, the liquid structure of  $\text{Fe}_{60}\text{Cu}_{40}$  alloy is studied in the light of its dependence on temperature to understand the atomic-scale phase-separation mechanism. The

**Table 1** Coordination number of Fe atoms and Cu atoms <sup>a)</sup>

$T$ (K)	$N_{\text{Fe}}$	$N_{\text{Fe-Fe}}$	$N_{\text{Fe-Cu}}$	$N_{\text{Cu}}$	$N_{\text{Cu-Fe}}$	$N_{\text{Cu-Cu}}$
1200	9.25	7.05	2.20	9.44	3.30	6.14
1600	9.31	6.14	3.17	9.38	4.76	4.63
1800	9.34	5.99	3.35	9.30	5.03	4.27
2200	9.39	5.90	3.50	9.31	5.24	4.06

<sup>a)</sup>  $T$  is temperature;  $N_{\text{Fe}}$ ,  $N_{\text{Fe-Fe}}$ ,  $N_{\text{Fe-Cu}}$ ,  $N_{\text{Cu}}$ ,  $N_{\text{Cu-Fe}}$ ,  $N_{\text{Cu-Cu}}$  are the coordination numbers of Fe, Fe surrounded by Fe atoms, Fe surrounded by Cu atoms, Cu, Cu surrounded by Fe atoms, and Cu surrounded by Cu atoms.

total PDFs indicate that the atomic structure is ordered in the short range and disordered in the long range at all the investigated temperatures. The atoms are distributed homogeneously in the liquid alloy if the atom types are not differentiated. However, with decreasing temperature, the segregation of Fe and Cu atoms is remarkable in terms of the atom number densities of the Fe and Cu atoms. Although complete phase separation does not occur, the partial PDFs and the coordination numbers confirm that atoms of the same type display a strong tendency to get together. These results provide some fundamental insights into the understanding of atomic-scale phase separation.

*The authors are grateful to Mr. Jian Chang, Mr. Baokun Lu, and Mr. Shangjiang Yang for their helpful discussions. This work was supported by the National Natural Science Foundation of China (50971103 and 50971105), the Program for New Century Excellent Talents, Natural Science Foundation of Shaanxi Province (2010JQ6004), Shaanxi Project for Young New Star in Science and Technology, and NPU Foundation for Fundamental Research.*

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