In situ observation of sintering in CaO-Fe₂O₃ system at high temperatures

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1 Introduction
Phase equilibrium of Fe₂O₃-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® (PILATUS ApparTU), was used in order to measure a part of diffraction Debye-ring in a short period.

Powder specimens, a mixture of Fe₂O₃ and CaO with various ratios, were mounted in the center of the reaction cell. They were heated in air up to \( T = 1773 \) K, and the change in the diffraction patterns were measured using an X-ray beam with a size of \( 1 \times 1 \) mm² and \( \lambda = 0.178897 \) 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 Fe₂O₃:CaO = 90:10 (mass%) when heated from 300 to 1773 K with a rate of \( 5.0 \times 10^{-1} \) 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 CaFe₂O₄ phase was formed at \( T = 1355 \) K because solid–solid diffusion becomes fast enough in the stable CaFe₂O₄ phase. On further heating, the CaFe₂O₄ reacted with \( \alpha\)-Fe₂O₃ and formed CaFe₄O₇ (CaFe₂O₄ + Fe₂O₃ \( \rightarrow \) CaFe₄O₇) at \( T = 1513 \) K. On further heating, the mixture of CaFe₂O₄, CaFe₄O₇, and Fe₂O₃ reacted with each other and formed a liquid phase at \( T = 1558 \) K. The overheating phenomena were clearly observed in situ for the reactions CaFe₂O₄ + Fe₂O₃ \( \rightarrow \) CaFe₄O₇ and CaFe₄O₇ + CaFe₂O₄ \( \rightarrow \) liquid.

In situ XRD measurements were carried out for specimens with different CaO/Fe₂O₃ 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-Fe₂O₃ 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 (Fe₃O₄), hematite (Fe₂O₃), and various types of calcium ferrite were formed. This concept can be a guideline for controlling sintering processes [1].

References

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