Supersaturation of Carbon in Austenite during Carburization by CO Gas

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1. Introduction

The new iron making processes using the carbon-composite pellets of iron oxides or the mixture of coal and iron ore particles have been developed in Japan. These processes have the advantage of rapid reduction of iron oxides to produce iron or pig iron within 15 min over 1 700 K. Nagata et al. investigated the reaction mechanisms of the carbon-composite pellets to produce pig iron. The rapid heating of pellets makes high oxygen potential near Fe/FeO equilibrium in the pellets. Reduced iron particles directly absorb carbon from solid carbon to produce molten pig iron and the pig iron particles suddenly agglomerate to form droplets over 1 600 K. Murakami et al. studied the mechanisms of carbon absorption into iron from CO gas. They reported that CO gas supersaturates the flat surface of austenite with carbon over the solubility by 0.019 mass% at 1 664 K. Murakami et al. investigated the mechanisms of carbon absorption into iron from solid carbon. When iron plate contacted with graphite plate, molten pig iron was rapidly produced at the interface and was accelerated by iron oxide scale on the surface of iron sample.

In the present study, the supersaturation of carbon in austenite fine particles and their melting behavior has been studied by means of a high temperature X-ray diffraction.

2. Experimental

Electrolytic iron particles were over 99.5 mass% in purity and the shape was almost bar with about 10 μm in diameter and about 100 μm in length. Reagent hematite was particles with the purity of 99.9 mass%. Hematite sample was milled by a wet vibration ball-mill and then treated by means of a spray-drying method. The shape was confirmed to be spherical with about 50 μm in diameter by microscopic observation.

A shallow flat vessel of alumina with 0.8 mm in depth, 17 mm in length and 9 mm in width was employed as a sample holder. A small graphite bar was set on the end of the vessel in the up-stream of CO gas for equilibrating with carbon. Sample was set on the vessel in the down-stream and was separated from the graphite bar with alumina bar. Electrolytic iron particles of about 400 mg or hematite particles of about 80 mg were stamped in the vessel. The vessel was horizontally set on the heating plate with Pt resistant heating wire in the center of furnace. The furnace was installed in the sample chamber of a high temperature X-ray diffractometer (RINT2000-TTR, Rigaku Denki Co.), as shown in Fig. 1.

X-ray beam passed through two windows of an outer film...
Particles were also reduced in He–10vol%H2 with the flow rate of 0.10 NL/min and were kept at a desired temperature in CO gas at 1 452 K, the gas was switched to CO with the flow rate of 0.20 NL/min. Hematite particles were reduced to iron and electrolytic iron and reduced iron particles absorbed carbon.

The concentration of carbon in the samples after the experiments was determined by a combustion-infrared absorptionmetry (CS-444LS, LECO Co). The standard samples of Fe–C alloy (from the Iron and Steel Institute of Japan) were employed for calibration of carbon content.

The spacing of lattice plane (111) of austenite, \( l_{111} \) (nm), is proportional to carbon content, C (mass%), and temperature, \( T(K) \), even in the supersaturation area, expressed as the following formula4):

\[
l_{111} = 4.69 \times 10^{-5} T + 9.74 \times 10^{-3} C + 2.05 \quad \ldots \ldots (1)
\]

### 3. Result

The spacing of lattice plane (111) of electrolytic iron particles in austenite state expanded with time by absorbing carbon from CO gas under constant temperatures, as shown in Figs. 2 and 3. The tendency was same for (200) plane. The expand rate of the spacing of lattice plane depended on the flow rate of CO gas and temperature. The spacing of lattice plane corresponds to carbon content in iron as shown in the Eq. (1). As listed in Table 1, the carbon content was in supersaturation for the flow rate of CO gas from 0.01 and 0.02 NL/min. The maximum carbon content decreased with increasing temperature.

The intensity of X-ray peaks of lattice plane (111) gradually decreased with time, as shown in the lower parts of Figs. 2, 3, 5 and 7. These samples did not melt throughout the experiment for about 7h except one case of Fig. 5. Figure 4 shows the samples of electrolytic iron particles; a) sintered in He–H2 gas atmosphere and b) carburized by CO gas after heating in He–H2 gas. The sintered iron particles are fine and dense.

