Structural Analysis of Molten Fe-Si Alloys by X-ray Diffraction*

By Yoshifumi KITA,** Masafumi ZEZE*** and Zen-ichiro MORITA**

Synopsis

Detailed measurements of X-ray diffraction on molten Fe-Si alloy, one of the fundamental systems in iron- and steelmaking, have been carried out over the whole concentration range at about 10 at% Si intervals at temperatures 50 °C above the liquidus.

The total interference functions $a(K)$ and the radial distribution functions $4\pi r^2 \rho_0 g(r)$ were estimated, from which the position K_1 , the height $a(K_1)$ and the half width W of the first peak of $a(K)$, and the nearest neighbour distance r_1 and the coordination number n_1 were also obtained. The partial interference functions $a_{\text{FeFe}}(K)$ and $a_{\text{SiSi}}(K)$ were estimated at 30 at% Si by a concentration method.

It was found that in the concentration range up to 40 at% Si, the overall feature of $a(K)$ and $g(r)$, together with K_1 , $a(K_1)$, W , r_1 and n_1 is almost similar to that of molten Fe. While for the alloys in the concentration range beyond 50 at% Si, with increasing Si content, the first peak of $a(K)$ becomes broader and more asymmetric, the first peak of $g(r)$ becomes narrower and the subsequent peaks are more strongly damped, and n_1 decreases.

From these facts, it was deduced that the structure of molten Fe-Si alloys is nearly close-packed in the range up to 40 at% Si, and then gradually changes to be more open, lower-coordinated with increasing Si concentration. The comparison of these results with other properties closely related to the liquid structure was also made.

I. Introduction

From the standpoint of iron- and steelmaking, especially in relation to properties of melts, it is important and interesting to obtain precise information on the atomic structure of molten Fe-based alloys. As is well known, in molten Fe-Si alloy, which is one of the fundamental systems in iron- and steelmaking, thermodynamic activities of Fe and Si show a remarkable negative deviation from Raoult's law,¹⁾ thus representing a strong interaction between Fe and Si atoms. Therefore, interest has been focused on the structure as well as various properties of this alloy system recently.

Formerly at the Fourth Japan-USSR Joint Symposium in 1973, Vatolin and Pastuhov²⁾ presented an X-ray study on the structure of molten alloys of Fe and Ni with Si and C, in which they suggested that experimental results on molten Fe-Si alloys can be explained by a structure model based on crystalline FeSi, FeSi₂, Fe and Si, and on quasi-eutectic versions.

On the other hand, more recently, Waseda and Tamaki,³⁾ and Waseda and Shiraishi⁴⁾ carried out X-ray diffraction analysis for molten Fe-Si alloys, and obtained three partial interference functions $a_{\text{FeFe}}(K)$, $a_{\text{FeSi}}(K)$ and $a_{\text{SiSi}}(K)$, using an anomalous scattering technique. In their results, it was shown that the partial interference functions were nearly independent

of the concentration of alloys, and that the Fe and Si atoms act, to the first approximation, as hard spheres in molten Fe-Si alloys.

Since both of X-ray diffraction studies quoted above had given results rather conflicting each other, it is considered that a study on the structure of molten Fe-Si alloys is still to be performed in detail and precisely, taking special care of the problem how the structure of these alloys changes with composition. In this study, from the above standpoint, the structure of molten Fe-Si alloys has been investigated in detail by X-ray diffraction over the whole concentration range at various compositions.

II. Experimental

The X-ray diffraction was carried out using a θ - θ diffractometer which is similar to that previously used.⁵⁾ The X-rays radiated from a Mo target and passed through a divergence slit (1/6 or 1 deg), were reflected from the free surface of the molten specimen. The scattered X-rays were then monochromatized by a curved graphite crystal after passing through a scattering slit (1 or 2 deg) and a receiving slit (0.6 mm wide), and finally counted by a scintillation counter. In order to collect the scattered X-rays more effectively, divergence and scattering slits were replaced by wider ones (1 and 2 deg, respectively) for scattering angles higher than about $\theta=15$ deg.

