Influence of Pre-oxidation on Carbothermic Reduction Process of Ilmenite Concentrate

Hai-Peng GOU,1,2) Guo-Hua ZHANG1,2)* and Kuo-Chih CHOU1,2)

1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Haidian District, Beijing 100083, China. 2) Collaborative Innovation Center of Steel Technology, University of Science and Technology Beijing, Haidian District, Beijing 100083, China.

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The pre-oxidation of Panzhihua ilmenite concentrate was investigated at 1 073 K and 1 273 K under air atmosphere. The products of the pre-oxidation at 1 073 K were Fe₂O₃, TiO₂ and Fe₂Ti₃O₉, while Fe₂O₃, TiO₂ and Fe₂TiO₅ at 1 273 K. The influences of pre-oxidation on the carbothermic reduction were studied at 1 473 K, 1 573 K, 1 673 K and 1 773 K under argon atmosphere. It was found that the main phases during the reduction process were Ti₃O₅, Fe, Fe₃C, Ti₂O₃ and TiCₓOᵧ. The pre-oxidation was beneficial to the formation of TiCₓOᵧ phase compared to the direct carbothermic reduction without pre-oxidation. And the pre-oxidation at 1 273 K was better for the carbothermic reduction than pre-oxidation at 1 073 K. The rate controlling steps for the carbothermic reduction obeyed the diffusion model. After being reduced for 2 h at 1 773 K, the product was changed to TiC with only little O content.

KEY WORDS: pre-oxidation; carbothermic reduction; Titanium oxy-carbide.

1. Introduction

Panzhihua ilmenite concentrate is a kind of important titanium resource, in which the titanium dioxide content is higher than 40 pct. Nowadays, the ilmenite concentrate is used to produce not only titanium dioxide and titanium metal but also Ti(C,N) powders and hard materials.1,2) No matter for what kind of products, the reduction process of ilmenite concentrate is crucial. Considering that ilmenite has a dense structure that is not benefit to the reduction, the oxidation process is used to change the mineral structure and improve its activity.3,4)

Over the past decades, the oxidation of ilmenite has been investigated by many researchers.5–9) Zhang et al.5) found that pre-oxidation of ilmenite concentrates changed their phase composition and caused a sharp decrease in specific surface area of raw materials and an increase in carburization temperature. Fu et al.6) studied the effects of oxidation conditions on the product phases, such as temperature, particle size and oxygen pressure. The oxidation products under air atmosphere from 773 K to 1 073 K included Fe₂Ti₃O₉, Fe, Fe₃C, Ti₂O₃ and TiCₓOᵧ. The pre-oxidation was beneficial to the formation of TiCₓOᵧ phase compared to the direct carbothermic reduction without pre-oxidation. And the pre-oxidation at 1 273 K was better for the carbothermic reduction than pre-oxidation at 1 073 K. The rate controlling steps for the carbothermic reduction obeyed the diffusion model. After being reduced for 2 h at 1 773 K, the product was changed to TiC with only little O content.

The rate of reduction and the size of the iron particles decreased with increasing degree of weathering of the concentrate at 1 273 K to 1 373 K.

In this paper, the influence of pre-oxidation on the carbothermic reduction process of ilmenite concentrate was examined, which is significant for the production of TiC powders or hard materials.

2. Experimental

2.1. The Pre-oxidation of the Ilmenite Concentrate

Panzhihua ilmenite concentrate was subject to X-ray fluorescence (XRF) to determine the chemical compositions, which is listed in Table 1. The main impurity element in ilmenite concentrate is Mg. The ilmenite concentrate was also examined by the X-ray diffraction (XRD), which is shown in Fig. 1. It shows that the main mineral phase of the ilmenite concentrate is FeTiO₅.

