In situ observation of sintering in CaO-Fe$_2$O$_3$ system at high temperatures

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1 Introduction

Phase equilibrium of Fe$_2$O$_3$-CaO system has a great importance in the process of iron making. Sintered iron ores with lime stone are used as raw material for a blast furnace. The process of sintering proceeds at a temperature higher than 1773 K and the sintered ores are cooled down before the thermal equilibrium attained. The required properties for sintered ores, such as the mechanical strength and the reactivity with reduction gas, are largely affected by the types of coexisting phases and their fractions, and its microstructure. Thus *in situ* observation of the change of structure during sintering processes is of a great importance.

2 Experiment

A special reaction cell for *in situ* X-ray diffraction was developed [1]. Powder specimens are heated in various gas up to T = 1773 K. The reaction cell was mounted on a special goniometer [2] which can maintain the specimen in a near-horizontal position while scanning a detector in both an in-plane and out-of-plane directions [3]. An area detector, PILATUS® (PIxeL ApparaTUs for the SLS, DECTRES and Rigaku), was used in order to measure a part of diffraction Debye-ring in a short period.

Powder specimens, a mixture of Fe$_2$O$_3$ and CaO with various ratios, were mounted in the center of the reaction cell. They were heated in air up to to T = 1773 K, and the change in the diffraction patterns were measured using an X-ray beam with a size of 1×1 mm^2 and λ = 0.178897 nm. Experiments were conducted at a bending beam-line of BL-6C at PF, KEK, Tsukuba, Japan.

In situ and real-time observation of microstructures were performed using an *in situ* laser microscope.

3 Results and Discussion

Figure 1 shows typical X-ray diffraction patterns measured by *in situ* XRD for the specimen with Fe$_2$O$_3$:CaO = 90:10 (mass%) when heated from 300 to 1773 K with a rate of 5.0×10^{-1} K/s. This rate was determined to simulate the heating condition of an industrial sintering process for iron making, and is rather faster than that to obtain the equilibrium state.

The CaFe$_2$O$_4$ phase was formed at T = 1355 K because solid–solid diffusion becomes fast enough in the stable CaFe$_2$O$_4$ phase. On further heating, the CaFe$_2$O$_4$ reacted with α-Fe$_2$O$_3$ and formed CaFe$_4$O$_7$ (CaFe$_2$O$_4$ + Fe$_2$O$_3$ → CaFe$_4$O$_7$) at T = 1513 K. On further heating, the mixture of CaFe$_2$O$_4$, CaFe$_4$O$_7$, and Fe$_2$O$_3$ reacted with each other and formed a liquid phase at T = 1558 K. The overheating phenomena were clearly observed *in situ* for the reactions CaFe$_2$O$_4$ + Fe$_2$O$_3$ → CaFe$_4$O$_7$ and CaFe$_2$O$_4$ + CaFe$_4$O$_7$ → liquid.

In situ XRD measurements were carried out for specimens with different CaO/Fe$_2$O$_3$ ratios. *In situ* microstructure observation was performed extensively for the cooling process, where crystallization of calcium ferrites from the molten oxide is affected by the specimen's composition and a cooling rate.

In situ observation both of crystal structure and microstructure successfully revealed the effects of heating and cooling rates on the sintering reaction in the CaO-Fe$_2$O$_3$ system with special attention to overheating and overcooling phenomena. The first continuous cooling transformation (CCT) concept for iron ore sintering was proposed to understand overcooling phenomena when the molten oxide cooled down to room temperature and magnetite (Fe$_3$O$_4$), hematite (Fe$_2$O$_3$), and various types of calcium ferrite were formed. This concept can be a guideline for controlling sintering processes [1].
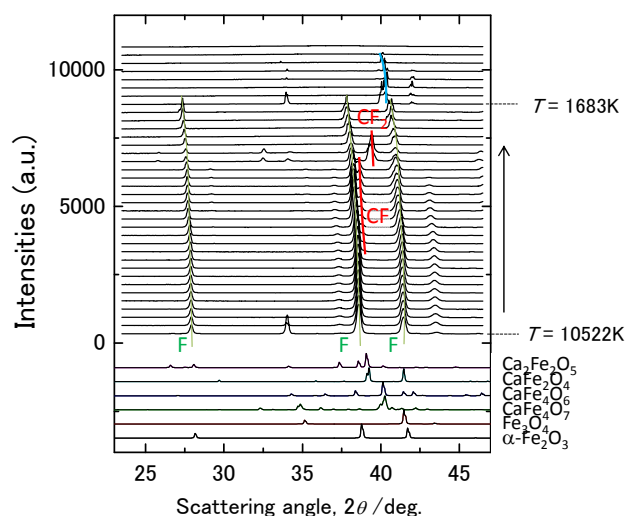

Figure 1 Temperature evolutions of X-ray diffraction patterns measured by *in situ* XRD for the specimen with Fe$_2$O$_3$:CaO = 90:10 (mass%) when heated from 300 to 1773 K with a rate of 5.0×10^{-1} K/s.

References
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