Effects of Preoxidation of Titania–Ferrous Ore on the Ore Structure and Reduction Behavior

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The paper examined an effect of preoxidation of titania-ferrous ore (New Zealand iron sand) on the ore structure and reduction by carbon monoxide. The major phase in iron sand is titanomagnetite, Fe$_3$O$_4$–Fe$_2$TiO$_4$ solid solution, with spinel cubic structure. In the non-isothermal preoxidation titanomagnetite was oxidized to cubic maghemite and then transformed to rhombohedral titanohematite, Fe$_2$O$_3$–FeTiO$_3$ solid solution. Isothermal preoxidation of the iron sand at 1 273 K transformed titanomagnetite to titanohematite and partly to pseudobrookite (Fe$_5$Ti$_3$O$_9$), however, complete oxidation of Fe$^{2+}$ to Fe$^{3+}$ in titanomagnetite was not achieved in the experimental condition.

The reduction of the titania–ferrous ore was investigated in non-isothermal and isothermal experiments using 75vol%CO–25vol%Ar gas mixtures in a laboratory fixed bed reactor. Samples in the course of reduction were characterized using XRD and EPMA. Preoxidation increased the rate of iron sand reduction.

KEY WORDS: preoxidation; titanomagnetite; titanohematite; reduction; carbon monoxide.

1. Introduction

Reduction of New Zealand titania–ferrous ore by carbon monoxide was studied by authors of this paper in Ref. 1). Titania–ferrous ore or iron sand, predominantly consists of titanomagnetite (TTM), which is a magnetite–ulvospinel solid solution, $(\text{Fe}_3\text{O}_4)_{1-x}(\text{Fe}_2\text{TiO}_4)_x$, with $x=0.27\pm0.02$. It was shown that reduction of iron sand was slower than of hematite or magnetite iron ore, what was attributed to the higher thermodynamic stability of TTM.

It is well known that reduction of magnetite ore is slower than of hematite ore, and that the reducibility of magnetite is greatly improved by its preoxidation to hematite before reduction. This is explained by volume increase of about 25% in transformation of hematite, in which oxygen atoms are arranged in the close-packed hexagonal structure, to magnetite, in which oxygen atoms form a face-centred-cubic structure, what opens up the structure and facilitates the reduction.2,3) Preoxidation of ilmenite is a broadly adopted practice in the processing of ilmenite ore for production of titania pigment and metallic titanium. It was established that preoxidation of ilmenite increases the rate of ilmenite reduction.4–7)

Preoxidation of iron sand is also expected to have a positive effect on the iron sand reduction. It was studied by McAdam et al.8) and Morozov et al.9) who confirmed that preoxidation of iron sand increases the reduction rate. However, the mechanism of the effect of preoxidation on iron sand reduction needs further elucidation.

This study employed an original experimental design for examination of gaseous reduction of ore in the solid state under well-controlled conditions (see Ref. 1)). The focus of this paper was on the effect of preoxidation on the iron sand morphology and phase composition in conjunction with iron sand reduction by carbon monoxide with the aim to gain a better understanding of the reduction mechanism of preoxidized titania-ferrous ore.

2. Experimental

The chemical compositions of iron sand and hematite iron ore examined in this paper are presented in Table 1. The particle size of ores was in the range of 125–212 μm. The surface area was 1.2 m$^2$/g for iron sand and 1.6 m$^2$/g for hematite iron ore. The mass of the ore in each experiment was 2 g. The oxygen associated with iron in the form of FeO and Fe$_3$O$_4$ (24.2 wt% Fe$^{2+}$ and 33.0 wt% Fe$^{3+}$) was calculated to be 21.1 wt%. The extent of reduction was calculated as a mass fraction of oxygen in iron oxides removed in the course of reduction.

Preoxidation of the TTM ore was conducted under air in a muffle furnace. The temperature was increased with the rate of 200 K/h in non-isothermal preoxidation experiments. In isothermal preoxidation, the iron sand was exposed to air at 1 273 K.