The pre-oxidation of the ilmenite concentrate was investigated by a vertical tube globar furnace under a flowing air atmosphere (0.6 L/min). The schematic diagram of the experimental apparatus is shown in Fig. 2. The temperatures of the pre-oxidation measured by a B-type thermocouple

Table 1. Chemical compositions of ilmenite concentrate (wt.%).

| Compositions | FeO | TiO₂ | SiO₂ | CaO | Al₂O₃ | MgO | SO₃ |
|--------------|-----|------|------|-----|-------|-----|-----|
| Content      | 39.30 | 43.68 | 3.15 | 1.28 | 2.91  | 7.99 | 0.62 |

| Compositions | Na₂O | MnO | Cr₂O₃ | ZnO | P₂O₅ | In₂O₃ | Total |
|--------------|------|-----|-------|-----|------|-------|------|
| Content      | 0.28 | 0.69 | 0.03  | 0.02 | 0.03 | 0.02  | 100  |

* Corresponding author: E-mail: ghzhang_ustb@163.com
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within ± 1 K were chose to be 1073 K and 1273 K, respectively. When the temperature reached the desired value, the alumina crucible with about 2 g sample was put into the hot zone of the globar furnace. The crucible was hung under a balance, which was connected to the computer that recorded the data every 20 seconds. When the readings tended to be stable, the pre-oxidations were kept to maintain 1 h to make the thermodynamic equilibrium achieved. Then the crucibles were taken out from the furnace to be cooled at ambient temperature. The pre-oxidation products at both temperatures were examined by XRD.

2.2. The Carbothermic Reduction of the Pre-oxidation Products

The pre-oxidation products were mixed homogenously with the graphite powder. And the molar ratio of C to Fe in mixtures was set to be 5:1. Then the mixtures of 2 g were made into cylindrical briquettes with the diameter of 18 mm. PVA (2%, wt) was used as a binder for the briquetting process. The briquette was placed in the alumina crucible with a graphite crucible outside. The temperatures for the isothermal carbothermic reduction were 1473 K, 1573 K, 1673 K and 1773 K respectively. When the temperatures of the vertical tube furnace reached the reduction tempera-

3. Results

3.1. The Thermogravimetric (TG) Curve of the Pre-oxidation

Isothermal TG plots of oxidation obtained at different temperatures are shown in Fig. 4. At 1073 K, the weight didn’t change obviously after 22 minutes. While at 1273 K, the weight didn’t change obviously after 12 minutes. It can be seen that the reaction rate of the oxidation increases as rising the temperature. The final mass gain was approximately 103.2%.

3.2. X-ray Diffraction

The XRD patterns of the pre-oxidation products at different temperatures are presented in Fig. 5. The pre-oxidation products at 1073 K were Fe₂O₃, TiO₂ and Fe₂Ti₃O₉, while the products at 1273 K were Fe₂O₃, TiO₂ and Fe₂TiO₅.

The XRD patterns of the pre-oxidation samples reduced at different temperatures for different time are presented in Figs. 6 and 7. In the case of the pre-oxidation at 1073 K, the main phases of the sample reduced at 1473 K were Ti₃O₅, Ti₂O₃, Fe, Fe₃C and TiC₂O₃. Whereas, only a small
amount of TiC$_x$O$_y$ phase appeared after 2 h at 1473 K. The main phases of the sample reduced at 1573 K were Ti$_2$O$_3$, Fe, Fe$_3$C and TiC$_x$O$_y$. Ti$_2$O$_3$ phase disappeared after 2 h at 1573 K. When the reaction temperatures were 1673 K and 1773 K, there were only Fe, Fe$_3$C and TiC$_x$O$_y$ left after 0.5 h.

In the case of the pre-oxidation at 1273 K, the main phases of the sample reduced at 1473 K were Ti$_3$O$_5$, Fe, Fe$_3$C and TiC$_x$O$_y$. Compared to Fig. 6(a), Ti$_2$O$_3$ phase did not appear with the increase of the reaction time. When the reaction temperature was 1573 K, the main phases of the products were Ti$_2$O$_3$, Fe, Fe$_3$C and TiC$_x$O$_y$. Compared to Fig. 6(b), Ti$_2$O$_3$ phase disappeared after 1 h, which happened earlier. When the reaction temperatures were 1673 K and 1773 K, the main phases were the same as the case of the pre-oxidation at 1073 K.

