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Investigation on Reaction Schemes of Iron Ore Sintering Process by High Temperature *in-situ* X-ray Diffraction and Micro-texture Observation

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Abstract

Iron ore sintering is a high-temperature, non-equilibrium reaction process that involves the formation of Ca-Fe-O melt. To clarify the mechanisms of liquid sintering, we observed the precipitation of iron oxide and calcium ferrite from liquid Ca-Fe-O by high-temperature in-situ X-ray diffraction and laser microscope observation. A continuous cooling transformation (CCT) diagram for iron ore sintering was devised based on the data on the cooling-rate dependence of the phase transition temperature obtained through the observation.

1. Introduction

Fine iron ore is sintered into lumps 5 to 50 mm in size called sintered ore, which is an important iron source accounting for more than 70% of the blast furnace burden in the Asia-Pacific region. Sintered ore is produced by mixing fine iron ore with limestone (flux) and coke breeze (heating fuel), granulating the mixture into pseudo-particles, heating them by combustion of the fine coke to 1450 to 1600 K, above the eutectic temperature according to the phase diagram for the CaO-Fe₂O₃ quasi-binary system (1478 K) (see **Fig.** 1(a)),¹⁾ and then holding them at the temperature range for several minutes. Part (b) of Fig. 1,²⁾ which was prepared based on general technical literature,³⁻⁶⁾ schematically illustrates the microstructural changes of the material during the sintering process.

The starting material, pseudo-particles, consists of fine iron ore, limestone and coke adhering to core particles of iron ore up to 10 mm in size. During the heating, oxides undergo phase transition and mutual diffusion at the interface between the adhering fines and nucleus grains, a molten liquid of an Fe-Ca-O system forms, and during the subsequent cooling, calcium ferrites precipitate, networks of pores form, and as a result, the structure of sintered ore is formed wherein Fe₂O₃ nucleus grains are fused together by calcium ferrites. The types, formation amounts and microstructures of the crystal phases of calcium ferrite, which change depending on process factors such as grain size, gangue content, temperature history, and oxygen partial pressure, affect the strength, reducibility, and other properties of sintered ore.³⁻⁹ Many researchers have studied the crystal structure of the Fe-Ca-O system and its stability, and there have been many reports on these aspects.¹⁾ Three different phases of calcium ferrite exist in the CaO-Fe₂O₃ quasi-binary system: Ca₂Fe₂O₅(C2F)¹⁰⁾, CaFe₂O₄(CF)¹¹⁾ and CaFe₄O₇(CF2)¹²⁾. (Henceforth C stands for CaO, F for Fe₂O₃, and W, which will appear soon, for FeO.) Of these three, CaFe₂O₄(CF) is a high-temperature phase, and is stable only in the temperature range of 1 428 to 1 499 K.

On the other hand, depending on oxygen partial pressure, α -CFF, β -CFF, and γ -CFF phases, all containing Fe²⁺, form at 1323 K,¹³⁾ and that of Ca₂Fe₉O₁₃(C2W5F2), Ca₂Fe₇O₁₁(C2W3F2), CaFe₃O₅(CWF), CaFe₄O₆(CW2F) and CaFe₅O₇(CW3F) phases form at 1393 K.^{14,15)} The above verifies that the types of phases appearing and the ratios of coexisting phases change depending on slight changes in the heating condition and chemical composition even under near-equilibrium conditions. Also, when gangues such as SiO₂ and Al₂O₃ are present, composite oxides of a continuous solid solution type containing Fe, Ca, Si, and Al form; such phases include SFCA (Ca₂(Fe, Ca)₆(Fe, Al, Si)₆O₂₀) and SFCA-I ((Ca, Fe)₄(Fe, Al)₁₆O₂₈).^{16,17}

The process of iron ore sintering is a non-equilibrium process that takes place within a very short time, and to clarify its process mechanisms, an analytical approach combining a phase diagram of a multi-component system and *in-situ* observation of high-temperature reactions is effective. However, *in-situ* observation of high-temperature reactions accompanying the formation of liquid phases has been little practiced because of the practical difficulties of high temperature (T>1473 K) and short reaction time (t<2×10² s). Some studies have been conducted on the formation of SFCA, a continu-

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Fig. 1 (a) Phase diagram for quasi-binary CaO-Fe₂O₃ system¹⁾ and (b) Schematic illustration of the sintering reactions during heating and cooling²⁾

ous solid solution phase containing SiO₂ and Al₂O₃, using scanning electron microscope observations (SEMs)¹⁸⁾ and *in-situ* X-ray diffraction measurements (XRD),^{19,20)} but they focused mainly on the reaction processes in a state of equilibrium, and there have been only a few findings on the reaction processes taking place under conditions of rapid heating and cooling as in real sintering plants. Moreover, there have been no reports on the observation of the changes of both the crystal structure and microstructure of the substances involved, although they are very important for clarifying the mechanisms of sintering reactions.