Reduction of ores using CO–Ar gas mixture was studied in a laboratory fixed bed reactor in a vertical tube electric furnace. Experimental set-up and the schematic of the reactor are presented elsewhere.1) After a sample was put into the reactor, it was purged with argon. Then the reactor was...
moved to the hot zone of the furnace. A sample was heated to a required temperature in argon atmosphere. Then the reducing gas mixture was introduced to the reactor. After certain reaction time, the reactor was pulled off from the hot zone of the furnace and quenched. In non-isothermal experiments, a sample was heated in the reactor from 473 to 1373 K with the rate of 100 K/h, and then kept at 1373 K until the completion of reduction of iron oxides. CO–Ar gas mixture was prepared from pure argon and carbon monoxide using mass flow controllers. Effect of temperature and gas composition on iron oxide reduction was presented in Ref. 1).

In this work, the reducing gas contained 75 vol% carbon monoxide and 25 vol% argon. The gases were purified before mixing by passing through traps filled with Drierite and 4A molecular sieve to remove moisture. The outlet gas was analyzed on-line by the mass spectrometer. The total gas flow rate was maintained at 800 mL/min.

Samples were analyzed with XRD (XRD, SIEMENS D5000) and microprobe spectrometer (EPMA, Cameca SX-50 Probe).

3. Results and Discussion

3.1. Preoxidation of Ironsand

3.1.1. Non-isothermal Oxidation

In the non-isothermal preoxidation experiments, a sample of ironsand was withdrawn from the furnace at a pre-set temperature and quenched in air. The change in the phase composition of ironsand during the non-isothermal oxidation was examined using XRD analysis. The XRD patterns of ironsand heated in air to different temperatures are shown in Fig. 1.

Fig. 1. XRD patterns of ironsand samples preoxidized by non-isothermal heating under air.

| Table 1. Chemical compositions of ironsand and hematite ore. |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Element         | FeO   | Fe^{3+}| Fe^{2+}| TiO₂ | Al₂O₃ | MgO   | SiO₂  | CaO   |
| Ironsand        | 57.2  | 24.2  | 33.0  | 7.43 | 3.59  | 2.94  | 2.17  | 0.67  | 0.51  |
| Hematite ore    | 62.7  | -     | 62.7  | 0.08 | 2.61  | -     | 4.81  | -     | 0.04  |
formed to TTH in a two-step process. In the first step, TTM was oxidized to titanium-containing maghemite ($\gamma$-Fe$_2$O$_3$) without a structural change. XRD peaks of maghemite were found in a sample heated to 873 K. The second step involved transformation of maghemite phase to TTH.

Increase in temperature to 1 273 K accelerated the rate of TTM oxidation. The oxidation rate of TTM to TTH increased dramatically in the temperature range between 1 073 and 1 273 K. Further increase in temperature from 1 273 to 1 373 K changed the XRD pattern of reduced samples quite marginally. At temperatures above 1 273 K, it seems that TTM was transformed to TTH without the maghemite formation, or to maghemite followed by very fast transformation of maghemite to TTH due to the instability of maghemite at high temperatures.

Pure magnetite is oxidized to maghemite and further to hematite at temperatures above 573 K. At temperatures above 773 K, magnetite is oxidized to hematite directly without maghemite formation.$^{10-12}$ However, maghemite formed from TTM in the oxidation of ironsand existed up to 1 073 K. The transformation of magnetite to maghemite involves an outward diffusion of Fe$^{2+}$ with creation of cation vacancies and the addition of oxygen atoms. This process is slower in ironsand due to high amount of Ti$^{4+}$ and other cations (Al$^{3+}$ and Mg$^{2+}$).$^{10,11,13}$

The XRD patterns of samples heated up to 1 273 and 1 373 K showed that titanium was present in TTM and TTH solid solutions. Ulvospinel (Fe$_2$TiO$_4$), ilmenite (FeTiO$_3$) or rutile (TiO$_2$) were not detected. However, a trace of pseudo-brookite (Fe$_2$TiO$_5$) was found in the XRD pattern after heating to 1 373 K as a result of the oxidation of TTH.

