Wettability and Interfacial Permeability between Prereduced Ilmenite and Molten Pig Iron

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The interfacial phenomena between molten pig iron and ilmenite prereduced with carbon and hydrogen were investigated. The wettability of prereduced ilmenite discs by molten pig iron was evaluated through measuring contact angle by the sessile droplet method. The effects of melting temperature, prereduction temperature and reduction degree on contact angle were examined. Molten pig iron could not be wetted by ilmenite prereduced with carbon and hydrogen, and the contact angle increases with increasing prereduction temperature. The contact angles of ilmenite prereduced with hydrogen are higher than that of ilmenite prereduced with carbon at the same reduction degree. The permeation of molten pig iron into porous ilmenite was observed at the interface of specimens prereduced with carbon and enhanced at higher reduction temperature. On the other hand, in the case of ilmenite prereduced with hydrogen, the permeation was not observed. These results indicate clearly that the separation between molten pig iron and reduced ilmenite can be enhanced by hydrogen reduction process, even at lower temperature than that of carbon reduction process.

KEY WORDS: wettability; interfacial permeability; prereduced ilmenite; carbon reduction; hydrogen reduction; sessile drop.

1. Introduction

The titanium minerals including ilmenite (FeO·TiO₂), leucoxene (Fe₂O₃·TiO₂), and rutile (TiO₂) have significant economic importance.1–4) Depleting of the natural rutile, the natural ilmenite is becoming the main resource to produce titanium dioxide pigments, titanium tetrachloride (feed stock for titanium metal production), and welding rod flux.5,6) The upgrading of ilmenite to form synthetic rutile (TiO₂) can be accomplished by various methods. These methods are classified into three main types, namely, thermal reduction, selective chlorination, and selective leaching.7,8) The thermal reduction is widely used to synthesize the upgrading titanias from ilmenite.9) Carbon is the most dominant reduction agent at present. However, this process will produce CO₂ which is responsible for global warming. As a result, the use of carbon in thermal reduction is hindered and hydrogen is attracting more and more attentions due to its environmental-friendly characteristic. Whatever carbon or hydrogen is used, the main product is composed of TiO₂ and iron. Therefore, the separation of TiO₂ from iron is the key step. However, few reports were found on this issue.10) The sessile drop method was employed generally to determine the surface tension of molten metal.11,12) Kapilashrami et al.13) and Kang et al.14) studied the wetting characteristics of molten iron on mullite by sessile drop technique. Valdez et al.15,16) measured the undercooling of a pure iron sessile droplet in contact with Al₂O₃, ZrO₂ and MgO substrates under controlled oxygen partial pressures by observing droplet recalescence. In the present work, the wetting behavior and contact angle of molten pig iron and ilmenite prereduced with carbon and hydrogen are investigated by using the sessile drop method.

2. Experimental

2.1. Raw Materials

The pig iron was machined into a column (diameter 8 mm, length 8 mm, about 0.7 g). The chemical composition of pig iron is shown in Table 1.

| Table 1. Chemical composition of pig iron (mass%). |
|--------|--------|--------|--------|--------|--------|--------|
| Fe     | C      | Si     | Mn     | P      | S      |
| 95.50  | 4.30   | 0.15   | 0.008  | 0.027  | 0.006  |

2.2. Ilmenite Prereduced with Carbon and Hydrogen

The ilmenite was ground and screened to particle size

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fraction from 71 to 150 μm. For carbon prereduction, total 10 g ilmenite and graphite were weighed precisely in which the molar ratio of carbon to oxygen from iron oxides ($N_C/N_O$) kept as unity in all experiments, corresponding to the complete carbon conversion to carbon monoxide. The raw materials were thoroughly mixed by stirring over 30 min with the addition of adhesive, and then pressed into the cylindrical discs (diameter 9 mm, length 8 mm) in a steel die under 15 MPa. The sample was placed into a vertical SiC furnace, and preheated at 823 K for 20 min to ensure the adhesive and moisture volatilized fully. Argon with the flow rate of 1 000 cm$^3$/min was purged to the tube to provide inert ambience. The reaction temperatures were varied from 1 373 to 1 673 K.

For hydrogen prereduction, about 2 g ilmenite powder were mixed with adhesive and pressed into cylindrical discs in a steel die. The sample was preheated at 823 K for 20 min to ensure the complete removal of adhesive and moisture. Then high purity $H_2$ was used as reducing agent with the flow rate of 1 000 cm$^3$/min. The reaction temperatures were varied from 1 073 to 1 273 K. At the end of each run, the pure argon was introduced into the furnace for the samples cooling.