In consideration of all of the above, we examined in real time the process of calcium ferrite formation in the CaO-Fe₂O₃ system through *in-situ* observation of (a) the changes in the crystal structure by high-temperature XRD and (b) the microstructure through a laser microscope. The present paper reports the findings obtained through these observations. In addition, it also proposes a diagram of the continuous cooling transformations (CCT) during sintering reactions, which was devised based on the findings from the above analyses.

2. Experimental

 α -Fe₂O₃ (99.99% purity) and CaCO₃ (99.99% purity) powder were mixed with an agate mortar and pestle at a mass ratio of 90:10 (Fe90Ca10), equivalent to the average composition ratio of typical sintered ore charged into blast furnaces. The grain size of the α -Fe₂O₂ powder was 1 to 2 μ m, and that of the CaCO₂ powder was 2 to 3 μ m. In a real sintering process, iron ore grains, several millimeters in size, are covered with fines of Fe₂O₃, CaCO₃, gangues, and coke. The chemistry in the portions where adhesive layers form changes greatly depending on how these fines are mixed and distributed. The size range of the above prepared mixture was selected such that it corresponded to that of the adhesive layer covering the surfaces of nucleus ore grains in the real sintering process in order to best simulate the reactions of the real process in the test.

2.1 High temperature in-situ X-ray diffraction analysis

The equipment of the quick X-ray diffraction system (Q-XRD) used for the present study consisted of (1) an X-ray source, (2) a two-dimensional hybrid pixel array detector (area detector), and (3) a heating furnace. **Figure 2** schematically illustrates the optical part of the system. A rotating anode for laboratory use (Co $\lambda_{K\alpha}$ =0.17889 nm) and a synchrotron radiation (λ =0.17889 nm) were used as the source of the incident X-ray as illustrated in parts (a) and (b), respectively, of Fig. 2; the beam size of the incident X-ray was set at 0.5 × 2.0 to 0.5 × 1.0 mm². When the synchrotron radiation was used, the test was conducted at BL6C of the Photon Factory (PF) of the Institute of Materials Structure Science, the High Energy Accelerator Research Organization (known as KEK in short). The incident X-ray was monochromated using a Si(111) double-crystal monochromator, and then focused onto the specimen using a curved cy-lindrical mirror coated with platinum.

The heating furnace equipped with a platinum wire heater was set at the center of the diffractometer. A beryllium foil was set at the incidence/diffraction window of the furnace, and the furnace wall portion around the window was water-cooled so that the wall temperature would not exceed roughly 350 K. The furnace wall was protected by a thermal radiation shield made of porous alumina, with a nickel foil 5 μ m in thickness set at the portion corresponding to the incidence/diffraction window: the nickel foil served also as a filter for fluorescence X-ray. When the rotating anode was used as the X-ray source, the source and the detector were arranged such that the specimen would be placed horizontally in the furnace, and when the synchrotron radiation was used, the furnace containing the specimen was tilted towards the incident beam by 5 to 8°. To minimize the volume decrease of the specimen by melting, the mixed powder was pressed into a box-shaped platinum container $18 \times 10 \times 1$ mm³ in inner dimension.



Fig. 2 X-ray geometry of the Q-XRD system²⁾ with X-ray sources of (a) rotating-anode and (b) synchrotron radiation

The specimen was heated in air atmosphere to 1773 K at a rate of 5.0×10^{-1} K/s, and then cooled to 673 K at a rate of -8.3×10^{-1} or -8.3×10^{-2} K/s. The specimen temperature was measured with an R-type thermocouple gage attached to a side of the container, and the difference between the monitoring by the thermocouple and the sample surface temperature was corrected using the temperature dependence of the lattice parameter of α -Al₂O₃. The two-dimensional hybrid pixel array detector, PILATUS100K[®], comprising 487 × 195 pixels, each 0.172 × 0.172 mm² in size, arranged in an effective area of 83.8×33.5 mm²,^{21,22}) was set at a camera length of 200 mm, and X-ray diffraction images were taken repeatedly at an exposure time of 10 to 20 s, covering a field of view of 2θ =23.5 to 46.5° and an arc angle of the Debye-Scherrer ring of $\Delta\beta$ =10°.