In a sample heated to 1 373 K, it was not possible to distinguish the XRD peaks of remaining TTM from peaks of TTH due to the peaks overlapping. The degree of oxidation was estimated by the measurement of the weight change in the preoxidation process. It showed that the transformation of TTM to TTH was not completed in non-isothermal heating to 1 373 K. The weight gained by a sample was approximately 2.0% of the initial weight of the raw ironsand; what means that only 60% of Fe$^{2+}$ was oxidized to Fe$^{3+}$.

3.1.2. Isothermal Oxidation

The ironsand was oxidized at 1 273 K under air in the muffle furnace. A sample was held in the muffle furnace for 2, 24 and 72 h. The change in the phase composition was studied using XRD and EPMA.

The complete transformation of Fe$^{2+}$ to Fe$^{3+}$ was not achieved in any case. The weight gained after 2-h oxidation was 2.2% while the complete oxidation of TTM would result in 3.45% weight gain. The XRD pattern of a sample oxidized for 2 h was composed of TTM and TTH peaks. Oxidation for 24 h resulted in the weight gain of 2.8%, what corresponds to 81.2% of the complete oxidation of TTM. 72 h oxidation increased the degree of oxidation to 84.1%.

The XRD patterns of preoxidized ironsand at different oxidation time are shown in Fig. 2. In the XRD pattern of a sample oxidized for 24 h, a pseudobrookite peak was observed. Its intensity slightly increased with increasing oxidation time.

The atomic distributions of iron and titanium in a particle of raw ironsand and samples oxidized for 2, 24 and 72 h were analyzed by EPMA (Fig. 3). The atomic iron to titanium (Fe/Ti) ratio along analyzed lines in the raw ironsand and samples oxidized for different times (Figs. 3(a) to 3(d)) are compared in Fig. 4.
Fig. 3. The change in the elemental distributions of Fe and Ti with oxidisation time at 1273 K: (a) Raw; (b) after 2 h; (c) after 24 h and (d) after 72 h. (The solid lines correspond to the linescan analyses shown in Fig. 4).

Fig. 4. The Fe/Ti ratios of the raw and preoxidized iron sand samples at 1273 K. (Each line analysis was made from the left end of the solid line of each particle in Fig. 3.)
Formation of a new TTH phase in oxidized samples seen from the mapping images (Fig. 3) and the Fe/Ti ratios (Fig. 4), started with a preferable orientation (lamellar). Its fraction increased with oxidation time (Figs. 3(b)–3(d)). In the beginning of the oxidation process (Fig. 3(b)), the exsolved TTH had higher Ti content than in the TTM matrix, which can be assigned to the higher mobility of Fe$^{3+}$ compared with Ti$^{4+}$. In the process of TTM oxidation, the concentration of Fe$^{3+}$ increased, causing a compressive stress in the TTM lattice and triggering the structural transformation of cubic spinel to rhombohedral TTH. During this transformation, Fe$^{3+}$ migrated out of the freshly formed rhombohedral lattice what accelerated further oxidation of TTM. This process is characterized by fluctuation of the Fe/Ti ratio at early stages of oxidation (Fig. 4(b)). At the late stages of the TTM to TTH transformation, titanium also migrated, resulting in the uniform Fe/Ti ratio in TTH phase. This is seen from the Fe/Ti ratio scans in samples oxidized for 24 h (Fig. 4(c)) and 72 h (Fig. 4(d)).

In samples oxidized for 24 and 72 h, EPMA did not detect the TTM phase. In these samples, EPMA showed the formation of pseudobrookite (PSB) in the core of the TTH phase. The Fe/Ti ratio for this phase in a sample oxidized for 24 h was close to 2 (Fig. 4(c)), which is the stoichiometric Fe/Ti ratio for PSB. The formation of PSB decreased Ti content in TTH. The average Fe/Ti ratio in titanohematite phase was 11.2, which was higher than the average Fe/Ti ratio of 10 for the raw iron sand ore. After 72 h (Figs. 3(d) and 4(d)), titanium was partly segregated, resulting in a further increase of Fe/Ti ratio in TTH phase to 11.6 (in average). The mapping image showed that titanium migrated towards the core of TTH.