3.3. The Percentage of Total Mass Loss during the Carbothermic Reduction

During the carbothermic reduction, the percentage of total mass loss ($W$) was calculated by Eq. (1), where $w_t$ is the mass of sample after time $t$, and $w_0$ is the initial mass of the sample. The dashed horizontal line (1) in Fig. 8 is the theoretical weight loss when the reduction products are Fe and TiC.

$$W = \frac{w_0 - w_t}{w_0} \times 100\% \quad \text{(1)}$$

As shown in Fig. 8, after the carbothermic reduction at the temperatures of 1473 K, 1573 K and 1673 K, $W$ is higher for the pre-oxidation sample at 1273 K than that at 1073 K. However, when the reaction temperature was 1773 K, $W$ are almost the same for both pre-oxidation samples. It can also be seen that the higher the reaction temperature is, the larger the $W$ will be. When the temperature was 1773 K, $W$ reached the theoretical weight loss after 2 h.

3.4. The Microstructure of the Reduction Product

The SEM morphology images of the products after pre-oxidation at 1073 K and 1273 K are shown in Figs. 9(a) and 9(b), respectively. After the pre-oxidation, there are many bumps on the surface of the mineral particles, which

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Fig. 5. XRD patterns of the oxidation products (a: 1073 K; b: 1273 K).

Fig. 6. XRD patterns of the samples (pre-oxidation at 1073 K) reduced at different temperature for different reaction time (1—Ti$_3$O$_5$, 2—Fe, 3—Fe$_3$C, 4—Ti$_2$O$_3$, 5—TiC$_x$O$_y$).
increase the specific surface area. The increase of the specific surface area is conducive to carbothermic reduction. Figures 9(c) and 9(d) display the SEM morphology images of the products which were reduced at 1773 K for 2 h. Figure 9(c) was dealt with the pre-oxidation at 1073 K, while Fig. 9(d) was dealt with the pre-oxidation at 1273 K. There are a lot of stomata on the reduction products. This is due to the generation of CO gas.

Backscattered electron (BSE) images of the samples reduced after 2 h at 1773 K are shown in Fig. 10. The phase compositions and morphology of the products with the pre-oxidation are very similar to those without the pre-oxidation.\(^{10}\) Energy Dispersive Spectrometer (EDS) analyses performed at different regions are shown in Table 2. Elements mass fraction by EDS analyses on the same regions for samples pre-oxidized at different temperatures.
are similar. For an element with a small atomic mass, such as carbon, the EDS result is not accurate and always has a large error. The carbon concentration in Table 2 could only qualitatively indicate the existence of C, but could not give its exact content. The O content in TiCxOy phase is so little that TiCxOy phase had been gradually reduced to TiC phase.

4. Discussion

Based on Fig. 5, the reduction mechanisms during the pre-oxidation are shown as follows:

\[
\begin{align*}
\text{FeTiO}_3 + \frac{1}{4} \text{O}_2 & \rightarrow \frac{1}{2} \text{Fe}_2\text{O}_3 + \text{TiO}_2 \quad (1073 \text{ K} \ 1273 \text{ K}) \ldots (2) \\
\text{FeTiO}_3 + \frac{1}{4} \text{O}_2 & \rightarrow \frac{1}{6} \text{Fe}_2\text{O}_3 + \frac{1}{3} \text{Fe}_2\text{TiO}_5 \quad (1073 \text{ K}) \ldots (3) \\
\text{FeTiO}_3 + \frac{1}{2} \text{Fe}_2\text{O}_3 + \frac{1}{4} \text{O}_2 & \rightarrow \text{Fe}_2\text{TiO}_5 \quad (1273 \text{ K}) \ldots (4) \\
\text{Fe}_2\text{O}_3 + \text{TiO}_2 & \rightarrow \text{Fe}_2\text{TiO}_5 \quad (1273 \text{ K}) \ldots (5)
\end{align*}
\]

The reacted fraction (\(\zeta\)) during the carbothermic reduction was calculated by the Eq. (6), where \(\Delta m'\) is the weight loss at time \(t\); \(\Delta m'_{\text{max}}\) is the maximum weight loss.