The scattering intensities were measured over the angular range, from $\theta=3$ deg to $\theta=42$ deg, with the step-scan mode at intervals of 0.25 deg over the first peak and at 0.5~2 deg intervals for the remaining part. The complete intensity curve was obtained from the scan of three times or more, finally accumulating more than 3×10^4 counts at each scattering angle, and the probable error of the mean curve was $\pm 2\%$ including a statistical error and an unavoidable error resulting from experimental conditions.

The specimens were heated by a Mo heater, melted in an alumina cell (meniscus area, 25×35 mm) in a purified Ar-10% H₂ atmosphere, and held at the given temperature with an accuracy of ± 5 °C. The alloy specimens were prepared from high-purity Fe (99.98 %) and Si (99.999 %).

In this study, measurements were carried out on molten Fe-Si alloys for the whole concentration range at intervals of about 10 at% Si, at temperatures about 50 °C above the liquidus. The compositions of the specimens and their temperatures at which measure-

* Based on the paper presented to The Eighth Japan-USSR Joint Symposium on Physical Chemistry of Metallurgical Processes, June, 1981, ISIJ, Tokyo, (1981), in English. Manuscript received March 31, 1981. © 1982 ISIJ

** Department of Metallurgical Engineering, Faculty of Engineering, Osaka University, Yamadaoka, Suita 565.

*** Graduate School, Osaka University.

ments were made are indicated in Fig. 1 by solid dots on the phase diagram of the Fe-Si system.¹⁾

III. Analysis of Intensity Patterns

Although the method of analysing the observed X-ray intensity is familiar in this field,⁶⁾ a brief description is given below for the convenience of discussion.

The scattering intensity was at first corrected for background counts and for polarization effect⁷⁾ occurring at both the molten specimen surface and the monochromator, then normalised to absolute units by two methods, *i.e.*, high angle method⁷⁾ and Krogh-Moe Norman method,^{8,9)} using atomic scattering factors for Fe and Si calculated by Cromer and Waber¹⁰⁾ with a correction for the anomalous dispersion.¹¹⁾ In this procedure, a correction for the incoherent scattering^{12,13)} was also taken into account.

The total interference function $a(K)$ was obtained from the resulting intensity of the coherent scattering per atom in electron units, $I_{\text{eu}}^{\text{coh}}(K)$, and expressed for a binary system as follows:

$$a(K) = \{I_{\text{eu}}^{\text{coh}}(K) - \langle f^2 \rangle + \langle f \rangle^2\} / \langle f \rangle^2 \dots\dots\dots(1)$$

where, $K = 4\pi \sin \theta / \lambda$; 2θ : the scattering angle,
 λ : the wave length

$$\begin{aligned} \langle f^2 \rangle &= c_i f_i^2 + c_j f_j^2 \\ \langle f \rangle &= c_i f_i + c_j f_j \end{aligned}$$

c, f : atomic concentration and atomic scattering factor with i and j referred to atomic species.

The partial interference functions required to characterise a binary system $a_{ii}(K)$, $a_{jj}(K)$ and $a_{ij}(K)$ were calculated by means of a concentration method¹⁴⁾ using $a(K)$ at three different concentrations over a limited range where the partial structure was assumed to be invariant, according to a generalised relationship:

$$\begin{aligned} a(K) &= \{c_i^2 f_i^2 a_{ii}(K) + c_j^2 f_j^2 a_{jj}(K) \\ &\quad + 2c_i c_j f_i f_j a_{ij}(K)\} / \langle f \rangle^2 \dots\dots\dots(2) \end{aligned}$$

The atomic radial distribution function (RDF) $4\pi r^2 \rho_0 g(r)$ was evaluated by the Fourier transformation of the interference function:

$$4\pi r^2 \rho_0 g(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty K \{a(K) - 1\} \sin(Kr) dK \dots\dots\dots(3)$$

where, r : the distance from origin
 ρ_0 : the average atomic density
 $g(r)$: the pair distribution function.