3.1.3. An Oxidation Path of TTM

The oxidation of TTM is illustrated by the FeO–Fe$_2$O$_3$–TiO$_2$ ternary diagram in Fig. 5. The oxidation path of TTM follows the horizontal line in Fig. 5, because only Fe$^{2+}$ in TTM is oxidized. Ulvospinel and magnetite form a solid solution, TTM (line [1]); ilmenite and hematite also form a solid solution, TTH (line [2]). There is a miscibility gap between TTM and TTH. The transformations during the oxidation process follow the reactions:

\[
\begin{align*}
Fe_{3-\frac{x}{2}}Ti_{\frac{x}{2}}O_3 + \frac{1}{4}TiO_2 + \frac{3}{2}Fe^{2+} + \frac{1}{2}Ti^{4+} & = \frac{3}{2}Fe^{2+} + \frac{1}{2}Ti^{4+} + \frac{3}{2}O_2 \quad \text{(1)} \\
Fe_{\frac{2}{3}}Ti_{\frac{1}{3}}O_3 + \frac{x}{6}TiO_2 + \frac{1}{x}Fe^{2+} + \frac{2}{3}Fe^{3+}TiO_3 & = \frac{2}{3}Fe^{2+}TiO_3 + \frac{2}{3}Fe^{3+}TiO_3 \quad \text{(2)}
\end{align*}
\]

Reaction (1) proceeds with the exsolution of rhombohedral TTH into the lamellar-shape phase similar to what was observed in naturally-weathered iron sand. Reaction (1) includes oxidation reaction Fe$^{2+}$→Fe$^{3+}$, migration of iron ions (Fe$^{3+}$ and Fe$^{2+}$) and structural transformation of spinel to rhombohedral phase.

Reaction (2) includes migration of titanium as shown in the mapping images of samples taken in the progress of oxidation (Fig. 5). In this study, reactions (1) and (2) did not go to completion, and proceeded only to the extent $\delta$ in accordance with the reaction:

\[
\begin{align*}
Fe_{\frac{2}{3}}Ti_{\frac{1}{3}}O_3 + \frac{x}{6}TiO_2 + \frac{1}{x}Fe^{2+} + \frac{2}{3}Fe^{3+}TiO_3 & = \frac{2}{3}Fe^{3+}TiO_3 + \frac{2}{3}Fe^{3+}TiO_3 \quad \text{(3)}
\end{align*}
\]

Reaction (2) starts at the intersection of the oxidation path with line [2] in Fig. 5 with the $\delta$ value (reaction (3)) of $2/3x$ and goes towards the thermodynamic equilibrium where $\delta=0$, which corresponds the complete oxidation of TTH to hematite and PSB.

The $x$ value found from analysis of TTM in raw iron sand, was approximately 0.27. TTM was about completely transformed to TTH (reaction (1)), however, the degree of trans-
formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB (reaction (2)) was quite low. The oxidation did not go beyond formation of TTH to PSB.

3.2. Effect of Preoxidation on the Reduction of Iron-sand

The effect of preoxidation of iron-sand on the reduction was investigated using iron-sand preoxidized at 1273 K for 72 h in air. The specific surface area of the iron-sand after the preoxidation was 0.05 m²/g. This was significantly lower than the specific surface area of 1.2 m²/g for raw iron-sand, as a result of a volume decrease in the TTM→TTH transformation and sintering.

3.2.1. Non-isothermal Reduction

Effect of preoxidation of iron-sand on non-isothermal reduction was investigated by comparison of rate and extent of reduction of preoxidized and raw iron-sands. Reduction curves obtained in the reduction experiments are shown in Fig. 6.

The reduction of the raw TTM iron-sand, described in Ref. 1), started at 1073 K with the maximum rate at about 1293 K. The reduction of iron oxides was close to completion; this stage has maximum rate at about 823 K, brought the total extent of reduction of iron oxides to 60%. Reduction at temperatures above 873 K can be related to the third reduction stage, at which the reduction of iron oxides was close to completion; this stage has maximum rate at 1023 K.