2.2 High temperature micro-texture observation

Observation of microstructure was conducted using a high-temperature laser microscope²⁾ made by Yonekura MFG Co., Ltd., wherein an IR heater equipped with two units of 1.5 kW halogen lamps and a confocal laser scanning microscope are combined; **Figure 3** schematically shows its configuration. It is capable of heating a specimen up to 1770 K, temperature control at a heating/cooling rate of \pm 500 K/min, and structural observation at a spatial resolution of 0.3 μ m. For the present study, an Fe90Ca10 powder specimen, about 50 mg in weight, was packed into a cylindrical container of platinum, 5 mm in diameter and 5 mm in height, heated up to 1770 K in a gas-flow environment of Ar-20vol%O₂, and after it melted completely, its micro texture was observed during cooling at the rate of -5 to -200 K/min. By properly controlling the gas flow around the specimen, it was possible to observe the structural change clearly even when the specimen emitted gas.

3. Results and Discussion

3.1 Reactions during heating process

Figure 4(a) shows the change in the X-ray diffraction pattern of

the Fe90Ca10 specimen during heating from 300 to 1773 K at a rate of 5.0×10^{-1} K/s, which is roughly a quarter that of heating from 1350 to 1600 K in a real sintering plant. Here, during heating up to the eutectic temperature, reactions advanced through solid phase diffusion between the powder grains, and the types of coexisting phases resulting from the reactions and their ratios changed depending on the temperature and the material structure. At 1355 K, the rate of solid phase diffusion became very high, and a stable CF phase formed.

During further heating, $CaFe_2O_4(CF)$ began to react with α -Fe₂O₃(F) at 1529 K to form $CaFe_4O_7(CF2)$. At the same time, a



Fig. 3 Schematic configuration of confocal laser scanning microscope combined with an image furnace²⁾



Fig. 4 High-temperature diffraction patterns of Fe90Ca10 caught *in-situ* by Q-XRD during (a) heating, (b) cooling at -8.3×10^{-1} K/s, and (c) cooling at -8.3×10^{-2} K/s² Legend: F=Fe₂O₄, WF=Fe₃O₄, C2F=Ca₂Fe₂O₄, CF=CaFe₂O₄, and CF2=CaFe₄O₇.

halo pattern due to liquid phase formation was observed, which suggested that the reaction rate was increased owing to the higher diffusion rate in the liquid phase. At yet higher temperatures, CF, CF2 and Fe₂O₂ reacted with each other, and at 1557 K, the liquid phase and Fe₂O₃ began to coexist. In the reactions of CF+F \rightarrow CF2 and $CF+CF2 \rightarrow$ liquid (L), the overheating temperature ΔT_1^{c} was 85 and ΔT_1^{c} was 80 K, respectively. (Here, ΔT_x^{Y} means the difference (overheat or overcool) between the temperature at which reaction X takes place under a heating or cooling rate Y and the phase transition temperature at equilibrium.) At 1678 K, Fe₂O₂ transformed into Fe₂O₄, but the temperature of this transformation was higher than the equilibrium temperature by 47 K (ΔT_{WF}^{c} =47 K). The superheat depends on the heating rate, the grain size of the starting material, and the state of mixing of the grains. When a specimen is prepared by thoroughly mixing fine powder of α -Fe₂O₂ and that of CaCO₂, the overheat will be negligibly affected by the diffusion rate, and be determined substantially by the heating rate.

3.2 Crystal structure and structural change during cooling

The formation process of calcium ferrite during cooling of the molten liquid was observed *in-situ* using a Q-XRD system and a confocal laser scanning microscope for high temperature use. The X-ray diffraction patterns of a starting material Fe90Ca10 taken *in-situ* during cooling from 1773 to 300 K at cooling rates of -8.3×10^{-1} and -8.3×10^{-2} K/s are shown, respectively, in parts (b) and (c) of Fig. 4. Both calcium ferrite (CF, CF2) and hematite (F) precipitated virtually simultaneously (L+F \rightarrow CF+CF2+F). This took place at 1483 K when the cooling rate was -8.3×10^{-1} K/s, and at 1491 K when it was -8.3×10^{-2} K/s; these precipitation temperatures were lower by 16 and 8 K, respectively, than the same in the state of equilibrium (1499 K).

