In situ observation of reduction kinetics and 2D mapping of chemical state for heterogeneous reduction in iron-ore sinters

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Abstract. Iron-ore sinters constitute the major component of the iron-bearing burden in blast furnaces, and the mechanism of their reduction is one of the key processes in iron making. The heterogeneous reduction of sintered oxides was investigated by the combination of X-ray fluorescence and absorption fine structure, X-ray diffraction, and computed tomography. Two-dimensional mapping of the chemical states (CSs) was performed. The iron CSs Fe_{III}, Fe_{II}, and Fe⁰ exhibited a heterogeneous distribution in a reduced sinter. The reduction started near micro pores, at iron-oxide grains rather than calcium-ferrite ones. The heterogeneous reduction among grains in a sinter may cause the formation of micro cracks. These results provide fundamental insights into heterogeneous reduction schemes for iron-ore sinters.

1. Introduction

Iron-ore sinters constitute the major component of the iron-bearing burden in blast furnaces in most countries in the Asia-Pacific region. They are formed by liquid-sintering at T > 1,500 K and are composed of an iron-oxide phase (mainly α-Fe₂O₃ and partially Fe₃O₄) and calcium ferrites (CFs) [1,2]. Iron-oxide grains with a diameter ranging from several tens to hundreds of µm are bonded by CFs such as CaFe₂O₄ and Ca₂Fe₅O₈. CFs contain many pores with diameters ranging from micrometers to millimeters (Figure 1). In industrial processes, the speed of reduction must be optimized, and the degradation due to the mechanical strength during the reduction must be minimized, as iron-ore sinters are piled up as high as 30–40 m and reduced in blast furnaces. Therefore, it is very important to understand where the reduction starts and how it progresses among sinters. We investigated the reduction process with respect to the iron chemical-state (CS) changes (Fe_{III}, Fe_{II}, and Fe⁰) and crack formation among sinters by using X-ray fluorescence (XF), X-ray absorption fine structure (XAFS), and X-ray computed tomography (X-CT) on the scale of a few tens of micrometers.
2. Experimental

The iron-oxide ores were mixed with limestone flux and coke breeze and heated by the combustion of the coke breeze, yielding heating up to temperatures of 1,450–1,600 K (above the eutectic temperature of CaO–Fe₂O₃: 1,478 K). The sinter was heated and reduced at \( T = 773 \text{ K} \) for 1 h in a gas with a molar ratio of CO:CO₂ ~ 1:1. To understand the intrinsic kinetics of the reduction of each phase, \textit{in situ} quick XAFS (QXAFS) measurements were conducted for a powder specimen at BL-9A and BL-9C of the Photon Factory (PF), IMSS, KEK. Iron K-edge and calcium K-edge XANES spectra were collected at 1,173 K in a He-20 vol. % H₂ atmosphere in the transmission mode with a typical time resolution of 15–30 s, and a reaction cell was used for the \textit{in situ} QXAFS [3,4].

Chemical mapping was performed at BL-15A1 [5] at the PF. XAFS and X-ray diffraction (XRD) were conducted for the sinter surface using an X-ray beam ~20 µm in diameter by scanning the specimen at room temperature. XAFS spectra were measured using a silicon drift detector (SDD) in the fluorescence geometry (Figure 2). To estimate the fractions of the iron chemical states (CSs)—Fe³⁺, Fe²⁺, and Fe⁰—the fluorescence intensities \((I)\) were measured at each point of the specimen, and the ratio of \(CS_{Fe} = \left(I_{at\ 7112\text{eV}} - I_{at\ 7100\text{eV}}\right)/\left(I_{at\ 7200\text{eV}} - I_{at\ 7100\text{eV}}\right)\) was used as an indicator of the CSs, as the iron K-edge energy shifted by ~5 eV around 7,112 eV among Fe³⁺, Fe²⁺, and Fe⁰.

X-CT measurements were performed for a sinter 2 × 2 × 10 mm³ in size using an in-house source with an X-ray energy of 70 keV. A charge-coupled device camera with a scintillator was used as a detector. The transmission image was measured with a step of 1 or 2° in a 360° rotation. The minimum special resolution was 0.7 µm.