On calculating RDF from this equation, the value of ρ_0 was estimated from the extrapolation of the density data of molten Fe-Si alloys measured by Gel'd *et al.*,¹⁵⁾ and $a(K)$ was extrapolated to $K=0$ smoothly by use of well-known thermodynamic relation $a(0) = \rho_0 \chi_T k T$, where χ_T , the isothermal compressibility, was taken from literature¹⁶⁾ for Fe and Si, and estimated by assuming additive law for alloy specimens.

The number of atoms in the first coordination shell, *i.e.*, coordination number n_1 was estimated by inte-

Fig. 1. The phase diagram of Fe-Si alloy system.

grating RDF:

$$n_1 = \int_{r_0}^{r_m} 4\pi r^2 \rho_0 g(r) dr \dots\dots\dots(4)$$

where, r_0 : the limit below which $g(r)$ is zero
 r_m : the value of r at which RDF has first minimum on the higher r side of the first peak.

Numerical calculation was carried out in Computation Center, Osaka University.

IV. Results and Discussion

The total interference functions $a(K)$ of molten Fe-Si alloys obtained by use of Eq. (1) are shown for various compositions in Fig. 2, where the compositions of alloys and the temperatures of measurements are numerically indicated. The variation of the first peak position K_1 of $a(K)$ with composition is given in Fig. 3 which contains, for comparison, the results of Vatolin and Pastuhov²⁾ given as the first peak positions of the intensity curves at about 30 °C above the liquidus, and those of Waseda *et al.* obtained for molten Fe and Fe-1, 5, 10 wt% Si alloys at 1 600 °C¹⁷⁾ and for molten Si at 1 460 °C.¹⁸⁾ The height $a(K_1)$ and the half width W of the first peak of $a(K)$ are also indicated in Fig. 3. $a(K)$ of molten Fe shows a sharp, almost symmetric first peak at 2.99 Å⁻¹, which agrees with the results by other investigators.^{2,17)} For molten Si, $a(K)$ shows an asymmetric first peak at 2.70 Å⁻¹ with its shoulder at 3.40 Å⁻¹, which is in agreement with the results of previous works.^{2,18)} As can be seen from Figs. 2 and 3, for the alloys in the concentration range of 10 to 40 at% Si, the overall feature of $a(K)$ as well as the first peak position K_1 , the height $a(K_1)$ and the half width W is almost similar to those of molten Fe. Since $a(K)$ in lower Si concentration range shows the contribution of Fe-Fe correlation predominantly, these facts indicate that Fe-Fe correlation like that in molten pure Fe still remains up to 40 at% Si in molten Fe-Si alloys. On the other side, for the alloys in the range of 50 to 80 at% Si, with increasing Si content, the shape of the first peak of $a(K)$ becomes broader and more asymmetric, its

Fig. 2. Total interference functions $a(K)$ for molten Fe-Si alloys at temperatures about 50 °C above the liquidus.

position K_1 is shifted toward the higher K side, the height $a(K_1)$ decreases and the half width W increases in a manner consistent with a more open liquid structure. Finally at 90 at% Si, a shoulder, characteristic of molten Si, comes to appear on the higher K side of the first peak. As is evident from Fig. 3, it should be pointed out that the first peak positions of $a(K)$ obtained in the present experiment, 3.02 Å⁻¹ for 50 at% Si and 3.11 Å⁻¹ for 67 at% Si, show remarkable difference from those obtained by Vatolin and Pastuhov,²⁾ 3.10 and 3.30 Å⁻¹ respectively, which were considered by them to correspond precisely to the positions of the diffraction lines from solid phases of ϵ -FeSi and ζ_α -FeSi₂.

