Effect of Thermal Cycle on Liquid Structure of Pure Iron at just above Its Melting Point

Qijie ZHAI, Jun LUO1) and Pei ZHAO2)

School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China. E-mail: qjzhai@mail.shu.edu.cn
1) Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, China.
2) Central Iron & Steel Research Institute, Beijing 100081, China.

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The effect of thermal cycle on liquid structure of pure iron was investigated by means of theta–theta type liquid metal X-ray diffractometer. The increase of thermal cycle times results in the reduction of the atomic cluster size and its atomic numbers, the expansion of the disorder areas, and the increase of the disorder degree of the liquid pure iron. The first sharp diffraction peak (FSDP) or pre-peak is found in the structure factor curve of liquid pure iron, which means there is medium-range order (MRO) in this melt. The FSDP or pre-peak directly relates to the correlation of Fe–Fe atoms on the MRO scale. It is concluded that the body-centered cubic (BCC) crystal structure of the previous δ-Fe is partly kept in the liquid pure iron, and the liquid pure iron is a mixture of atomic clusters and disorder areas.

KEY WORDS: liquid structure; pure iron; X-ray diffraction.

1. Introduction

The solidification process and solid structure of steel has a great effect on quality of slab in continuous casting. Recent researches show that solidification process and solid structure of metals has close relationship with their liquid structure, so material scientists show great interests on studying liquid structure and its heredity.1–3) In order to control the solidification process and solid structure of steel, it is very helpful to learn its liquid structure and its relationship with melting process. Because of its high melting point and easy oxidation at high temperature, the study on liquid structure of steel is very difficult and there is no report about the effect of melting process on liquid structure of steel.

Currently, MRO structure in liquids and amorphous solids is a subject with much interest.4–8) However, it is difficult to derive unambiguous information on extent of MRO in the liquid or non-crystalline materials from experimental measurements.9) Luckily, there exists one celebrated structural feature, which is often taken to be a signature of MRO, that is FSDP or pre-peak in the structure factor curve, S(Q), in certain classes of liquid or amorphous solids. The FSDP occurs at a value of Q smaller than the position of the main peak of S(Q). In general, the presence of FSDP or pre-peak corresponds to compounds-forming behavior,10) or it can be attributed to the atomic clusters with a certain structure. In this paper, we report the effect of thermal cycle on liquid structure of pure iron at just above its melting point. It is noticeable that the liquid pure iron during the thermal cycle processing is corresponded to the transient state but not the equilibrium state.

2. Experimental Procedure

Figure 1 shows the schematic diagram of the high temperature X-ray diffractometer. The molten sample with the mass of 27.65 g was prepared from high purity iron (99.97%) and it was heated in an alumina crucible (20×18×10 mm) by a tantalum heating element held between water-cooled electrodes. Measurements were carried out in
high purity helium atmosphere before the chamber was cleaned by vacuum equipment. The sample temperature was measured by a Pt–Rh thermocouple which was inserted into a hole at the side of the crucible. The sample was first heated to 1 813 K at the rate of 0.33 K/s and held at 1 813 K for 9 ks, and then the scattering intensities were collected. Then the same thermal cycle processes as follows were carried out for three times: the molten sample is superheated up to 1 853 K at the rate of 0.17 K/s and held at 1 853 K for 1.2 ks, and then cooled down to 1 813 K at 0.17 K/s and held at 1 813 K for 1.8 ks, and then collect the scattering intensities.

The X-ray scattering intensities from the molten sample of pure iron were measured using a theta-theta diffractometer with a graphite monochromator in the diffraction angle 5° to 90° which covers the values of wave vector \( Q = 4\pi \sin \theta \lambda \) between 5 to 120 nm\(^{-1}\). Mo-K\(\alpha\) radiation was reflected from the free surface of the liquid specimen, the X-ray then reached the detector through a graphite monochromator in the diffraction beam. During the measurements, the surface of the specimen was fixed to one horizontal position by means of a laser calibrator.

3. Data Processing

The scattering intensity measured in arbitrary units can be converted into the coherent scattering intensity per atom in electron units \( I_{eu}^{coh}(Q) \) by means of the generalized Krogh–Moe–Norman method. Corrections for absorption, Compton scattering, irradiated volume etc. are done before data processing. Details can be found in Ref. 11). Pure iron can be assumed as a simple substance with only one type of atoms. Thus \( I_{eu}^{coh}(Q) \), which is related to the structurally sensitive part of the X-ray scattering intensity from a liquid sample, is written as

\[
I_{eu}^{coh}(Q) = Nf^2 + \sum_{j=0}^{\infty} 4\pi^2 \rho(r) - \rho_0 d\rho \sin(Qr) dr \quad \text{(1)}
\]

\[
S(Q) = \frac{I_{eu}^{coh}(Q)}{f^2} \quad \text{...................................(2)}
\]

Where \( N \) is the number of atoms in the scattering bulk, \( f \) is the atomic scattering factor, \( \rho(r) \) is the radial density function, \( \rho_0 \) is the average number density of atoms, and \( S(Q) \) is the structure factor.