More detailed procedure on the preparation of ilmenite discs prereduced by carbon and hydrogen was described elsewhere.$^{4,17–19}$

2.3. Wettability Measurement

Contact angle was measured by using sessile drop equipment, which composed of a horizontal furnace, a digital camera for the image manipulation and observation of the contact angle, a deoxidation furnace and a gas manometer system for controlling the atmosphere, as schematically illustrated in Fig. 1.

The pig iron was polished to mirror, rinsed in acetone by an ultrasonic cleaner and dried afterward. The iron and the substrate were put into the middle of corundum tube and then sealed. Argon which was purified firstly to high purity (99.999%) was introduced into the tube to purge oxygen at a flow rate of 400 cm$^3$/min. The specimen was heated to prescribed temperature at the rate of 5 K/min. More than five photographs of droplets were captured at each desired experimental temperature as a function of time. The contact angles were calculated by analyzing these photos with self-made software. The mean value of those data at the same temperature has been considered as the contact angle at this temperature. The contact angle was measured by the sessile droplet of molten pig iron on the prereduced ilmenite substrate, and the uncertainty of the measured contact angle was estimated less than 0.5% as described in the previous papers.$^{12,20–22}$

The interfacial topography was observed by optical microscope (Leitz Wetzlar-307) and JSM scanning electron microscopy which is equipped with energy dispersive spectroscopy (EDS) to observe the distribution of elements. The phases in reduced ilmenite were investigated by using XRD (Philips 1 140, $CuKα$, 40 mA current, 30 kV voltage).

3. Results

3.1. Interface of Ilmenite Prereduced with Carbon

Figure 2 shows a typical morphological evolution of wetting couples between molten pig iron and ilmenite prereduced with carbon at 1 573 K.

![Fig. 2. Morphological evolution of wetting couples between molten pig iron and ilmenite prereduced with carbon at 1 573 K.](image)

Figure 3 shows the contact angles of molten pig iron with ilmenite discs. The substrates were prereduced by carbon at temperatures of 1 473, 1 573 and 1 673 K, resulting reduction degrees of 86.97, 93.18 and 99.07%, and remaining carbon of 0.63 mass% of total weight of the ilmenite substrates, respectively. All contact angles are much higher than 90°, indicating the poor wettability between pig iron and reduced products. The experimental
temperature and the prereduced temperature distinctly influenced the contact angle between the ilmenite prereduced with carbon and molten pig iron. As shown in Fig. 3, the contact angle between molten pig iron and prereduced ilmenite decreased with the increase of the experimental temperature. The changes of contact angles were more obvious at lower experimental temperature. The contact angle increased significantly with increasing prereduction temperature of the ilmenite. It indicated that the complete separation of molten pig iron from ilmenite in carbon thermal reduction process could be achieved at higher reduction temperature.

Figure 4 shows the variation of contact angle with time when ilmenite substrates prereduced with carbon were used at 1553 K. It was seen clearly that the contact angle of molten pig iron with prereduced ilmenites is time-independent, indicating the wetting is non-reactive process.

The interface between ilmenite prereduced with carbon and solidified pig iron was observed by optical microscope, as shown in Fig. 5. The interfacial permeability was found in these specimens, obviously for the ilmenite substrates prereduced at 1573 and 1673 K. It can be seen that the permeable layer thickness increased with increasing prereduction temperature. High prereduction temperature would result in the increase of carbon consumption, and high porosity of reduced ilmenite, as reported in Ref. 4). Therefore, molten pig iron would penetrate more easily into reduced porous ilmenite discs to form permeability layer. In fact, molten pig iron was non-wettable with titanium oxide. However, since the pores in reduced ilmenite were enough big, the penetration force of molten pig iron into the pores depending on its gravity could overcome the interfacial tensile between molten pig iron and titanium oxides. Therefore, large amount of titanium oxides were surrounded by molten pig iron.

The SEM was employed to investigate further the interfacial layer between pig iron and ilmenite prereduced with carbon, as well as distribution of elements observed by EDS, as shown in Fig. 6. An interfacial layer is observed obviously with thickness of about 300 μm, which is consistent with the observation with optical microscopy. The layer structure was characterized by that molten pig iron was penetrating into substrate and surrounding large amount of titanium oxide particles, confirmed by the element mapping of Fe, Ti and O by EDS.

3.2. Interface of Ilmenite Prereduced with Hydrogen

Figure 7 shows the variation of contact angle between

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**Fig. 3.** Variation of contact angle between molten pig iron and ilmenite prereduced with carbon at 1473, 1573 and 1673 K as a function of experimental temperature.

