Pre-peak in the structure factor of liquid Al-Fe alloy

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Abstract.   Based on the study of the positions and heights of the pre-peaks on the structure factors of liquid Al–Fe alloys, it is found that the heights are higher in the region on the phase diagram where nearly all the intermetallic compounds with higher melting temperature gather, and the highest at Fe_2Al_5; while the positions are smaller, and a minimum at Fe_2Al_5. These results reveal the close relationship between the liquid structure and the Al–Fe alloy phase diagram. Two types of atomic configuration are constructed, and the origin of the pre-peaks is found to be the Fe–Fe correlation or the Al–Al correlation, or their mixture at different compositions.

1. Introduction

The fast-solidified Al–Fe-based alloys and Al–Fe–Re metallic glasses [1, 2] show excellent specific strength. Some metallic glasses can be formed with aluminum content up to 90%. Fe_3Al-based iron aluminides [3] have been of interest for many years because of their excellent oxidation and sulphidation resistance. Until now, there is only a little work [4, 5] on the structure of liquid Al–Fe alloys. The study of the atomic structure of Al–Fe alloys should be helpful to the understanding of the formation and structure of the above materials.

The static structure factor $S(Q)$ can be obtained through x-ray diffraction. The typical $S(Q)$ ([6], p 62) has a sharp first peak with several peaks whose height decreases successively on the large-Q side of the first peak. Most liquid metals and alloys have such an $S(Q)$.

With the development of the research work on the liquid structure, a new feature in the $S(Q)$ of some liquid alloys [7, 8] begins to attract more and more attention. The feature is a pre-peak on the small-Q side of the first peak, which is much smaller than the first peak in height and stands in the region of 10–16 nm^{-1}. Some Al-based alloy liquids, for example liquid $Al_x[Mn_y(FeCr)_{1-y}]_{1-x}$ [9] and $Al_{80}Ni_{20}$ [10], exhibit a pre-peak in both total and partial structure factors. The pre-peak is often more obvious on the $S(Q)$ of amorphous materials than that of liquid alloys. The physical origin of the pre-peak has not been defined yet. In general, the presence of a pre-peak corresponds to compound-forming behaviour [11], or can be attributed to the structure of clusters constituted of unlike atoms, and means that not only short-range order but the medium-range order [12] exists in the melt.

In this article the changes in the pre-peak with Fe content are studied, and compared with the phase diagram. The local atomic structure is also constructed.

2. Experimental procedure

The alloy specimens were prepared from high-purity Al (99.999%) and Fe (99.98%) in a crucible made of Al_2O_3 of size $8 \times 25 \times 30$ mm^3. Measurements were carried out at the constant temperature 1550 °C with an accuracy of ± 5 °C.

The x-ray scattering intensity from the molten alloys was measured using a θ–θ diffractometer which allowed the sample to be held in a stationary horizontal position and the x-ray tube and detector moved in opposite directions. The intensity profiles were obtained by Mo Kα radiation ($\lambda = 0.071$ nm) coupled with a graphite monochromator in the diffraction beam, in the scattering angle 2θ from 5 to 90° which covers the values of wavevector $Q = 4\pi \sin\theta/\lambda$ between 5 and 120 nm^{-1}.

The scattering intensity measured in arbitrary units can be converted into the coherent scattering intensity per atom in electron units $I_{eu}^{coh}(Q)$, using the generalized Krogh–Moe– Norman ([6], p 10) method with the atomic scattering factor including the anomalous dispersion factor compiled in the *International Tables for X-ray Crystallography IV* [13]. Compton scattering is also corrected using the values reported by Cromer and Mann [14].

The total structure factor can be obtained through equations

$$S(Q) = I_{eu}^{coh}(Q)/\langle f^2(Q)\rangle \tag{1}$$

$$\langle f^2(Q)\rangle = c_1 f_1^2(Q) + c_2 f_2^2(Q). \tag{2}$$

Here $c_i = N_i/N$. N_i is the number of type i atoms in the scattering volume in which the total atom number is N. $f_i(Q)$ is the type i atomic scattering factor. $i = 1, 2$.
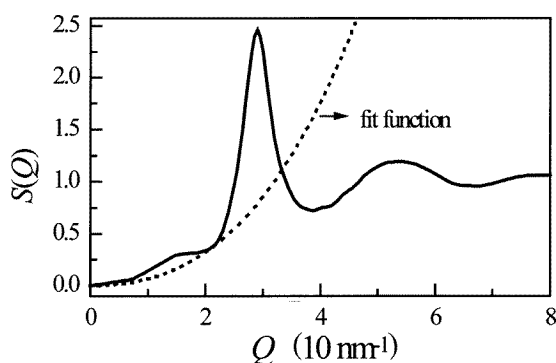

Figure 1. Separation of the pre-peak.