The radial distribution function (RDF) \( 4\pi r^2 \rho(r) \) or the pair distribution function (PDF) \( g(r) = \rho(r)/\rho_0 \) is calculated by the following Fourier transformation.

\[
4\pi^2 \rho(r) = 4\pi^2 \rho_0 + \frac{2r}{\pi} \int_{Q=0}^{\infty} Q^2 i(Q) \sin(Qr) dQ \quad \text{....(3)}
\]

4. Results and Discussion

Figure 2 shows the X-ray scattering intensity of liquid pure iron, and Fig. 3 shows the structure factor derived from the measured X-ray scattering intensity data. A significant pre-peak can be found in the small \( Q \) region (5 < \( Q < 20 \) nm\(^{-1}\)) of the X-ray diffraction profile and of the structure factor curve respectively, which indicates the existence of MRO structure in the tested liquid. MRO means that some atomic clusters with certain size exist in the liquid pure iron. The structural unit size corresponding to the pre-peak may be estimated according to the formula \( D = 7.725/Q_p \), where \( D \) is a characteristic distance related to the structural unit size and \( Q_p \) is the position of the pre-peak. The unit size of atomic clusters or the topologic order \( R \) reflecting the pre-peak is obtained by Scherrer formula \( R = 2\pi\Delta Q/\Delta Q \), where \( \Delta Q \) is the half-width of FSDP. The calculated results are listed in Table 1. Topologic order can be used to determine whether there is a MRO structure in the melt. It shows that the size of atomic clusters or the topologic order in the system is about 1 nm, so that the pre-peak indicates the existence of the MRO structure.

Figure 4 shows the PDF of liquid pure iron calculated from the structure factor. Table 2 lists the value of the peak position in the structure factor curve and PDF curve together.
er with some relevant information. It shows that these values are very close to those in Ref. 16), and the thermal cycle effect on the liquid pure iron can not been identified from Table 2. Waseda et al.17) investigated the liquid structure of silicon near its melting point (1 713 K, 1 733 K and 1793 K), and found that the peak position of structure factor and PDF had no obvious difference either.

The position of the first peaks in PDF, shown in Fig. 4, is the nearest distance \( r \) of atoms. It can be seen from Fig. 4 that the PDF of liquid pure iron has a sharp first peak at about 0.260 nm, a second broad one at about 0.505 nm and the subsequent oscillations which almost completely disappear at distance beyond 1.0 nm. The size of atomic clusters can also been estimated by the PDF. Generally, the maximum \( r_{\text{max}} \) is taken to be the radius of the atomic cluster when \( g(r) \) is between \((1+0.02)\) and \((1-0.02)\). When the atomic clusters are regarded as spheres, the atomic number in atomic cluster \( n_{s} \) can be calculated using the equation

\[
N_{s} = \frac{4 \pi \rho}{3 M} \int_{r_{\text{min}}}^{r_{\text{max}}} r^{2} g(r) dr
\]

where \( \rho \) is the density of liquid pure iron. The value of \( \rho \) is about 7.03 g/cm³ for the liquid pure iron near its melting point.18) The coordination number is also an important parameter, but its concept is somewhat unclear in liquids comparing with crystals. Nevertheless, the coordination number for only a few near neighbors gives a convenient picture of the near neighbor structure in liquids and it is usually estimated from the area under a corresponding peak in the distribution function.17) In this work, the nearest neighbor coordination number \( N_{\text{min}} \) is obtained by integrating the PDF from the first non-zero point to the minimum of the first peak in the PDF.

\[
N_{\text{min}} = \rho \int_{r_{\text{min}}}^{r_{\text{max}}} 4 \pi r^{2} g(r) dr \quad \text{.............(4)}
\]

The size of atomic clusters and atomic number in atomic cluster under different thermal cycle times are shown in Figs. 5 and 6 respectively. It can be seen that \( r_{s} \) and \( n_{s} \) decrease with increasing thermal cycle times, which indicates that the liquid pure iron becomes more disordered. It is worth mentioning that an abrupt change is found during the second and third thermal cycle processing in Figs. 5 and 6. This seems imply a sharp change on the structure of the liquid pure iron. A similar structure change of liquid iron has been found in the temperature range from 1 873 to 1973 K.19–21) The thermal cycle may result in the structure change of liquid iron as increasing temperature. It is obvious that thermal cycle processing can affect the liquid structure of melt, but it has an optimum value for the thermal cycle times. For example, the third time of thermal cycle processing has inconspicuous effect in this work.

We have calculated the coordination number \( N \) of the liquid pure iron and the value is about 8 (see Table 3), which is very close to that of the BCC unit. As a result, we conclude that the structural unit in the liquid pure iron is a BCC. The reason is that the \( \delta \)-Fe has a BCC crystal structure, and the BCC crystal structure is partly preserved in the liquid pure iron. The nearest neighbor distance of atoms is 0.260 nm, hence the body diagonal is 0.520 nm, which is very close to the calculation result of 0.515 nm. When two
BCC structures combine themselves together via vertex sharing one atom along a body diagonal, they can form an atomic cluster with the size of 1.040 nm, which is very close to the size of atomic clusters in Table 1. Such many atomic clusters in the liquid pure iron will be attributed to the MRO. The structure model of liquid pure iron is shown in Fig. 7. The actual structure of liquid pure iron should be a mixture of atomic clusters and disorder areas.

5. Conclusion

In this paper, the effect of thermal cycle on liquid pure iron and MRO structure in the liquid has been investigated using X-ray diffraction for the liquid system at 1813 K. It is found that the size of atomic cluster and atomic number in atomic clusters decrease with increasing thermal cycle, which indicates that the liquid becomes more disordered.

We also report the structural feature of the atomic clusters in the liquid pure iron. The pre-peak, a signature of MRO, is shown in the diffraction profile and structure factor of the liquid. BCC units are found in liquid pure iron. The atomic cluster with a size of about 1.0 nm is composed of two BCC units. The origin of the pre-peak can be explained that the BCC crystal structure of $\delta$-Fe is partly persisted in the melt. The liquid pure iron is a mixture of atomic clusters and disorder areas.

Acknowledgments

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