Hematite particles were reduced to \( \gamma \)-Fe through magnetite, wustite and \( \alpha \)-Fe by CO gas. During heating up, \( \gamma \)-Fe started to absorb carbon above 1 100 K due to the larger solubility of carbon than \( \alpha \)-Fe. In Fig. 5, the spacing of lattice plane of reduced iron under the flow rate of 0.05 NL/min rapidly expanded during heating up until 1 050 K. Above 1 050 K it thermally expanded with increasing temperature like electrolytic iron particles in He–H2 and iron particles reduced from hematite by He–H2. The carburized particles were not dense, as shown in Fig. 4(c).

Under the flow rate of CO gas from 0.08 to 0.20 NL/min, the spacing of lattice plane expanded rapidly during heating up, attained maximum at about 1 300 K and decreased until about 1 400 K, followed by expansion again. After reaching at 1 550 K, these samples were carburized by CO gas for about 3h at the temperature. Figure 4 shows the sample (d) carburized in the gas flow rate of 0.10 NL/min and melted partially as well as that with the flow rate of 0.08 NL/min. The sample (e) melted to make droplets in the gas flow rate of 0.20 NL/min. As shown in Fig. 5(c), the intensity of X-ray diffraction peaks of lattice plane (111) of iron reduced by CO gas decreased with increasing temperature and time.

![Fig. 1. Schematic diagram of a furnace in XRD and a specimen holder.](image-url)
The intensity of reduced iron under the gas flow rate of 0.20 NL/min disappeared near the maximum spacing of lattice plane because of carbon deposition from CO gas. In this case, Fe$_3$C was detected above 1 122 K, as shown in Fig. 6. The intensities of electrolytic iron and reduced iron by He–H$_2$ showed the maximum near 1 400 K.

4. Discussion

4.1. Diffraction Intensity of X-ray from Iron Particles in a Sample Layer

The effective depth, $x$, of X-ray penetration can be calculated by the following equation;

$$x = -0.5 \ln(1 - G_x) \cdot \sin \theta \cdot \mu^{-1}$$  \hspace{1cm} (2)

where $G_x$ is the usage rate of X-ray diffraction energy at the effective depth and $\theta$ is the diffraction angle of X-ray. $\mu$ is a linear absorption coefficient and is calculated from the product of mass absorption coefficient and density. The mass absorption coefficient of powder iron is proportional to the ratio of the apparent density of powder to the density of iron. The mass absorption coefficient of iron is 52.8 cm$^2$/g. $^{5)}$ The apparent densities are about 3.0 g/cm$^3$ for electrolytic iron powder and about 1.1 g/cm$^3$ for reduced iron powder. The density of steel can be estimated to be 7.8 g/cm$^3$ at 1 473 K from the handbook data. $^{6)}$ For 99% of $G_x$, the effective depth is calculated to be 140 and 340 μm for electrolytic iron powder and 1 010 and 2 440 μm for reduced iron at 45 and 135 degree in 2$\theta$, respectively, which is one third or over the thickness of samples. The carbon contents of samples estimated from the spacing of lattice plane represent the average values. As the distribution of carbon concentration in a sample after reaction was con-
firmed to be uniform by an electron micro probe analyzer.

The intensity of X-ray generally decreases with increasing temperature and XRD cannot detect for fine crystallite under about 5 nm in diameter, liquid and glass. In the lower parts of Figs. 2, 3 and 7, electrolytic iron particles were carburized by CO gas or solid carbon under constant temperatures. The diffraction intensity of X-ray of lattice plane \((111)\) for these iron particles gradually decreased with carburization. In Fig. 5(c), for reduced iron from hematite particles by CO gas or He–H\(_2\) gas, the intensity of X-ray decreased gradually at constant temperature, though the carbon content in iron did not exceed the solidus line of iron-carbon system. These phenomena indicate that the size of crystallite in iron particles gradually decreases. The X-ray intensity for reduced iron particles also decreased during heating up in Fig. 5(c). This may be caused by both temperature increase and crystallite size decrease. Further discussions will be made in the Sec. 4.5.