The total pair distribution functions $g(r)$ obtained by Eq. (3) are shown in Fig. 4. The first peak position r_1 of RDF, *i.e.*, the nearest neighbour distance, and the coordination number n_1 are given in Fig. 5 together with the previous data.^{2,4,17,18)} The nearest

Fig. 3. Composition dependency of the position K_1 , the height $a(K_1)$ and the half width W of the first peak of $a(K)$ for molten Fe-Si alloys.

neighbour distances r_1 for molten Fe and Si are found to be 2.55 and 2.53 Å respectively, which agree fairly well with the results by previous investigators^{2,4,17,18)} except the case for molten Si by Vatolin and Pastuhov²⁾ (2.47 Å). It can be seen from Figs. 4 and 5 that, for the alloys in the range up to 40 at% Si, the pair distribution functions $g(r)$ have prominent first peaks and successive well-defined maxima. Besides, the nearest neighbour distance r_1 (2.55~2.58 Å) and the coordination number n_1 (11.3~11.7) are nearly invariant from those of molten Fe (2.55 Å and 11.2, respectively), thus indicating that molten Fe-Si alloys in the range up to 40 at% Si have a nearly close-packed structure like that of molten Fe. For the alloys with concentration beyond 50 at% Si, with increasing Si content, the width of the first peak of $g(r)$ becomes narrower and the subsequent peaks are more strongly damped, and the coordination number n_1 decreases rapidly from 10.6 for 50 at% Si to 6.5 for pure Si. These facts suggest that there appears the more open structure like that of molten Si with increasing Si concentration. The nearest neighbour distance r_1 decreases with Si content from 2.55 Å for 50 at% Si to 2.48 Å for 80 at% Si which is smaller compared to that of molten Si (2.53 Å).

These behaviours of both $a(K)$ and $g(r)$ mentioned above lead us to deduce that the structure of molten Fe-Si alloy system is nearly close-packed like that of molten Fe in the range up to 40 at% Si, and gradually changes to be more open, lower-coordinated with increasing Si concentration.

From the above mentioned, it follows that the partial interference functions for molten Fe-Si alloys may be independent of composition in the range up to 40

Fig. 4. Total pair distribution functions $g(r)$ for molten Fe-Si alloys at temperatures about 50 °C above the liquidus.

at% Si where the nearly close-packing of atoms is maintained, while they may vary with composition in the range beyond 40 at% Si due to the appearance of the more open, lower-coordinated structure in Si-rich concentration range. These deduction may not agree with the previous conclusion that the partial structures are independent of the concentration in liquid Fe-Si.³⁾ Accordingly, it may not be correct to derive the partial interference functions for these alloys in the range beyond 40 at% Si by a concentration method which necessarily involves the assumption that the three partial functions are independent of composition. Therefore, the partial interference functions $a_{\text{FeFe}}(K)$ and $a_{\text{FeSi}}(K)$ were evaluated by Eq. (2) only at the lower concentration of Si, i.e., 30 at% Si, using $a(K)$ for 10, 30 and 50 at% Si alloys*, and shown in Fig. 6, where the vertical lines indicate the uncer-

Fig. 5. Composition dependency of the nearest neighbour distance r_1 and the coordination number n_1 for molten Fe-Si alloys.

tainty, an inevitable consequence of the experimental error. $a_{\text{SiSi}}(K)$ obtained similarly has much more uncertainty than others in such a low Si concentration range since the atomic scattering factor of Si is about a half of that of Fe; therefore, it was not shown in the figure. $a_{\text{FeFe}}(K)$ and $a_{\text{FeSi}}(K)$ calculated for the random mixture of hard spheres using Percus-Yevick equation,¹⁹⁾ together with $a(K)$ for molten Fe obtained from the experiment, were also shown in Fig. 6 for comparison. As can be seen from the figure, the overall feature of the first peak of $a_{\text{FeFe}}(K)$ is in agreement with that of $a_{\text{FeFe}}(K)$ obtained from P-Y calculation and also with that of $a(K)$ for molten Fe. The peak positions for three functions are found at 2.98, 2.99 and 2.99 Å⁻¹, respectively. On account of the uncertainty for $a_{\text{FeSi}}(K)$ larger than for $a_{\text{FeFe}}(K)$, the height of the first peak of $a_{\text{FeSi}}(K)$ does not agree with those of $a_{\text{FeSi}}(K)$ obtained from P-Y calculation. However, the first peak position of $a_{\text{FeSi}}(K)$ at 3.05 Å⁻¹ agrees fairly well with that of $a_{\text{FeSi}}(K)$ at 3.02 Å⁻¹ obtained from P-Y calculation. These facts encourage us to believe that the structure of molten Fe-Si alloys in the range up to 40 at% Si could be, to the first approximation, explained by the random mixture of hard spheres.