3. Results and discussion

3.1. \textit{In situ} XAFS observation for intrinsic kinetics of reduction

The change in the X-ray absorption near edge structure (XANES) spectra around the iron K-edge energies for pellets of Fe₂O₃, Fe₃O₄, and CaFe₂O₄ at 1,173 K with a gas flow of H₂/He = 20/200 ccm was obtained by \textit{in situ} QXAFS at the time \( t \) after the gas was switched from O₂/He to H₂/He. A detailed analysis, including a linear combination, was performed for each XANES spectrum, revealing that the total periods of the reduction (Fe³⁺ → Fe⁰) of Fe₂O₃ (RedTime\textsubscript{Fe₂O₃}), Fe₃O₄ (RedTime\textsubscript{Fe₃O₄}), and CaFe₂O₄ (RedTime\textsubscript{CaFe₂O₄}) had the following relationship: RedTime\textsubscript{Fe₂O₃} < RedTime\textsubscript{Fe₃O₄} ≈ RedTime\textsubscript{CaFe₂O₄}.

As the results of the simple analysis of the change in the iron K-edge energies are consistent with the results of the detailed analysis, the change in the iron K-edge energies at the maximum of the first
derivation for the specimens is shown in Figure 3. According to the detailed analysis, the periods corresponding to Fe$_{\text{III}}$ + Fe$_{\text{II}}$ and Fe$_{\text{III}}$ + Fe$_0$ are shown in pink and green, respectively, in Figure 3. The period of Fe$_{\text{III}}$ → Fe$_{\text{II}}$ in Fe$_2$O$_3$ was ∼5 times faster than those of Fe$_2$O$_3$ and CaFe$_2$O$_4$. In Fe$_2$O$_3$, Fe$_{\text{III}}$ atoms were located at the centers of Fe$_{\text{III}}$-O$_4$ tetrahedrons and (Fe$_{\text{II}}$, Fe$_{\text{III}}$)-O$_6$ octahedrons, and Fe$_{\text{II}}$ atoms that were not reduced in the first step existed between Fe$_{\text{III}}$ atoms that were to be reduced. In CaFe$_2$O$_4$, the stacks of Fe$_{\text{III}}$-O$_6$ octahedrons were adjacent to the stacks of Ca$_{\text{II}}$-O$_6$ octahedrons. The existence of other atoms that were not reduced at the first step may explain why it took longer for Fe$_{\text{III}}$ to be reduced in Fe$_2$O$_3$ than in Fe$_2$O$_4$.

No induction period was observed in CaFe$_2$O$_4$ by the calcium K-edge XANES measurements for CaFe$_2$O$_4$. Figure 4 shows the change in the absorption intensity at 4.047 eV, corresponding to the white line, at the time t. No induction period, as is observed in the iron K-edge XANES in Figure 3(c), was observed at the calcium K-edge. This suggests that the structure around calcium changed but the iron CS did not change in the period of t = 0 to 2 min. A detailed analysis of the XAFS spectra after the reduction and the in situ XRD measurements during the reduction (to be submitted elsewhere) suggested that the following reaction occurred: 2 CaFe$_2$O$_4$ → 2FeO + Ca$_2$Fe$_2$O$_5$ + 1/2O$_2$ → 4Fe + 2CaO + 3O$_2$.

![Figure 3](image.png)

Figure 3. Change in the iron K-edge energies of pellets at 1.173 K with a gas flow of H$_2$/He = 20/200 ccm for (a) Fe$_2$O$_3$, (b) Fe$_3$O$_4$, and (c) CaFe$_2$O$_4$. The dotted lines show the iron K-edge energies at the maximum of the first derivation for the reference materials, i.e., Fe$_2$O$_3$, FeO, and Fe (foil).

3.2. Ex situ two-dimensional mapping of chemical states of iron and X-CT measurements

Two-dimensional (2D) mapping by XAFS and XRD showed that the prepared sinter was composed of α-Fe$_2$O$_3$ (∼55 vol. %), Fe$_3$O$_4$ (∼20 vol. %), CaFe$_2$O$_4$ (∼20 vol. %), and Ca$_2$Fe$_2$O$_5$ (∼5 vol. %) over an area of 3 × 3 mm$^2$. Identical 2D mapping was performed for the reduced sinter. We attempted a linear-combination analysis for all the points in the 2D mapping, but this was rather difficult because the XANES spectra were measured with the fluorescence geometry in spite of the high iron concentration. Therefore, we introduced the chemical states (CSs) index of CS$_{\text{Fe}}$, which corresponds to the shift of the iron K-edge energies at the maximum of the first derivation, between Fe$_{\text{III}}$ (CS$_{\text{Fe}}$=0.0) and Fe$_{\text{II}}$ (CS$_{\text{Fe}}$ = 1.0). The CS of CS$_{\text{Fe}}$ = 0.5 corresponds to Fe$_2$O$_3$.