A parabolic-like function $f(x) = ax^2 + bx^3$, in which b is often much smaller than a, was used to fit the small-angle part of $S(Q)$, as shown in figure 1. Separation of the pre-peak is executed by $S(Q)$ minus the fit function. Such a method has been used in [12] and mentioned in [15].

3. Results

Parameters of the pre-peaks at different Fe contents are given in table 1. Structure factors at 1550 °C are shown in figure 2 where the pre-peak can be seen from 12.50% Fe to 87.40% Fe, but disappears suddenly when the iron content is less than 8.00%. The height of the pre-peak (HPP) at 87.40% Fe is only about 1/12 of the maximum.

Table 1. Parameters of the pre-peaks at different Fe contents.

Fe content (at.%)	Symbol	Q_p ($10\ \mathrm{nm}^{-1}$)	$S(Q_p)$	d_p (nm)
0.00	A	—	—	—
8.00	B	—	—	—
12.50	C	1.28	0.117	0.491
25.00	D	1.36	0.144	0.462
28.57	E	1.30	0.198	0.483
33.34	F	1.45	0.110	0.433
40.00	G	1.48	0.122	0.425
50.00	H	1.45	0.110	0.433
60.00	I	1.53	0.056	0.410
75.00	J	1.60	0.020	0.393
87.40	K	1.63	0.017	0.385
100.00	L	—	—	—

Q_1, which is the first peak position of $S(Q)$, is shown in figure 3. Al_7Fe, Fe_2Al_5 and Fe_3Al are the turning compositions of Q_1.

As shown in figure 4(a) the position of the pre-peaks shifts towards large Q with increasing Fe content, but has a minimum at Fe_2Al_5, while in figure 4(b) HPP decreases in the Fe rich direction; a maximum is still at Fe_2Al_5.

4. Discussion

The sudden disappearance of the pre-peak at 8.00% Fe is very strange, which was also found by another author [5]. There must be a liquid structural transformation in the range of 8.00% Fe–12.75% Fe.

The higher the HPP, the better the compound-forming behaviour [11]. It is obvious that in figure 4(b) this ability is better around Fe_2Al_5, and best at Fe_2Al_5.

According to the phase diagram [3] shown in figure 5, nearly all the intermetallic compounds gather around Fe_2Al_5, among which Fe_2Al_5 has the highest melting temperature $1171\,°C$, while Al_3Fe and $FeAl_2$ about $1157\,°C$. Correlation can be found between figure 4(b) and the phase diagram. In the region which has most of the intermetallic compounds, the HPP has a larger value. Fe_2Al_5 has the highest melting temperature, and the largest value of HPP. It can be speculated that in the melt the distribution of the atoms of Al and Fe is not random: the structure of the solid in the medium range persists into the melt. Fe_2Al_5-like clusters that are more stable in structure and composition may be found in the melts in a wide range of Fe content.

The calculation [16] by quantum physics shows that the attraction between Al and Fe atoms is very strong. This is the reason why there is pre-peak and liquid–solid structure correlation. In addition, from figure 3 structural transformation is present at Al_7Fe, Fe_2Al_5 and Fe_3Al. The opinion in the article [5] was that in the Al–Fe melts there was intermetallic compound Fe_2Al_5, because in the pre-peaks stood the lines of crystalline Fe_2Al_5.

In this work, measurements were performed at a constant temperature of $1550\,°C$. When Fe content increases, the temperature becomes close to the liquidus curve. But neither the first peak position [17] nor the position of the pre-peak [18] of the structure factor is visibly affected by temperature changes.

