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Application News

EPMA-8050G Electron Probe Microanalyzer

State Analysis of Iron Oxides in Sintered Ore for Steel Manufacturing after Hydrogen Reduction

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User Benefits

- The mineral structure of sintered ore can be investigated by quantitative mapping of Al, Mg, Si, Ca, and Fe.
- EPMA analysis is a useful technique in research on the composition of the calcium ferrite phase due to differences in the reduction reaction depending on the furnace temperature.
- Investigation of the oxidation state of iron is useful in study of the production conditions for sintered ore, such as oxidation and reduction.

■ Introduction

Reduction of carbon dioxide (CO_2) emissions is being promoted with the aim of achieving carbon neutrality in 2050. In the hydrogen reduction ironmaking process, iron ore is reduced with hydrogen (H_2) in place of coke (C), forming water (H_2O) instead of CO_2, thereby reducing CO_2 emissions. Targeting a reduction of 10 % or more in CO_2 emissions, research on a hydrogen reduction technology using hydrogen in the blast furnace is now underway in the Japanese national project COURSE50, focusing on reduction of the heat requirement and optimization of the reaction conditions of the raw materials, together with circulating use of gas with a regenerated reduction capacity, by promoting hydrogen reduction, which is a smaller endothermic reaction than direct reduction by coke. Development of a Super COURSE50 technology has also begun, and will make it possible to inject a larger amount of hydrogen into the blast furnace.

This article introduces a state analysis of the iron oxides in sintered ore, which was carried out by measuring the detailed spectra of micro-regions in sintered iron ore after hydrogen reduction using an EPMA™ electron probe microanalyzer (EPMA-8050G).

■ Sintered Ore Structure after Hydrogen Reduction

One issue for increasing hydrogen reduction in the blast furnace process is maintaining a high temperature in the Since reduction reaction by hydrogen is an endothermic reaction that absorbs heat, the temperature distribution in the furnace changes, and the low temperature region expands, resulting in remarkable low-temperature reduction powdering of the burden materials. Heat compensation is necessary to suppress this type of powdering, but leads to an increase in coke consumption.

The element distribution images in Fig. 1 and Fig. 2 show the result of conversion of the various elements in sintered ore to the mass percentage concentration (wt%) of a simple oxide (in case of Fe, Fe_2O_3).

Fig. 1 shows the results for sintered ore sintered at a low temperature of up to 600 °C under a high H_2 blast furnace condition. Since the reduction reaction was incomplete, the COMPO image contains iron oxides, which appear as regions of bright contrast. Silica (SiO_2) shows a correlation with the calcium oxide (CaO) of the calcium ferrite phase, while a trace amount of magnesium oxide (MgO) was also detected. In the high MgO region, the main element is iron (Fe), and is predicted to be a magnesium ferrite phase. As the content of alumina (Al_2O_3) in the calcium ferrite increases, the content of iron oxides decreases.

Fig. 2 shows the results for sintered ore reduced at a high temperature of up to 1000 °C under the high H_2 blast furnace condition. Here, the formation of metallic iron (Fe) in the iron oxide particles can be seen, indicating that reduction of the iron oxides has proceeded.