\[
\zeta = \frac{\Delta m'}{\Delta m'_{\text{max}}} \times 100\% \quad \ldots (6)
\]

Chou model\(^{11,12}\) (Eq. (7)) under the rate controlling step of diffusion in the solid product layer was used for dynamic

![Fig. 10. BSE images of the samples reduced at 1 773 K for 2 h (a: the pre-oxidation at 1 073 K; b: the pre-oxidation at 1 273 K).](image)

![Table 2. EDS results of the elements mass fraction on different regions.](image)

| Phase | Figure 10(a) | Figure 10(b) |
|-------|--------------|--------------|
| FeC   | 80.44%Fe 10.74%C 5.59%Si | 81.64%Fe 11.29%C 4.52%Si |
|       | 2.09%Ti 1.15%Mn | 2.55%Ti |
| TiCxOy| 85.95%Ti 12.05%C 1.35%Fe 0.64%V 0.01%O | 86.91%Ti 10.01%C 1.60%O 0.97%Fe 0.51%V |
|       | 29.93%O 22.18%Ti 15.86%C | 31.19%Al 25.03%O 14.46%C |
| Impurities | 14.23%Mg 8.73%Ca 6.34%Si | 11.31%Ti 7.20%Ca 4.84%Fe 1.80%Fe 0.61%Al 0.32%V |
|       | 4.71%Mg 1.27%Si |

![Fig. 11. Comparisons of calculated and measured reacted fractions vs time curves at different temperatures (a: the pre-oxidation at 1 073 K; b: the pre-oxidation at 1 273 K; \(r\) is the correlation coefficient).](image)


The comparisons of calculated and measured reacted fractions vs time curves at different temperatures are shown in Fig. 11. As shown in Fig. 11, the model calculated curves agree well with the experiment measured curves. It can be found that the rate controlling steps for the pre-oxidation products reduced from 1 473 K to 1 773 K are the diffusion. Compared with the carbothermic reduction without pre-oxidation, the rate controlling steps are same. While the activation energy with pre-oxidation is lower than that without pre-oxidation, the activation energy with pre-oxidation is lower than that without pre-oxidation. It also suggests that pre-oxidation is conducive to the carbothermic reduction. From the reacted fraction and the activation energy, it can be seen that pre-oxidation at 1 273 K was better for the carbothermic reduction than pre-oxidation at 1 073 K. Without the pre-oxidation, the lowest temperature for the generation of TiC02 was 1 573 K. But for both cases of pre-oxidations, TiC02 phase appeared after being reduced for 2 h at 1 473 K. Especially, when the pre-oxidation temperature is 1 273 K, TiC02 phase appeared after 1 h at 1 473 K, which is earlier than that with the pre-oxidation at 1 073 K.

5. Conclusions

The isothermal pre-oxidation of Panzhihua ilmenite concentrate and its influence on carbothermic reduction was investigated in this article. Experiments for different pre-oxidation temperatures, different reduction temperatures and different reduction time were carried out to study their influences. The conclusions could be drawn as follows:

1. The main phases of the pre-oxidation at 1 073 K were Fe2O3, TiO2 and Fe2Ti3O8, while Fe2O3, TiO2 and Fe2TiO3 at 1 273 K. The pre-oxidation could increase the specific surface area and reduce the activation energy, which is beneficial to the carbothermic.

2. When the carbothermic reduction temperatures were 1 473 K, 1 573 K and 1 673 K, the reacted fraction is higher for the pre-oxidation sample at 1 273 K than that at 1 073 K. Whereas, when the reaction temperature was 1 773 K, the reacted fractions for both pre-oxidation samples were almost the same. The rate controlling steps for the carbothermic reductions from 1 473 K to 1 773 K are the diffusion.

3. For both pre-oxidations, the temperature for the generation of TiC02 was 1 473 K, which is lower than the carbothermic reduction without pre-oxidation. After being reduced for 2 h at 1 773 K, TiC02 phase could be reduced to TiC phase with very little oxygen.

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