**Fig. 4.** Contact angles between molten pig iron and ilmenites prereduced with carbon as a function of time at 1553 K.

**Fig. 5.** Morphologies of interfaces between solidified pig iron and ilmenite prereduced with carbon (CPI) at (a) 1373 K, (b) 1473 K, (c) 1573 K and (d) 1673 K (all specimens were heated to 1553 K and held for 30 min).
molten pig iron and ilmenite prereduced with hydrogen with experimental temperature. The ilmenite specimens were prereduced uniformly, and the reduction degrees of ilmenite with hydrogen were 46.98, 64.43, 80.65 and 97.84% at temperatures of 1 073, 1 123, 1 173 and 1 223 K, respectively. It can be seen that the ilmenites prereduced with hydrogen were non-wettable with molten pig iron. The contact angle decreased with the increase of the experimental temperature, while increased obviously with the increase of prereduction temperature, which is similar to the case of ilmenite prereduced with carbon. Figure 8 shows the change of contact angles with holding time when the prereduced ilmenite substrates were kept at 1 553 K. The time-independency of contact angle between molten pig iron and prereduced ilmenite was also observed clearly.

Figure 9 shows the interfacial morphologies between solidified pig iron and ilmenite prereduced by hydrogen (HPI) at (a) 1 073 K and (b) 1 123 K (both specimens were heated to 1 553 K and held for 30 min).
formed, indicating the different structure from that of ilmenite prereduced with carbon. The SEM observation confirmed the absence of permeable layer at the interface, as shown in Fig. 10.

It should be reasonable to propose that the absence of permeable layer in ilmenite substrates prereduced with hydrogen is associated with higher density of product than that prereduced with carbon. This could be seen clearly by the comparison of SEM morphologies of both specimens, as shown in Figs. 6(a) and 10. For carbon prereduction, graphite powder was mixed into ilmenite. Accordingly, the consumption of graphite during reduction process could leave large amount of pores. On the other hand, this did not occur during hydrogen reduction process, leading to higher product density prereduced with hydrogen.

4. Discussion

From Figs. 3 and 7, it can be summarized that the separation between pig iron and reduced product of ilmenite was improved at higher reduction temperature, no matter whether carbon or hydrogen was used as reducing agent. Figure 11 shows the influence of reduction temperature on the phase composition of reduced product by pure hydrogen. The sample reduced at 1 123 K contained iron, ilmenite, rutile and pseudobrookite. At 1 173 K, peaks regarding ilmenite became invisible and reduced rutiles appeared, while the intensity of peaks for rutile and pseudobrookite increased. TiO phase appeared at 1 223 K and the intensity regarding pseudobrookite decreased evidently, which suggested the pseudobrookite was reduced and decomposed. Increase of the peak intensities regarding TiO phase at 1 273 K suggested the reduction reaction was enhanced further. These results show that high temperature is beneficial to produce Ti oxides by reduction. It was reported that Ti oxides have the poor wettability with most transition metals.23,24 This might be associated with the increase of contact angles with increasing prereduction temperature for both ilmenites prereduced with carbon and hydrogen, as shown in Figs. 3 and 7.

The reduction degrees of ilmenites prereduced with carbon and hydrogen have been measured at different temperatures in our previous research.4,17,18 Figure 12 shows the relationship between contact angle and reduction degree measured at 1 553 K. It can be seen that the contact angle increases when reduction degree increases. The specimen prereduced with hydrogen always possesses higher contact angle than that prereduced with carbon. This result indicates clearly that better separation between molten pig iron and reduced ilmenite can be achieved by the reduction process with hydrogen. Furthermore, temperatures of reduction with hydrogen at 1 023 to 1 223 K are much lower than those of reduction with carbon at 1 473 to 1 673 K, which is feasible to develop the environmental-friendly processes. The absence of permeability layer at interface between ilmenite prereduced with hydrogen and molten pig iron as mentioned in the context is another evidence to confirm the merit of hydrogen reduction process.

5. Conclusions

The interfacial phenomena between molten pig iron and ilmenite prereduced with carbon from 1 473 to 1 673 K and with hydrogen from 1 073 to 1 223 K were investigated. In both cases, molten pig iron was non-wettable with reduced product and the contact angle increases when the prereduction temperature increases. The permeation of molten pig iron into porous ilmenite substrate was observed at the interface between molten pig iron and specimens prereduced with carbon and enhanced at higher reduction temperature.
With the same reduction degree, the contact angle between molten pig iron and ilmenite pre-reduced with hydrogen is higher than that between molten pig iron and ilmenite pre-reduced with carbon. These results indicate clearly that better separation between molten pig iron and reduced ilmenite can be achieved by hydrogen reduction process, even at lower temperature than that of carbon reduction process.

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