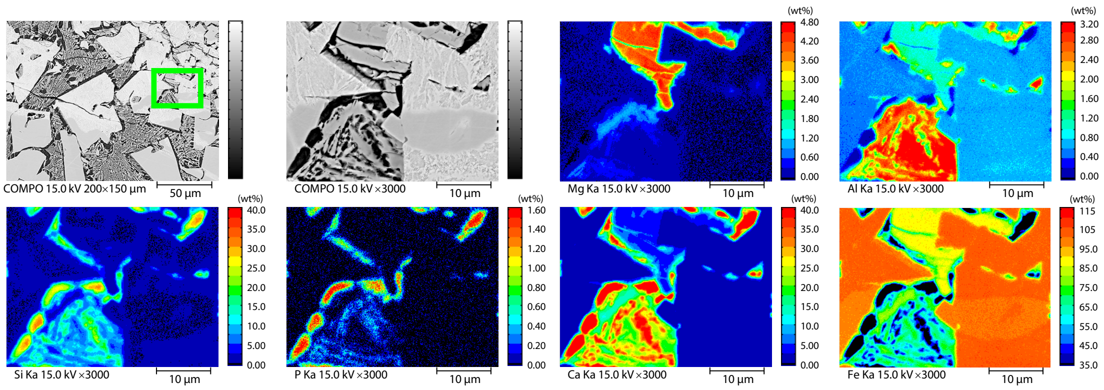


Fig. 1 Mapping of Sintered Ore after Reduction at 600 °C

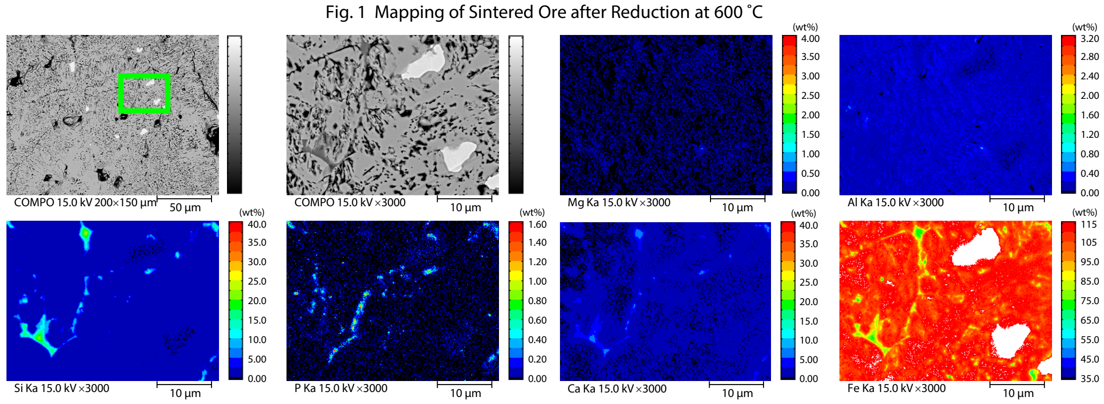
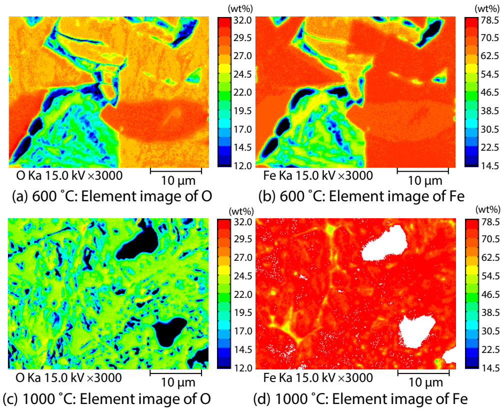


Fig. 2 Mapping of Sintered Ore after Reduction at 1000 °C

■ Phase Analysis of Sintered Ore after Hydrogen Reduction

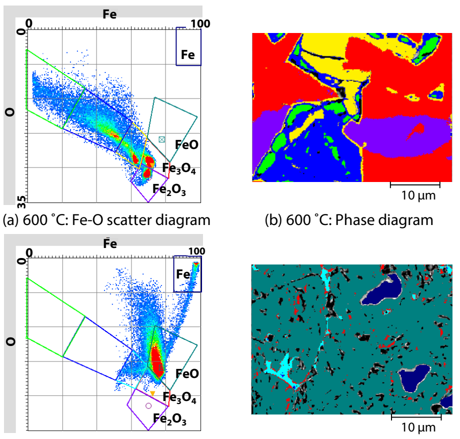
To identify differences in the oxidation valence, the element distribution images in Fig. 3 show oxygen (O) and iron (Fe) by the mass percentage concentration (wt%) of the simple elements.

Fig. 4 (a) and (c) are Fe-O scatter diagrams showing the positions of the compounds by the theoretical concentration of iron oxide under low temperature and high temperature reduction, respectively. In Fig. 4 (a), the symbols ○ and ▼ represent hematite (Fe_2O_3) and magnetite (Fe_3O_4), respectively, while in Fig. 4 (c), clusters (point-sets) can be seen in regions showing ⊠ wustite (FeO) and compounds of iron (Fe). Fig. 4 (b) and (d) are phase diagrams in which filters were set by the Fe-O scatter diagrams (see Related Applications 3). In the phase diagrams, the purple regions are hematite, red regions are magnetite, green regions are wustite, dark blue regions are iron, yellow regions are magnesia ferrite, blue regions are calcium ferrite, and yellow-green regions are slag. The sintered ore contains hematite and magnetite before reduction, but in the reduction reactions at the different furnace temperatures, the species of iron oxides are different depending on the furnace temperature. From the element distribution images and phase diagrams, it can be understood that metallic iron (Fe) has formed in the sintered ore subjected to hydrogen reduction at the high temperature of 1000 ˚C. The light blue region in Fig. 4 (d) is considered to be slag.



