In situ QXAFS observation of the reduction of Fe$_2$O$_3$ and CaFe$_2$O$_4$

Masao Kimura$^{*1}$, Yohei Uemura$^2$, Toru Takayama$^1$, Reiko Murao$^1$, Kiyotaka Asakura$^3$ and Masaharu Nomura$^1$

1 Nippon Steel Corporation, Futsu, 293-0011, Japan
2 Photon Factory, KEK, Tsukuba, 305-0801, Japan
3 CRC, Hokkaido University, 001-0021, Japan

E-mail: kimura.masao@nsc.co.jp

Abstract In situ QXAFS studies of the reduction of $\alpha$-Fe$_2$O$_3$ and CaFe$_2$O$_4$ were conducted to determine their reduction kinetics and mechanisms. The reduction of $\alpha$-Fe$_2$O$_3$ involved two steps, the first being a very fast process in which Fe$^{3+}$ was reduced to Fe$^{2+}$, and the second being the reduction of Fe$^{2+}$ to Fe metal over a longer period. In contrast, the reduction of Fe in CaFe$_2$O$_4$ was a single first-order reaction, although an induction period was clearly observed at the beginning of the reduction process. The reduction processes were successfully studied using a combination of in situ QXAFS spectra at the Ca and Fe K-edges.

1. Introduction

Iron is one of the most indispensable metals. It has been used for thousands of years and is used in numerous materials that we use in our day-to-day lives. Demand for iron is still increasing today. To make the best use of iron resources, most pig iron is now produced in blast furnaces by reducing sinters made from fine grains of various iron ore types ($\alpha$-Fe$_2$O$_3$, $\alpha$-FeOOH, and/or Fe$_3$O$_4$) and CaCO$_3$. Small iron ore grains are mixed with CaCO$_3$ and sintered to make relatively large “heterogeneous” sinters (typically a few tens of mm in diameter).

Reduction kinetics, averaged over sinters, have been monitored by quenching sinters during the reduction process and determining the amount of reduced iron by chemical analysis. However, sinter bonding phases, e.g., calcium ferrite and SFCA (silicoferrite of calcium and alumina) play important roles in determining the sinter quality parameters, such as reducibility [1-3] and the reduction degradation index (RDI) [4,5]. At high temperatures (e.g., 1273 K), an increase in surface area and the presence of pores less than 1 $\mu$m in diameter are important to the reduction properties of the whole sinter [3]. Information on changes in the atomic structures of various Fe-Ca-O phases is, therefore, crucial to our ability to control the reduction properties of the sinter, although these processes have not yet been studied sufficiently. The X-ray absorption fine structure (XAFS) can reveal local structures and the electronic states of target atoms under reaction conditions. In this study, we performed in situ QXAFS experiments on the reduction of $\alpha$-Fe$_2$O$_3$ and CaFe$_2$O$_4$ and investigated their reduction mechanisms.

2. Experimental

In situ QXAFS[6] experiments were conducted at Photon Factory, KEK (KEK-PF), Japan. BL-9A and BL-12C were used for the Fe K-edge XAFS. At BL-9A, high energy resolution and high flux are both achieved; the flux at 6.5 keV was as high as $7 \times 10^{11}$ photons/s at the maximum stored current of 450 mA. At BL-12C, a fairly high flux, $1 \times 10^{10}$ photons/s was achieved. A 170-mm-long ion chamber was used for measuring the incident X-ray intensity and a 310-mm-long ion chamber was for measuring the transmitted intensity. Each in situ QXAFS spectrum of the Fe K-edge was measured in 20 s with the Si(111) monochromator rotated from 16.90° to 14.20°. BL-9A was used to measure the
Ca K-edge XAFS. Each QXAFS spectrum of the Ca K-edge was measured in 51 s with the Si(111) monochromator rotated from 31.00° to 26.50°. Ni-coated double mirrors were used for eliminating the high harmonic waves. The beam size was cut using slits to $1 \times 1 \text{mm}^2$ at the specimen.