### 4.2. Influence of CO Gas Flow Rate on Supersaturation

CO gas decomposes to produce carbon and CO\(_2\) on the surface of iron particle, as follows;

\[
\text{CO(g)} \rightarrow \text{C(in Fe)} + \text{O(ad)} \quad \text{.........(3)}
\]

\[
\text{CO(g)} + \text{O(ad)} \rightarrow \text{CO}_2(g) \quad \text{.........(4)}
\]

where O(ad) is oxygen atom adsorbed on the surface. Carbon is transferred by the interdiffusion of CO and CO\(_2\) in a boundary layer near the surface of particle. CO gas decomposes into C(ad) and O(ad). Carbon atoms are absorbed from the surface and dissolve into iron. In this case,
the transfer of carbon can be controlled by the mixed processes of CO gas diffusion in a boundary layer and diffusion in iron particle, because the chemical reactions of (3) and (4) are generally faster than the diffusion processes.2)

The boundary layer theory indicates that the thickness of boundary layer near sample is proportional to the root square of the velocity of gas. As shown in Fig. 8, the final concentration of carbon in electrolytic iron particles is proportional to the root square of the flow rate of CO gas. Thus, the carbon concentration in iron particles is proportional to the thickness of boundary layer. This means that the interdiffusion of CO and CO₂ in gas phase controls the carbon concentration. As the activity of carbon on the surface of iron particles mixed with graphite is unity, carbon diffuses into iron faster and the spacing of lattice plane of iron expands faster than iron particles carburized by CO gas.

4.3. Cause of Supersaturation

The solute supersaturation ratio is defined as

\[ s = \frac{C}{C_s} \] .............................(5)

where \( C \) is the concentration of solute and \( C_s \) the solubility. For the present results, \( s \) is from 1.2 to 1.8, as listed in Table 1. Murakami et al.2) showed that the radius of embryo of liquid iron appearing on the flat surface of solid iron is about 141 \( \mu m \) with the supersaturation of 0.019 mass\% of carbon during carburizing by CO gas. The radius of embryo, \( r^* \), can be calculated as

\[ r^* = \frac{-2\gamma}{\Delta G_v} \] ..................................(6)

where \( \gamma \) is the surface tension of a Fe–C liquid alloy and \( \Delta G_v \) is the volume free energy which is expressed as

\[ \Delta G_v = \left( \frac{\rho}{M} \right) (\Delta G_{M}^{eq} - \Delta G_{ss}^{M}) \] ..................................(7)

\( \rho \) is density, \( M \) molecular weight of iron and \( \Delta G_{M}^{eq} \) and \( \Delta G_{ss}^{M} \) the free energy of mixing of equilibrated and supersaturated states, respectively. The free energy of mixing is expressed as

\[ \Delta G^{M} = RT(X_{Fe} \ln a_{Fe} + X_{C} \ln a_{C}) \] .................(8)

where \( X \) and \( a \) are the mole fraction and activity of component \( i \), respectively.

The radius of embryo of liquid is calculated for the supersaturation of 0.25 mass\% C from the solubility of austenite (Fe–1.75mass\%C (\( X_{C} = 0.0814 \))) at 1 500 K. The density of Fe–2mass\%C (\( X_{C} = 0.0930 \)) at 1 500 K is 7.25×10³ kg/m³. The surface tension of Fe–2mass\%C at 1 823 K is about 1.8 N/m and the temperature dependency of surface tension of pure iron is \(-0.62 \times 10^{-3} N/m \cdot K\).7) Then, the surface tension of Fe–2mass\%C at 1 500 K is es-

Fig. 6. Peak profiles of XRD reduced iron from hematite by CO gas with the flow rate of 0.20 NL/min during heating up. Fe₃C was detected.

Fig. 7. Comparison of (a) the spacing of lattice plane (111) and (b) the intensity of X-ray peaks between electrolytic iron particles in CO gas in equilibrium with carbon and iron particles mixed with graphite.
The activity of carbon in austenite at the solubility is 0.7 and that in supersaturation is extrapolated to be 0.8. The activity of iron in austenite is 0.95 from 0.9 to 1.8 mass% C.9) The radii of embryo is calculated to be \(0.24 \text{ mm}\) and becomes smaller with increasing the solute supersaturation ratio. The estimated radii of embryo is smaller than the average diameter of 10 \(\text{mm}\) of bar-type particles of electrolytic iron. Thus the diameter of particles does not cause austenite to be supersaturated with carbon.