(a) 600 ˚C: Element image of O
(b) 600 ˚C: Element image of Fe
(c) 1000 ˚C: Element image of O
(d) 1000 ˚C: Element image of Fe

Fig. 3 Mapping of O and Fe of Sintered Ore after Reduction



(a) 600 ˚C: Fe-O scatter diagram
(b) 600 ˚C: Phase diagram
(c) 1000 ˚C: Fe-O scatter diagram
(d) 1000 ˚C: Phase diagram

Fig. 4 Phase Analysis of Sintered Ore after Reduction

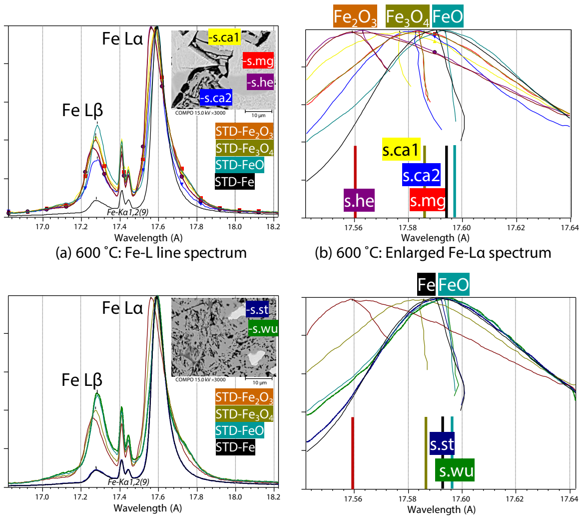
■ State Analysis of Iron Oxides in Sintered Ore after Hydrogen Reduction

In the case of iron, it is known that state analysis of iron oxides from the wavelength shift, waveform, and other features is possible by using the Fe-L line spectrum.

Here, Fig. 5 (a) and (c) show the Fe-L line spectra of standard samples of iron oxides and the sintered ore structure normalized by the spectral intensity of Fe-Lα, and Fig. 5 (b) and (d) show the analysis lines by the midpoint method in the apex region of the F-Lα peaks.

At 600 ˚C, the hematite structure (s.he) is in good agreement with the wavelength of Fe_2O_3, and the magnetite structure (s.mg) is in good agreement with the wavelength of Fe_3O_4. Furthermore, since the calcium ferrite structure (s.ca1) displays a peak wavelength between the wavelengths of Fe_2O_3 and Fe_3O_4, the oxidation state is considered to be an intermediate state between Fe_2O_3 and Fe_3O_4. On the other hand, a different calcium ferrite structure (s.ca2) can also be observed, and is almost in agreement with the wavelength of Fe_3O_4. Its valence ratio of Fe (Fe^{2+} : Fe^{3+}) is considered to be (1 : 2).

At 1000 ˚C, the wustite structure (s.wu) is in agreement with the wavelength of FeO, while the s.st structure is consistent with the wavelength of Fe, indicating completely reduced iron. Thus, although the structure of the sintered ore contains hematite and magnetite before reduction, reduction does not proceed at the low temperature of 600 ˚C, whereas reduction proceeds at the high temperature of 1000 ˚C, and the formation of wustite and metallic iron (Fe) can be confirmed from the spectra.



(a) 600 ˚C: Fe-L line spectrum
(b) 600 ˚C: Enlarged Fe-Lα spectrum
(c) 1000 ˚C: Fe-L line spectrum
(d) 1000 ˚C: Enlarged Fe-Lα spectrum

Fig. 5 State Analysis of Fe in Sintered Ore after Reduction

■ Conclusion

Quantitative mapping analysis and phase analysis of sintered ores after hydrogen reduction can be used not only in identification of iron oxide species and calcium ferrite, but also in structural analysis and research and development of the reduction process by utilizing state analysis from the detailed spectra of micro-regions.

<Acknowledgement>

The authors wish to express their heartfelt gratitude to Prof. Taichi Murakami of Tohoku University Graduate School of Environmental Studies (GSES) for his generous cooperation in providing the samples and instructions regarding the data analysis in the preparation of this Application News article.

<Related Applications>

1. Analysis of Sintered Ore for Steel Making, Application News No.01-00584-EN
2. State Analysis of Iron Oxides in Sintered Ore for Steel Making, Application News No.01-00663-EN
3. Analysis of Sintered Ore for Steel Manufacturing after Hydrogen Reduction, Application News No.01-00843-EN

01-01029-EN First Edition: Nov. 2025

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