A flow type in situ cell was used, details of which have been published previously [7]. The cell was equipped with four rod heaters, and the cell could be heated to above 900 °C. The cell temperature was measured using a K-type thermocouple. A mixture of hydrogen and helium (H$_2$:He = 20:80 vol. %) was used to reduce the iron oxides. This gas composition was selected for experimental reasons, even though the composition of this reductive gas is different from that of in a real blast furnace (70–90 vol. % CO). The gas flow rate was 100 sccm, and the reduction temperature was 900 °C. A mixture of oxygen and helium (O$_2$:He = 20:80 vol. %) was introduced into the cell, at 100 sccm, until the reduction temperature was reached.

Normalized XANES data ($\Delta \mu_t = 1$) were used to calculate the reduction rate constants. EXAFS data analyses were performed using Athena software [8].

3. Results and Discussion

Figures 1 (a) and (b) shows the evolution of XANES spectra over time around the $\alpha$-Fe$_2$O$_3$ Fe K-edge, obtained by in situ QXAFS at time $t$ after the gas was switched from O$_2$/He to H$_2$/He, at 900 °C. The XANES spectrum changed dramatically as soon as the H$_2$–He mixture was introduced, with the white-line intensity of $\alpha$-Fe$_2$O$_3$ (peak at 7129 eV) decreasing and the edge energy shifting to a lower energy. After this, another peak appeared at 7125 eV. The in situ XANES features at $t = 0.3$ and 3.3 min resembled the FeO feature, although the peak intensity at 7125 eV, at $t = 0.3$ min, was greater than that of FeO. Therefore, it appears that the Fe$^{2+}$ species may be produced with a different local structure from FeO. It is notable that the XANES at 3.3 min after the reduction process began was quite similar to that of FeO. The main peak decreased and the pre-edge region increased as the reaction proceeded, and the shape became similar to that of Fe metal. In summary, the reduction of $\alpha$-Fe$_2$O$_3$ consisted of at least two steps, the first being fast reduction from Fe$^{3+}$ to Fe$^{2+}$, which finished by 0.3 min. At 0.3 min, the peak intensity of the in situ spectrum at 7125 eV was greater than that of FeO, while the overall XANES feature of both spectra resembled each other. This implies that the first step was the reduction of Fe$^{3+}$ to form compounds such as FeO. The second step was a slow reduction process from Fe$^{2+}$ to Fe metal.

Figure 1 (c) shows the dependence of the X-ray absorption coefficients, at specific energies, on time $t$. Time 0 was when the reduction gas was first introduced. The isosbestic point was found at 7142 eV and another weak isosbestic point was found at 7117 eV. The intensity at 7125 eV (circles) quickly increased and then gradually decreased. The increase was too fast to be analyzed, but the X-ray absorption variation during the decay processes fitted well with first order kinetics, with a rate constant of 0.19(1) min$^{-1}$.

Figure 2 (a) shows the in situ XANES of CaFe$_2$O$_4$. An isosbestic point was found at 7142 eV from 3 min after H$_2$ was introduced. The XANES spectra did not change dramatically immediately after the H$_2$ mixture was introduced, as it did for $\alpha$-Fe$_2$O$_3$ (see Fig. 2 (b)). Figure 2 (c) shows the X-ray absorption variations at 7117 eV, 7125 eV, and 7142 eV. Absorption at 7125 eV did not change in the period $0 < t < 3$ min, then the intensity gradually decreased. The reduction of CaFe$_2$O$_4$ appeared to consist of at least two reaction steps. The first step was an induction period in which the local structure and Fe atom electronic states changed. The second step was reduction to Fe, shown by the variation at 7125 eV, which fitted a single exponential function with a 3 min delay. The rate constant for this step was 0.21 min$^{-1}$. 



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Fig. 1 (a) Time evolution of XANES spectra around the α-Fe₂O₃ Fe K-edge, obtained by *in situ* QXAFS at time \( t \) after the gas was switched from O₂/He to H₂/He (20% H₂ and 80% He, 100 sccm), at 900 °C, (b) Fe K-edge XANES of α-Fe₂O₃ and during its reduction (at 0.3 min and at 3.3 min) and the Fe K-edge XANES of FeO, (c) variation in X-ray absorption at 7117 eV (squares), 7125 eV (circles), and 7142 eV (triangles).