Some possible suggestions on the variation of the structure with composition for molten Fe-Si alloy system can also be obtained from the concentration dependency of the physical or thermodynamic proper-

* On evaluating the partial interference functions for Fe-Si alloys, it is desirable to use three $a(K)$'s, all being within the concentration range up to 40 at% Si. However, it is obvious from Eq. (2) that the use of three $a(K)$'s at concentrations too close to one another leads to an extraordinarily large error in the resultant partial interference functions. According to the estimation of the error based on the determinant⁶⁾ of the weighting factor in Eq. (2), for example, the use of $a(K)$'s at 10, 30 and 50 at% Si gives the error in $a_{\text{FeSi}}(K)$ increased by 16 times that of $a(K)$, while the use of $a(K)$'s at 20, 30 and 40 at% Si causes the larger error in $a_{\text{FeSi}}(K)$ amounting to 60 times that of $a(K)$. Therefore, in order to have possible determination of the partial interference functions, we did use $a(K)$'s at 10, 30 and 50 at% Si at the sacrifice of uncertainty derived from the fact that the partial interference functions at 50 at% Si may vary slightly from those up to 40 at% Si.

Fig. 6. Partial interference functions $a_{\text{FeFe}}(K)$ and $a_{\text{FeSi}}(K)$ for molten Fe-30at%Si alloy evaluated from $a(K)$ for Fe-10, 30 and 50at%Si alloys by a concentration method and those calculated from P-Y equation for the random mixture of hard spheres, together with $a(K)$ for molten Fe obtained by the experiment. Vertical lines indicate the uncertainty.

ties which are closely related to the liquid structure. For example, the molar volume²⁰⁾ and the excess stability²¹⁾ for molten Fe-Si alloys are shown in Fig. 7. As can be seen in the figure, the molar volume V_m increases with Si content gradually up to 50 at% Si, and then rapidly in the range beyond 50 at% Si. The partial molar volume of Fe, $\bar{V}_{\text{Fe}}$, decreases, and that of Si, $\bar{V}_{\text{Si}}$, increases abruptly at 50 at% Si. These

Fig. 7. Composition dependency of the molar volume V_m , the partial molar volumes of Fe and Si ($\bar{V}_{\text{Fe}}$, $\bar{V}_{\text{Si}}$) and the excess stability for molten Fe-Si alloys.

facts suggest that the more open, lower-coordinated structure may appear and its influence gradually increases with Si content in the range beyond 50 at% Si. The excess stability, which represents thermodynamic stability of solution with reference to ideal solution, decreases abruptly at 60 at% Si. This fact also indicates that the more open, lower-coordinated structure may occur in the Si-rich concentration range.

Our deduction on the structure of molten Fe-Si alloy system derived from the X-ray diffraction study, corresponds well and does not conflict with suggestions given by the variation of these properties with composition.

V. Conclusions

Detailed analysis of X-ray diffraction has been carried out on molten Fe-Si alloy which is one of the fundamental systems in iron and steelmaking. The total interference functions $a(K)$ and the radial distribution functions $4\pi r^2 \rho_0 g(r)$ were determined from intensity patterns obtained for molten Fe-Si alloys over the whole concentration range at about 10 at% Si intervals at temperatures about 50 °C above the liquidus.

(1) In the concentration range up to 40 at% Si in molten Fe-Si alloy system, the overall feature of $a(K)$ and $g(r)$, and the short range order parameters are almost similar to those of molten Fe and nearly invariant with composition. While, for the alloys in the range beyond 50 at% Si, the overall feature of $a(K)$ and $g(r)$, and the short range order parameters vary with increasing Si concentration.