It is well known that the medium-range order in liquid is enhanced when the temperature is close to the liquidus curve. In this study the temperature of Fe_3Al is much closer to the
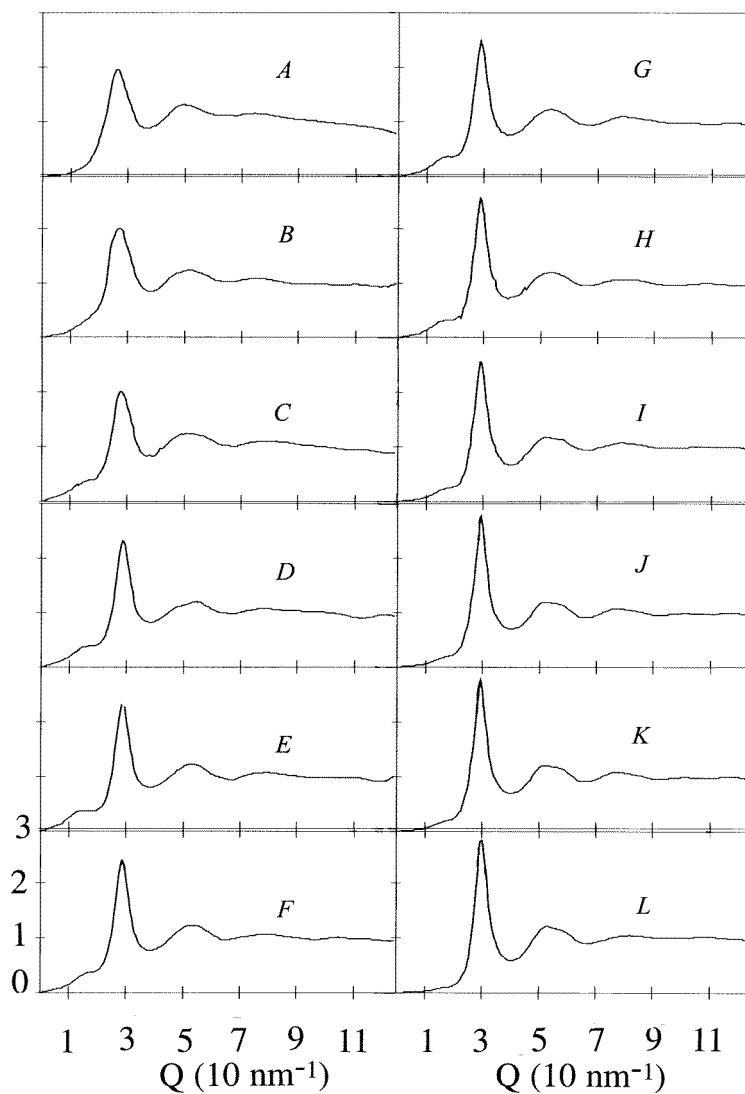
Figure 2. Structure factors of different alloys at 1550 °C. The letters A–L indicate the composition as listed in table 1. The scales of different layers are the same as that in layer F.

liquidus curve than that of Fe_2Al_5; however, the pre-peak is much weaker in Fe_3Al than in Fe_2Al_5. This situation indicates medium-range order is really stronger in Fe_2Al_5 than in Fe_3Al and maybe the types of medium-range order are different in liquid Fe_3Al and Fe_2Al_5.

