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In situ Observation of Reduction Kinetics of Iron Oxides

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1 Introduction

In a steel making process, iron-ore sinters made of iron ore, lime stone, and coke, are reduced to Fe metal by CO-based reduction gas and pig iron is produced in a reaction furnace called a "blast furnace". Because 10,000 tons level of pig iron is manufactured in one blast furnace per day and the energy required for the reduction process is very large, information on the reaction mechanism is important to achieve a higher efficiency of the process. On the other hand, reactions that progress in a blast furnace are very complicated because of multiple processes. To comprehend its overall behavior, it is essential to understand each reaction that comprises the reaction. Therefore, various iron oxides were reduced with different reductant, and the reduction process was measured by in situ-QXAFS.

2 Experiment

A sample was prepared by diluting α-Fe_2O_3 with BN in SUS sample holder. In situ flow cell reported previously [1] was used in consideration of continuity with previous experiments. Under He gas flow (100 sccm), the temperature was elevated from room temperature to 800 °C at 0.667 °C s^{-1} (40 °C min^{-1}) and then to 900 °C at 0.167 °C s^{-1} (10 °C min^{-1}). After reaching 900 °C, reaction was initiated by introducing a reduction gas. Reduction gas, which is H_2 or CO diluted to 20 vol% by He gas, was introduced into the reaction cell at 100 sccm. The absorption around Fe *K*-edge was measured by a transmission method using QXAFS method to obtain a spectrum at 20 s intervals. All XAFS experiments were carried out at the High Energy Accelerator Research Organization (KEK), Photon Factory (PF), BL-9C.

3 Results and Discussion

Figure 1a shows the spectrum changes of α-Fe_2O_3 under H_2 gas atmosphere at 900 °C. As the reduction reaction proceeds, the spectra of α-Fe_2O_3 (Fe^{III}) → FeO (Fe^{II}) → Fe metal (Fe^0) was observed. The reduction rate of Fe^{III} to Fe^{II} is extremely fast, and the reaction is completed in about 2 spectrum measuring period of QXAFS (20 - 40 s). In the process of second-stage, $Fe^{II} \rightarrow Fe^0$, since the isosbestic point was observed in the spectrum, the reaction is considered to proceed without metastable intermediate phase. The reaction rate of Fe^{II} to Fe^0 was estimated from the change in absorbance. To derive the apparent reaction rate constant, time change of absorbance (μt) at 7124 eV, which is the white line of α-Fe_2O_3 was obtained (Figure 1b). As isosbestic points were clearly observed and the change in absorbance decreased exponentially, reduction of FeO is considered to be the first-order reaction with respect to Fe(II) concentration. Based on the fitting results of the plot in Figure 1b, the apparent reaction rate constant k was determined to be $3.8 \times 10^{-1} \pm 0.01\ min^{-1}$.

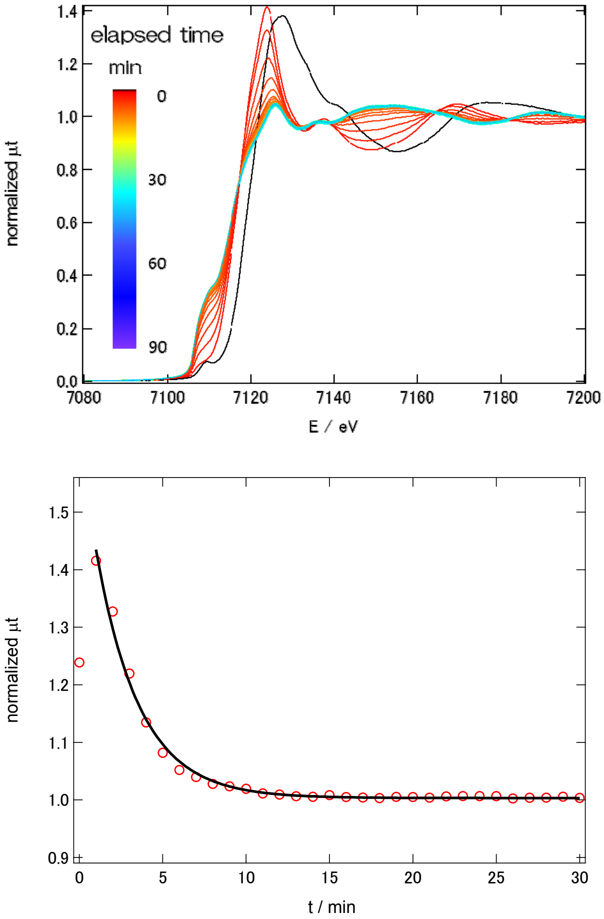

Figure 1 (a) Time evolution of XANES spectrum at K edge of α-Fe_2O_3 under H_2 (20 %) balanced with He (total flow rate 100 sccm), (b) the absorbance change according to the reaction time (at 7124 eV).We accept users' reports throughout the year. Please submit your report as soon as it is ready.