Cohen et al.8) found the very large supersaturation ratio of 2 to 3 for KCl and KBr solutions using an electrodynamical balance. They concluded that this supersaturation was the result of the decline of heterogeneous nucleation sites per unit volume. In the present study, the large supersaturation is probably caused from the smooth surface of particle due to the surface diffusion of elements during carburizing at elevated temperature, as shown in Fig. 9.

4.4. Supersaturation Limit of Carbon in Austenite

As the carbon activity in gas phase was fixed to unity, carbon content in solid iron particles could be supersaturated over liquidus line of austenite in iron-carbon system. The experimental results however showed that the supersaturated contents of carbon in iron particles were always under the liquidus line.

The supersaturation of carbon in austenite indicates that there is metastable austenite in large carbon concentration. Figure 10 shows the chemical potential of carbon in austenite, \(\mu_c\), as a function of carbon concentration, \(X_c\). The chemical potential is calculated from the activity of carbon, \(a_c\), in austenite and liquid state9) and estimated in the supersaturation area from the thermodynamic condition, as follows;

\[ \int_{\text{liquidus-line}}^{\text{solidus-line}} X_c d\mu_c = 0 \]

From the thermodynamic stability, a stable area satisfies \((\partial \mu_c / \partial X_c)_T > 0\) and an unstable area \((\partial \mu_c / \partial X_c)_T < 0\).

Figure 11 shows the metastable and unstable area of austenite and liquid among liquidus line and solidus line. When the carbon content increases over the metastable area in austenite, it is necessary to make heterogeneous nucleation sites of liquid. Thus, the supersaturated carbon content in austenite is limited in metastable area and decreases with increasing temperature.

4.5. Abnormal Expansion of Spacing of Lattice Plane of Reduced Iron by CO Gas before Melting

During heating up, the spacing of lattice planes of reduced iron particles in austenite from hematite by CO gas expanded rapidly. The rate of expand was independent on CO gas flow rate from 0.08 to 0.20 NL/min as well as 0.05 NL/min until 1 050 K. Figure 11 shows the changes of apparent carbon content in austenite estimated from the spacing of lattice planes during heating in CO gas until 1 550 K. The metastable and unstable area of austenite and liquid is also drawn in the phase diagram of Fe–C alloy.

\[ \int_{\text{liquidus-line}}^{\text{solidus-line}} X_c d\mu_c = 0 \]
internal strain and crystallite size calculated using the peaks of (111) and (200) planes of reduced iron during heating up. The maximum effective strain is at about 1300 K corresponding with the spacing of lattice planes. The crystallite size is about 0.1 μm and is less than the radius of embryo mentioned above.

There are two interstitial sites in fcc crystal structure of γ-Fe with 4 and 6-coordination of iron atoms. The former site is unstable and the latter stable. As iron reduced at lower temperature has more atomic defects in its crystal structure, it is possible that a part of carbon atoms sits in 4-coordination sites. From the hard sphere model, the radius of iron atom is calculated to be 0.130 nm using the lattice parameter of 0.368 nm for fcc-iron at 1550 K. When a carbon atom with the radius of 0.0583 nm sits in the interstitial site of 4-coordination, the expand rate of lattice is 1.02. When it sits in the 4-coordination site, the rate is 1.77. This means that at the maximum spacing of lattice planes, 18% of carbon atoms sit in the interstitial sites of 4-coordination. Above about 1300 K, iron lattice relaxed to the stable structure and carbon atoms gradually move to 6-coordination sites from 4-coordination sites.

5. Conclusion

Electrolytic iron particles were supersaturated in the temperature between 1452 and 1599 K under CO gas in equilibrium with carbon with a flow rate from 0.05 to 0.20 NL/min. The solute supersaturation ratio was very large and was from 1.2 to 1.8. The cause of the supersaturation is the decline of heterogeneous nucleation sites per unit volume. Iron particles reduced from hematite by CO gas absorbed carbon and the spacing of lattice planes of iron largely expanded during heating up. The phenomena could be explained that 18% of carbon atoms were distributed into the interstitial sites of 4-coordination of iron atoms and others into 6-coordination. The former atoms relaxed to move into the stable 6-coordination sites during heating. The iron particles reduced by CO gas were not supersaturated and melt at the solubility of austenite by carbon dust acting as nucleation sites of liquid phase.

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