The fact that, when the cooling rate was as described above, all

CF, CF2 and F formed nearly at the same time from the molten liquid of the oxide seems to indicate that the solidification of CF directly from the liquid takes place in preference to the solid-phase reaction of CF2 \rightarrow CF+F (Fig. 1 (a)), which seems to occur at a temperature lower than 1428 K. The relative amounts of the precipitated CF, CF2 and F changed only slightly during cooling to room temperature. Considering the fact that the cooling rate of the present study is nearly on the same order of magnitude as the typical cooling rate of industrial ore sintering, the findings obtained through the *in-situ* Q-XRD observation seem to indicate that the formation of calcium ferrite during overcooling in a temperature range of 1480 to 1500 K significantly affects the type and amounts of coexisting phases in the sintered ore by industrial production.

At equilibrium state, a phase transition of $L \rightarrow L+WF$ takes place at 1733 K, but when the molten oxide was cooled at a rate either of -8.3×10^{-1} or -8.3×10^{-2} K/s, no clear diffraction patterns were obtained at the ranges above 1483 and 1491 K, respectively. This is presumably because the amounts of the primary crystals of Fe₃O₄ and Fe₂O₃ precipitating from the liquidus phase were less than the detection limit of the equipment. It follows, therefore, that, in order to clarify the reaction processes in a liquid phase of oxides containing small amounts of initial precipitates, it is also important to use a technique for *in-situ* micro texture observation such as a high-temperature laser microscopy. In fact, the phase transformation temperature was defined in the present study through the combination of two different *in-situ* observation techniques: the Q-XRD to detect the change in crystal structure, and the high-temperature laser microscope to sense the change in microstructure.

Figure 5 shows some photomicrographs of Fe90Ca10 specimens taken during cooling from 1 770 to 300 K at a rate of (i) -3.3 K/s and another of (ii) -8.3×10^{-1} K/s; these two cooling rates cor-



Fig. 5 Change in microstructure of Fe90Ca10 during cooling from 1773 to 300 K at cooling rates of (i) -3.3 K/s and (ii) -8.3 × 10⁻¹ K/s²)



Fig. 6 CCT diagram for Fe90Ca10²⁾

Solid curves in black are time-temperature curves during cooling at (i) -3.3 K/s, (ii) -8.3×10^{-1} K/s, and (iii) -8.3×10^{-2} K/s. Horizontal dotted lines in blue show the phase transformation temperatures of $L \rightarrow L+WF$, $L+WF \rightarrow L+F$, $L+F \rightarrow CF2+F$, and $CF2+F \rightarrow CF+F$ at equilibrium. Symbols $\Delta T_{A \rightarrow B}$ we and the supercool for the reaction $A \rightarrow B$ to take place at a cooling rate Y (= i, ii or iii). Broken lines (red) show those of $L \rightarrow L+WF$ and $L+WF \rightarrow L+F$ under non-equilibrium cooling conditions determined in this study. The dotted bold line (red) shows that of $L+F \rightarrow CF2+CF+F$ under non-equilibrium cooling set this study. Boundaries determined by laser microscopy are shown by diamonds. Cross marks show the time and temperature where typical microstructures obtained by *in situ* laser microscopy shown in Fig. 5.

respond to the plotting in **Fig. 6**. When Fe90Ca10 is cooled, acicular crystals of magnetite (Fe₃O₄, WF) precipitate in the first place from the liquid through a reaction of $L \rightarrow L+WF$. These crystals grow in specific angles from the nuclei to form triangular grains; this is because magnetite has a spinel type face-centered cubic (FCC) crystal structure. The characteristic feature of this crystal growth is closely related to the diffraction from the {*hkl*} = {006} plane detected in the L+WF zone (see parts (b) and (c) of Fig. 4).

The overcool $\Delta T^i_{L\rightarrow L+WF}$ causing the magnetite precipitation at a cooling rate of (i) -3.3 K/s and that of $\Delta T^{ii}_{L\rightarrow L+WF}$ at a cooling rate of (ii) -8.3×10^{-1} K/s were -63 and -36 K, respectively. The phase transformation of L+WF \rightarrow L+F took place during further cooling, crystal grains of magnetite grew in 3 to 8 s, and large crystal grains of hematite formed (see parts (i-2) and (ii-2) of Fig. 5). At the larger cooling rate of -3.3 K/s (i), precipitated crystal grains had triangular shapes as seen in part (i-2). In contrast, at the lower cooling rate of -8.3×10^{-1} K/s (ii), the crystal grains tended to take rather random shapes. This is presumably because, when cooling is slow, the shape of magnetite grains is easily changed by the phase transformation of hematite, and moreover, other precipitates from the liquid settle and grow on the surfaces of the triangular magnetite grains to make their shape random.