On the other hand, when using CO as reduction species, as shown in Figure 2, it can be seen that the reaction proceeds very slowly compared to H_2. Also in this case, because the attenuation curve of absorbance can be approximated by an exponential function (Fig. 2b), it can be regarded as going through a pseudo-first order reaction with respect to iron oxide concentration. Concentration of reduction species at the oxide surface, in other words, the difference in the diffusion rate to the oxide surface according to the type of gas, would not have a significant impact on the reaction rate, at least under the conditions of this experiment (reduction gas partial pressure, feed rate). The apparent reaction rate constant determined from the absorbance change was $4.0 \times 10^{-2} \pm 0.001\ \mathrm{min}^{-1}$.

It is considered that a reduction reaction of the iron oxide particles is a series of reactions including absorption of reduction species onto iron oxide surface, diffusion/reduction of oxygen atoms within the oxide (oxidation of reduction species), and desorption of oxidized/reduced species. It is unlikely that diffusion of oxygen atoms in the oxide is dependent on the difference in reduction species. In the case of this research, the reduction reaction at the iron oxide surface was found to be the rate-limiting processes. In this study, the measurement was performed under the condition, in which the reduction gas concentration was sufficiently high at the oxide surface. Hence, the rate constant obtained in this report is relevant to the rate of electron transfer from the reduction gas to the oxide. In other words, it is suggested that the energies of absorption of H_2 or CO to the surface of α-Fe_2O_3 and their reaction energies are different.

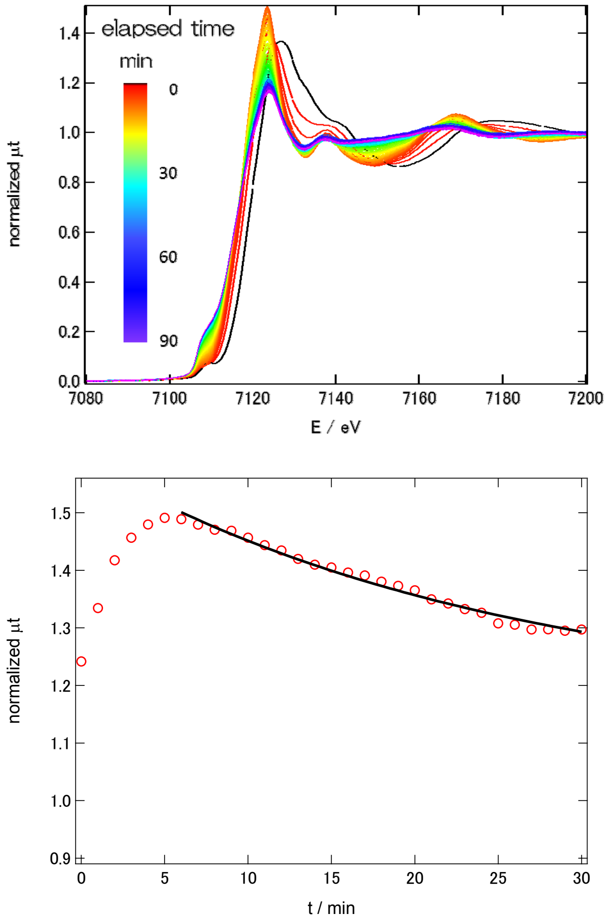

Figure 2 (a) Time evolution of XANES spectrum at K edge of α-Fe_2O_3 under CO (20 %) balanced with He (total flow rate 100 sccm), (b) the absorbance change according to the reaction time (at 7124 eV). The experiment conditions were the same as those in Fig.1 except reduction gas.

In this study, reduction reaction mechanism of α-Fe_2O_3 was studied using different reduction gases (H_2 and CO). The large difference of the reaction rates constant was successfully obtained. For further studies, conditions of reduction gas on the oxide surface, such as concentration of reduction gas and temperature dependency, will be examined.

Acknowledgement

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References

[1] M. Kimura, Y. Uemura, T. Takayama, R. Murao, K. Asakura, M Nomura, "In situ QXAFS observation of the reduction of Fe_2O_3 and $CaFe_2O_4$", Journal of Physics: Conference Series, **430**, 012074 (2013).

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