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ガスジェット浮遊炉による溶融酸化鉄の水素還元速度 測定手法の開発

Development of a Measurement Method for Assessing the Hydrogen Reduction Rate of Molten Iron Oxide using Aerodynamic Levitation Furnace

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1. Introduction

The operation of blast furnaces significantly contributes to CO_2 emissions, primarily due to the use of carbonaceous materials as reducing agents for iron ore. To reduce these emissions, efforts have been made to replace carbon-based reducing agents with hydrogen-based alternatives. However, the reported hydrogen reduction rate of molten iron oxide is inconsistent¹⁻³, potentially due to chemical reactions between the sample and its container at high temperatures.

In this study, molten iron oxide was maintained under a flowing hydrogen-mixed gas in a containerless state using an aerodynamic levitation (ADL) technique. The purpose of this study was to investigate the possibility of accurately measuring the hydrogen reduction rate of molten iron oxide using ADL.

2. Experimental procedure

Electrolytic iron with a mass purity of 99.99%, weighing between 35-40 mg, was chemically cleaned in a nitric acidethanol solution using an ultrasonic cleaner, followed by a cleaning in acetone. The cleaned iron was then melted in air on a copper hearth using a semiconductor laser beam and maintained at 2000 K for 45 seconds before being rapidly solidified into a spherical Fe-14.8%O sample. This sample was placed on the nozzle of the ADL and levitated by a jet of Ar-H₂ gas mixture, injected from the bottom at a flow rate of approximately 1.4 L·min⁻¹. The oxygen partial pressure of the gas was confirmed by a zirconia-type oxygen sensor, operating at 1008 K at the inlet. The levitated sample was irradiated with a semiconductor laser beam, melted, and maintained at 1960 K for a certain period of time before rapid solidification. The reduction behavior of the molten iron oxide sample was monitored at 6000 frames·sec⁻¹ using a highspeed video camera, in conjunction with the temperature measured by a monochromatic pyrometer The oxygen content of the solidified sample was analyzed using the inert gas fusion-infrared absorption method to calculate the hydrogen reduction rate *r* [kg-O·m⁻²·s⁻¹].

3. Result and discussion

Figure 1 shows typical time-lapse images of molten iron oxide being reduced at 1960 K under a flow of Ar-5%H₂ mixed gas, observed from above. The oxygen partial pressure (Po_2) of the gas was estimated to be ~10⁻²³ atm, derived from the standard Gibbs energy of the formation of H₂O(g). This estimation was based on the measured Po_2 value from a zirconia-type oxygen sensor, assuming that the ratio of partial pressures of H₂O(g) to H₂(g) remains constant regardless of temperature. Under this gas flow condition, the molten iron oxide gradually reduced, resulting in the formation of a low-emissivity liquid iron phase at around 45 seconds.



Fig.1. Typical time-lapse images of molten iron oxide being reduced at 1960 K under a flow of Ar-5%H₂ mixed gas.

Subsequently, the levitated molten iron oxide was completely reduced by the 58-second mark. In addition, the volume of the droplet decreased as the reduction progressed.

Figure 2 illustrates the oxygen concentration in the solidified sample as a function of the exposure time of the levitated droplet to the Ar-5% H₂ gas mixture. For comparison, it also depicts results obtained under high-purity Ar gas, where the oxygen partial pressure is maintained at 10^{-7} atm. While the oxygen content of the molten sample maintained under high-purity Ar gas remains nearly constant even after 90 seconds, it decreases linearly under the Ar-5% H₂ gas mixture with time. This confirms that the levitated molten iron oxide was reduced under the flow of Ar-5% H₂ mixed gas. Moreover, an increase in hydrogen concentration of the gas enhances the reduction of the sample.

Figure 3 displays the time-dependent changes in the surface area of the levitated droplet during the hydrogen reduction reaction. These changes were estimated from the droplet images observed from above, under the assumption that the droplet retains a spherical shape. Based on these droplet images, the molten iron oxide covered the sample surface until the liquid iron phase appeared. From the observed changes in the surface area prior to the formation of liquid iron phase and the corresponding amounts of reduced oxygen, the hydrogen reduction rate of molten iron oxide sample was calculated to be 0.10 kg-O·m⁻²·s⁻¹. Thus, the ADL technique enabled the accurate measurement of the reduction rate of molten iron



Fig.2. Time dependence of oxygen concentration in a molten sample maintained at approximately 1960 K under an Ar-H₂ gas flow of 1.4 L/min.



Fig.3. Typical time dependence of the surface area in the levitated droplet of molten iron oxide during its reduction under an Ar-H₂ gas flow of $1.4 \text{ L} \cdot \text{min}^{-1}$.

oxide, unaffected by any sample contamination from the container, even at elevated temperatures. At this stage of the research, however, the possibility that hydrogen supply might be the rate-determining step in the reduction process cannot 2 of 3

be dismissed. Further studies involving increased hydrogen gas concentration and flow rate are essential for advancing our understanding in future work.

4. Summary

Using the ADL technique, the Fe-14.8%O sample was levitated and melted under a flow of Ar-5%H₂ mixed gas, with the objective of developing an accurate method for measuring the hydrogen reduction rate of molten iron oxide without sample contamination from the container at high temperatures. The results clearly showed the reduction of the molten sample, as evidenced by a marked transition from molten iron oxide to a liquid iron phase, coupled with a noticeable decrease in sample volume. In our experimental setup, which maintained an Ar-5%H₂ gas flow rate of 1.4 L·min⁻¹, we tentatively determined the hydrogen reduction rate of molten iron oxide to be $0.10 \text{ kg-O·m}^2 \cdot \text{s}^{-1}$.

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