(2) From these behaviours of $a(K)$ and $g(r)$, it is deduced that the structure of molten Fe-Si alloys is nearly close-packed like that of molten Fe in the range up to 40 at% Si, and then gradually changes to be more open, lower-coordinated with increasing

Si concentration.

(3) The partial interference functions $a_{\text{FeFe}}(K)$ and $a_{\text{FeSi}}(K)$ of molten Fe-30 at% Si alloy obtained from the experiment agree with those obtained from Percus-Yevick calculation, suggesting that the structure of molten Fe-Si alloys in Fe-rich concentration range can be explained, as the first approximation, by the random mixture of hard spheres.

(4) These deductions on the structure of molten Fe-Si alloys correspond well with composition dependency of the molar volume and the excess stability.

Acknowledgements

The authors wish to express their appreciation to Prof. H. Endo, Department of Physics, Kyoto University, for valuable discussion and comments.

REFERENCES

- 1) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley: Selected Values of the Thermodynamic Properties of Binary Alloys, Metals Park, Ohio, (1973), 871.
- 2) N. A. Vatolin and E. A. Pastuhov: Spec. Rep. No. 19 The Forth Japan-USSR Joint Symposium on Physical Chemistry of Metallurgical Processes, ISIJ, Tokyo, (1973), 1.
- 3) Y. Waseda and S. Tamaki: *Commun. Phys.*, **1** (1976), 3.
- 4) Y. Waseda and Y. Shiraishi: *Tetsu-to-Hagané*, **63** (1977), 1476.
- 5) Y. Kita, M. Ueda, Z. Morita, K. Tsuji and H. Endo: Liquid Metals, 1976, Conference Series; No. 30 (Proceedings of the 3rd Int'l Conf. on Liquid Metals, July, 1976), Inst. Physics, Bristol and London, (1977), 245.
- 6) Y. Waseda: The Structure of Non-crystalline Materials, McGraw-Hill Inc., New York, (1980), 27.
- 7) N. S. Gingrich: *Rev. Mod. Phys.*, **15** (1943), 90.
- 8) J. Krogh-Moe: *Acta Cryst.*, **9** (1956), 951.
- 9) N. Norman: *Acta Cryst.*, **10** (1957), 370.
- 10) D. T. Cromer and J. T. Waber: *Acta Cryst.*, **18** (1965), 104.
- 11) D. T. Cromer: *Acta Cryst.*, **18** (1965), 17.
- 12) D. T. Cromer: *J. Chem. Phys.*, **50** (1965), 4857.
- 13) H.H.M. Balyuzi: *Acta Cryst.*, **A31** (1975), 600.
- 14) S. I. Filippov, N. B. Kazakov and L. A. Pronin: *Izv. VUZ av, Cher. Met.*, (1966), 8.
- 15) P. V. Gel'd, P. V. Kocherov, E. S. Levin and B. A. Baum: *Fiziko Khimicheskie Osnovy Proizvodstva Stali*, Nauka, Moskva, (1968), 9.
- 16) N. C. Halder and C.N.J. Wagner: *J. Chem. Phys.*, **47** (1967), 4385.
- 17) Y. Waseda, M. Tokuda and M. Ohtani: *Tetsu-to-Hagané*, **61** (1975), 54.
- 18) Y. Waseda and K. Suzuki: *Z. Physik*, **B20** (1975), 339.
- 19) N. W. Ashcroft and D. C. Langreth: *Phys. Rev.*, **156** (1967), 685.
- 20) N. K. Dzhemilev, S. I. Popel' and B. V. Tsarevsky: *Fiz. Metal. Metalloved.*, **18** (1964), No. 1, 83; Translation: *Phys. Met. Metallogr.*, **18** (1964), No. 1, 77.
- 21) L. S. Darken: *Trans. Met. Soc. AIME*, **239** (1967), 80.