Figure 6 shows the correlation distance d_p determined by the position of the pre-peak Q_p, using the equation $d_p = 2\pi/Q_p$ [12]. The first three alloys C–E have a d_p around 0.49 nm, F–H alloys about 0.43 nm and I–K alloys near 0.40 nm indicated by dotted lines respectively in figure 6. A pre-peak originates from the correlation between the minor species atoms [11, 12]: then the distance between such atoms is available. This information can be used to construct the model structure of the clusters in the liquid. Firstly for the C–E alloys, Fe is a minority, so its nearest neighbours are preferentially Al atoms and in
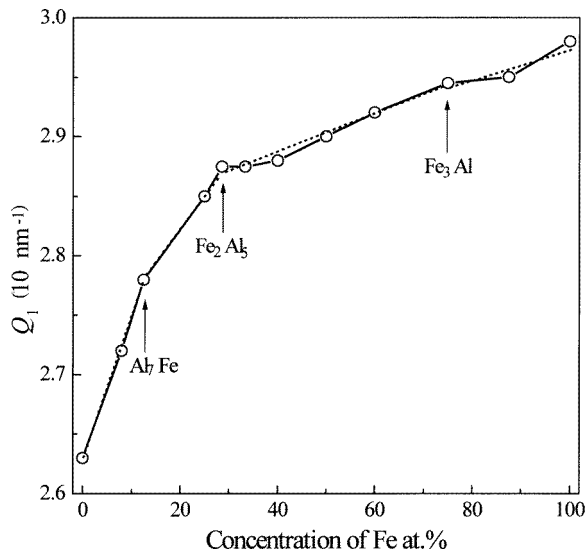
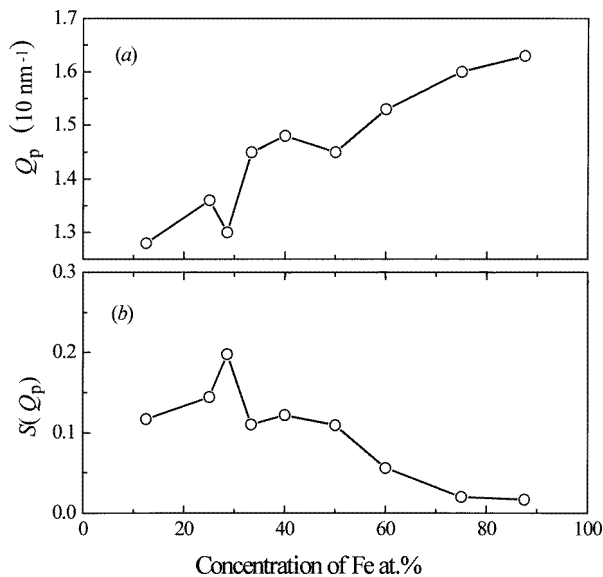**Figure 3.** The first peak positions of the $S(Q)$s at different Fe contents.

Figure 4. (*a*) Positions of the pre-peaks, (*b*) HPPs at different Fe contents.

specific clusters Fe may have ultimately only Al nearest neighbours. Secondly, for the I–K alloys, Al is a minority, so its nearest neighbours are preferentially Fe atoms, and also, in specific clusters Al may have only Fe nearest neighbours.

Taking the crystalline structure as the first-order approximation of the liquid structure, the primarily model structures of clusters are constructed on the basis of the above analysis. For the C–E alloys the polyhedrons containing one Fe atom which is coordinated by 6–12 Al atoms are tested respectively. Among these units only the unit shown in figure 7 (type I) can meet the requirement of the pre-peak position. In figure 7 eight Al atoms (type I) form
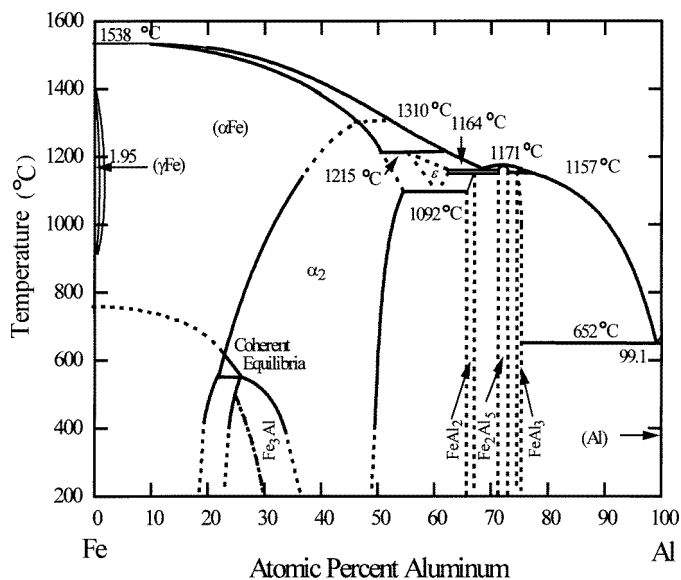
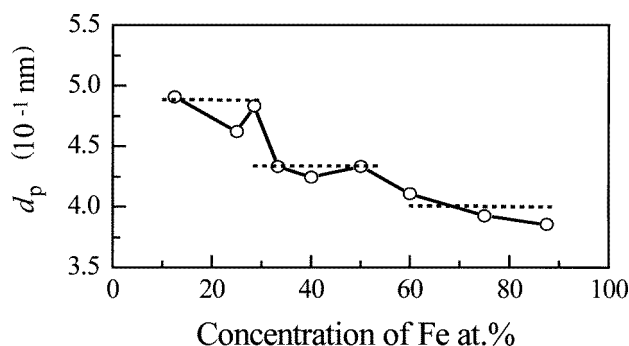**Figure 5.** Schematic phase diagram of iron–aluminum.