Figure 5 shows a typical example of the 2D mapping at the iron K-edge, showing the CS index of CS$_{\text{Fe}}$ for the cross section of the reduced sinter. The observed area (Figure 5) corresponds to an interface area where Fe$_2$O$_3$ grains were sintered to each other with CFs (bonding phases). The CS index of CS$_{\text{Fe}}$ was ∼0.5, corresponding to Fe$_2$O$_3$, in most parts of the specimen, which is consistent with the macroscopic XRD measured over an area of 3 × 3 mm$^2$ at $E = 7.080$ eV. The attenuation lengths in these measurements were ∼20 and 8 μm at energies lower and higher than the iron K-edge, respectively. Microscopic XRD measurements with an X-ray beam of ∼20 μm were also performed,
but the type of the diffraction pattern largely depended on the grain size, and it was difficult to obtain the 2D mapping of the crystal structure, which was available in the CS mapping.

Among the region corresponding to Fe₃O₄, as shown in Figure 5, the CSFe values were higher in certain regions, such as those indicated by the blue bold lines, and lower in others, such as those indicated by the pink dotted lines. The regions with lower CSFe values, where the reduction progressed at a relatively slow speed, may correspond to CaFe₂O₄ grains in the as-prepared state (i.e., before reduction) because the intrinsic kinetics of reduction are high in Fe₂O₃ and low in CaFe₂O₄, as described in Section 3.1. The formation of the regions with higher CSFe values, where the reduction progressed at a relatively high speed, is attributed to the pores and/or micro cracks, which may have enhanced the diffusion of the reductive gas. Thus, a microstructural analysis using X-CT was performed.

**Figure 4.** Change in the absorption intensity at 4,047 eV for CaFe₂O₄. The line is a visual guide.

**Figure 5.** CS mapping of iron, where the CSFe value is indicated by a color scale. The pores are colored white for simplicity, according to optical microscopy measurements. The gray lines with dots show the positions of the cracks observed in Figure 6.

This kind of heterogeneous reduction in the bulk sinters is expected to easily cause micro cracks because the reduction yields a large volume decrease [6]. The three-dimensional microstructure of the other side of the specimen used in the 2D mapping (Figure 5) was investigated by X-CT (Figure 6). Because of the cutting process, the results shown in Figures 5 and 6 do not correspond exactly to the same surface but rather nearby regions. The cracks shown in Figure 6 were located near the boundaries of the high CSFe regions and/or pores. This suggests that the interface between the reduction-advanced and the reduction-delayed areas and that between the reduction-advanced area and the pre-existing pore are possible sites for cracking. The heterogeneous progress of the reduction may trigger cracking, and further investigation of the correlation of the heterogeneity and the crack initiation is in progress.

**Figure 6.** X-CT image for the reduced sinter. Cracks are indicated by arrows. The blue square shows the corresponding area in the 2D mapping (Figure 5).

### 4. Conclusion

The heterogeneous reduction reaction of iron-ore sinters was investigated by the combination of XF and XAFS, XRD, and X-CT. To estimate the fractions of iron chemical states (CSs) —Fe³⁺, Fe²⁺, and
Fe$^0$—we performed 2D mapping of the ratio of the fluorescence intensities at different energies and successfully showed the heterogeneous distribution of the CSs within the reduced sinter. It is suggested that the reduction proceeded at iron-oxide grains rather than CF ones, which is consistent with the intrinsic reduction-kinetics of the individual phase that were obtained by in situ QXAFS. The heterogeneous reduction can be also attributed to the existence of pores and/or micro cracks, which may have enhanced the diffusion of the reductive gas. The behavior of the heterogeneous reduction in sinters may be deeply related to the reduction speed and the degradation of the mechanical properties. The approach shown in this study provides fundamental insights for designing an ideal microstructure for iron-ore sinters, which may save energy and natural resources.

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References

[1] Ahsan S N, Mukherjee T and Whiteman J A 1983 Ironmak. Steelmak. 10 54.
[2] Lu L, Holmes R J and Manuel J R 2007 ISIJ Int. 47 349-58.
[3] Kimura M, Uemura K, Nagai T, Niwa Y, Inada Y and Nomura M 2009 J. Phys: Conf. Ser. 190 012163.
[4] Kimura M, Uemura Y, Takayama T, Murao R, Asakura K and Nomura M 2013 J. Phys: Conf. Ser. 430 012074.
[5] Igarashi N, Shimizu N, Koyama A, Mori T, Ohta H, Niwa Y, Nitani H, Abe H, Nomura M and Shioya T 2013 J. Phys. Conf. Ser. 425 072016.
[6] Turkdogan E, Olsson R and Vinters J 1971 Metall. Mater. Trans. B 2 3189.