During further cooling, a solid-solid reaction of CF2+F \rightarrow CF+F advances; this reaction was clearly observed by the Q-XRD. The overcool of this reaction was -16 K when the cooling rate was (ii) -8.3×10⁻¹ K/s, and -8 K when the cooling rate was (iii) -8.3×10⁻² K/s.

4. CCT Diagram for Sintering Process

The overcool in the sintering reactions defined through the *in-situ* observation by the Q-XRD and the laser microscope can be understood quantitatively by applying the concept of continuous cooling transformation (CCT) diagrams, which are widely used for heat treatment of steel materials.²³⁾ Based on the findings obtained

through the observations, we compiled CCT diagrams for the first time in the field of iron ore sintering. Figure 6 shows the diagram for Fe90Ca10. The graph shows time-temperature curves for cooling rates (i) -3.3, (ii) -8.3×10^{-1} and (iii) -8.3×10^{-2} K/s in black solid lines, and the temperatures of four transformation reactions, namely $L \rightarrow L + WF$, $L + WF \rightarrow L + F$, $L + F \rightarrow CF2 + F$, and $CF2 + F \rightarrow CF+F$, at equilibrium in blue dotted lines.

The symbols ΔT_x^{Y} mean the overcool for the transformation reaction X to take place during cooling at the cooling rate Y (=i, ii or iii). The red dotted curves show the temperatures at which the reactions of L→L+WF and L+F→CF2+CF+F take place during cooling in a non-equilibrium condition defined based on the findings of the present study, and the diamonds, half white and half black, represent the phase boundaries defined through structural observation. Note that the cross symbols (+) marked with (i-1), (ii-2), etc. indicate the time and temperature at which the corresponding frames of Fig. 5 were taken.

The following two issues are understood from the diagram: (1) the larger the cooling rate Y, the larger the overcool (ΔT_X^{Y}) of a specific reaction X tends to be; and (2) the following relationship holds true between the overcool values ΔT_X^{Y} of different reactions X at a given cooling rate Y:

 $\Delta T^{\rm Y}_{\rm L+F\to CFx+F} \ll \Delta T^{\rm Y}_{\rm L\to L+WF} \leq \Delta T^{\rm Y}_{\rm L+WF\to L+F}$

The hatched area in green in Fig. 6 corresponds to the range of cooling rates commonly practiced at commercial iron ore sintering. ^{3–6, 8)} In this range of overcool, the temperature at which reactions $L+WF \rightarrow L+F$ and $L+F \rightarrow CF2+F$ take place depends largely on the cooling rate, which indicates that the ratios of coexisting phases and the structure of the final sintered ore change substantially depend on small changes in the cooling pattern.

It follows, therefore, that, in order to obtain a desired microstructure of sintered ore, it is possible to design the temperature curve for the industrial sintering process based on a CCT diagram. Given a target temperature pattern, it is possible to control heating and cooling of the sintering process by changing, for example, the coke mixing ratio and the combustion conditions, and verifies the adequacy of the control by examining the texture of the products.

5. Summary

The recent advance in sensing and monitoring technologies has enabled hitherto impossible observation of rapidly developing reactions in real time. Sintered iron ore has been the principal blast furnace feed for many years, but the sintering reaction steps involving gangue materials and the mechanism through which a specific product property appears are so complicated that many process aspects still remain unclear. The techniques for high-temperature, in-situ observation of process phenomena presented herein are effective at clarifying those aspects. Simplifying various mechanisms of industrial processes requires combined use of mutually supplementing approaches. In addition to X-ray diffractometry, etc., techniques such as thermal analysis and thermodynamic calculation were used in a complementary manner for the present study, which led to proposals of methods and indicators (such as the CCT diagram) for comprehensive and quantitative understanding of data collected through tests. The process in real sintering plants involves a multi-component system containing Al₂O₂, SiO₂, etc. besides the main raw materials, and to properly understand process phenomena it is necessary to begin by clarifying the state of equilibrium.

Understanding of the reaction mechanisms of liquid sintering between pseudo-particles, one of the most important element reac-

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tions of the iron ore sintering process, is advanced by developing and using quantitative indicators like those introduced herein. Along this route, it will be possible to clearly and quantitatively explain the complicated relations of reaction conditions (temperature, oxygen partial pressure, element distribution between pseudo-particles, etc.) and optimize the process.

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