Figure 6. Real space manifestation of Q_p.

a cube with an edge of 0.286 nm (this study), whose centre is occupied by an Fe atom. Then the d_{FeAl} is 0.2477 nm, very close to the value 0.248 nm [4]. If another unit with the same structure is connected with this one and shares one Al atom along a body diagonal, the distance d_{FeFe} between these two units is 0.495 nm, very close to the value of 0.49 nm from figure 6. Hereafter the structure formed in this way of connection is called type I structure.

For the I–K alloys, following the same procedure as for the C–E alloys, it is found that only the unit shown in figure 7 (type II) can well describe the pre-peak position. The unit also has an edge of 0.286 nm, and a d_{FeAl} of 0.248 nm. Two such units sharing an edge in the plane of the two body diagonals give a d_{AlAl} of 0.404 nm, rather close to the value of 0.40 nm from figure 6. The structure formed in this way of connection is called the type II structure.

It is worth noticing that type II structure is similar to DO_3 structure [3] of the ordered Fe_3Al alloy. The unit involved in type II structure is nearly the same as that in DO_3
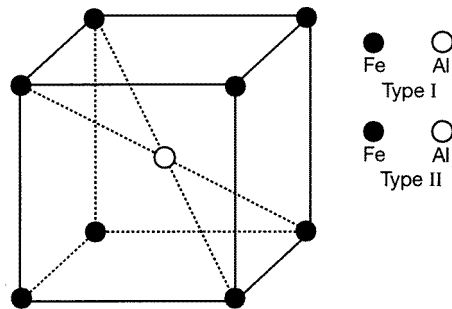
Figure 7. Unit of the structure model.

structure; so is the way of connection of such units. The unit in DO_3 has an edge of 0.289 nm, and a d_{FeAl} of 0.250 nm. The difference between the unit in type II structure and that in DO_3 with one Al atom is negligible.

This implies that the pre-peaks of the F–H alloys may be related to B_2 structure [3] for ordered FeAl alloy, since the H alloy can be a B_2 structure in solid state. The primitive cell of B_2 structure is the same as the unit in DO_3 structure with an Al atom. In B_2 structure Fe and Al atoms have identical sites. Each atom has two like atoms in the distances of 0.408 nm and 0.50 nm respectively. Hence the pre-peaks observed in the F–H alloys are the linear sum of the pre-peaks from the two distances. The pre-peak position should be near the average distance 0.454 nm but on the side of 0.408 nm, since the correlation on 0.408 nm must be stronger than that on 0.50 nm. Indeed, for the F–H alloys the distance of about 0.43 nm from figure 6 falls in the region of 0.408 to 0.454 nm and close to 0.408 nm.

The model structure based on the cubic clusters is an approximation of the liquid structure, and it is likely that the clusters occupy only a part of the volume of the melt. In order to prove the clusters, at least three partial radial distribution functions are necessary which are unavailable in the present x-ray diffraction pattern.

5. Conclusion

In the Al–Fe alloy system, there is liquid–solid structure correlation in the range 12.75% Fe–87.40% Fe; the atomic configuration persists into the melts in the medium range; the Fe_2Al_5 type cluster is the most stable one in the melts.

Unlike atoms are predominately coordinated, the Fe–Al distance in liquid Fe–Al alloys is nearly the same as that in the solid state.

The origin of the pre-peak is the Fe–Fe correlation in Al-rich alloys and the Al–Al correlation in Fe-rich alloys, but a mixture of Fe–Fe and Al–Al correlation around the composition of FeAl alloy.

Acknowledgments

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