Fig. 2 (a) Time evolution of XANES spectra around the CaFe₂O₄ Fe K-edge, obtained by *in situ* QXAFS at time \( t \) after the gas was switched from O₂/He to H₂/He (20% H₂ and 80% He, 100 sccm), at 900 °C, (b) Fe K-edge XANES of Ca₂Fe₂O₄ before and during the reduction process (before reduction, 2.7 min, 8.6 min, and 51.3 min) and the Fe K-edge XANES of α-Fe₂O₃, (c) variation in X-ray absorption at 7122 eV (squares), 7125 eV (circles), and 7143 eV (triangles).

Fig. 3 (a) Ca K-edge XANES of CaFe₂O₄, CaFe₂O₄ (after reduction), CaFe₂O₅, CaO, and Ca(OH)₂, (b) time evolution of XANES spectra around the CaFe₂O₄ Ca K-edge, obtained by *in situ* QXAFS under reduction gas flow, at 900 °C, (c) the dependence of X-ray absorption at 4047 eV on time \( t \).
Figure 3 (a) shows Ca K-edge XANES spectra of CaFe$_2$O$_4$, CaFe$_2$O$_4$(after reduction), Ca$_2$Fe$_3$O$_5$, CaO, and Ca(OH)$_2$ at R.T. Before reduction, the CaFe$_2$O$_4$ XANES spectrum features were different from those of CaO or Ca(OH)$_2$ because the CaFe$_2$O$_4$ crystal structure is composed of layers of Fe-O and Ca-O and is different from the CaO and Ca(OH)$_2$ crystal structures. After reduction, the CaFe$_2$O$_4$ XANES resembled the Ca(OH)$_2$ XANES, indicating that the chemical states of the Ca atoms in CaFe$_2$O$_4$ changed to Ca(OH)$_2$-like states. Figure 3 (b) shows the evolution of XANES spectra, over time, around the Ca K-edge, obtained by \textit{in situ} QXAFS, with a measuring time of 51 s, under the reducing atmosphere, at 900 °C. The absorption intensity at 4041 eV decreased, and the intensity at 4047 eV increased, after the reduction gas was introduced.

The intensity at 4047 eV was plotted against the reaction time in Fig. 3 (c). It should be noted that an induction period, which was seen at the Fe K-edge XANES in Fig. 2 (b), was not observed. Ca atoms changed once the reaction gas was introduced, and this change started several minutes before the reduction of Fe ions started. In other words, the decomposition of Fe-O and Ca-O layers may precede the reduction of Fe ions. The variation at 4047 eV fitted a single exponential function, and the rate constant was estimated as 0.24 min$^{-1}$. This value was slightly higher than the rate constant for Fe in CaFe$_2$O$_4$.

4. Summary

\(\alpha\)-Fe$_2$O$_3$ and CaFe$_2$O$_4$ reduction processes were studied using \textit{in situ} QXAFS experiments, and we have suggested the reduction mechanisms involved. The reduction of \(\alpha\)-Fe$_2$O$_3$ involved two steps. The first step was a very fast process in which \(\alpha\)-Fe$_2$O$_3$ changed to a FeO-like structure, and the second step involved the reduction of Fe$^{2+}$ to Fe$^{0}$ metal over a longer period.

In contrast, the reduction of Fe in CaFe$_2$O$_4$ was a simple first-order reaction, although an induction period, in which decomposition to Ca(OH)$_2$ and Fe compounds occurred, was clearly observed at the beginning of the reduction process. This was successfully shown by the combination of \textit{in situ} QXAFS at the Ca and Fe K-edges. Although further research is necessary, the existence of Ca atoms appears to have a great effect on the reduction of Fe.

A combination of QXAFS with different edges was used to successfully elucidate the reduction kinetics of Fe-Ca-O phases for specimens in fine powders. The reaction rates are intrinsic to each phase, giving us fundamental information that can be used to distinguish microstructure and porosity factors for sinters from the factors related to the types and amounts of co-existing phases. This will allow us to improve the over-all reduction properties of sinters by controlling each factor.

5. References

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