Figure 7 presents the XRD patterns of samples of the preoxidized iron-sand reduced and quenched at different temperatures. As discussed above, the preoxidized iron-sand was composed of TTH and small amount of PSB. There was no change in the phase composition up to 673 K. In the first reduction stage, TTH was reduced to TTM. This is shown by the XRD pattern of a sample heated up to 773 K: Some amount of TTM was reduced to metallic iron. The metallic iron was transformed further to iron carbide. At T=823 K, the experimental extent of reduction was 45%. In the second stage, TTM was reduced to metallic iron. The main reaction in the first reduction stage is the following:

$$Fe_{2-\gamma}Ti_{\gamma}O_{3+y} + \frac{3}{2}CO = \frac{2}{3}Fe_{\gamma} + Ti_{\gamma}O_{3+y} + \frac{1}{5}CO_2$$ \hspace{5cm} (5)

The y value in the TTH in the preoxidized iron-sand was approximately 0.16.

Calculated extent of reduction by reaction (5) is 11.1%. In the second reduction stage, TTM was reduced to ilmenite and metallic iron. The metallic iron was transformed further to iron carbide. At T=823 K, the experimental extent of reduction was 45%. In the second stage, PSB was also reduced. In the XRD pattern of a sample heated to 873 K, after the completion of the second reduction stage, the peak for PSB phase disappeared. The main reactions in the second reduction stage were as follows:

$$Fe_{3-\gamma}Ti_{\gamma}O_{4+y} + \left(4-\frac{9}{2}y\right)CO = (3-3y)Fe + \frac{3}{2}yFeTiO_3 + \left(4-\frac{9}{2}y\right)CO_2$$ \hspace{5cm} (6)

$$Fe_2TiO_3 + CO = Fe + FeTiO_2 + CO_2$$ \hspace{5cm} (7)

$$3Fe + CO = Fe_3C + CO_2$$ \hspace{5cm} (8)

In the third reduction stage, TTM was reduced to metallic iron and rutile. This reduction could occur through wustite and ulvospinel, although XRD did not detect their formation. It can be suggested that wustite and ulvospinel were reduced very quickly what made them "invisible". The main reactions in the third reduction stage are as follows:

$$Fe_{3-\gamma}Ti_{\gamma}O_{3+y} + \left(1+\frac{3}{2}y\right)CO = 3\left(1-\frac{3}{2}y\right)“FeO”$$ \hspace{5cm} (9)

$$“FeO” + CO = Fe + CO_2$$ \hspace{5cm} (10)

$$Fe_2TiO_3 + CO = Fe + FeTiO_2 + CO_2$$ \hspace{5cm} (11)
Metallic iron was partly transformed to iron carbide by the reaction (8). Reactions (9)–(11) were completed by about 1 073 K, while reaction (12) continued to 1 373 K.

The final sample contained iron, iron carbide, rutile and a small amount of unreduced TTM. Further reduction of rutile phase to lower titanium oxides was not detected.

The overall reaction during the reduction process can be described by the following reactions:

\[ \text{Fe}_2\text{Ti}_y\text{O}_3 + \text{CO} = \text{Fe} + \text{TiO}_2 + \text{CO}_2 \] ..........................................................(13)

\[ 3\text{Fe} + \text{CO} = \text{Fe}_3\text{C} + 2\text{CO}_2 \] ..........................................................(8)

Formation of iron carbide was not observed in the non-isothermal reduction of raw iron sand\(^1\) when metallic iron appeared at relatively high temperatures (the reduction only started at 1 073 K), at which carbon activity in the reducing gas was not high enough to form iron carbide under given experimental conditions (ramping rate 100 K/h).

3.2.2. Isothermal Reduction

Isothermal reduction experiments were conducted for raw and preoxidized iron sand, hematite and magnetite iron ores using 75 vol% CO–Ar gas mixture at 1 373 K.

Reduction curves, presented in Fig. 8, show that preoxidation of iron sand accelerated its reduction. It was reduced faster than magnetite iron ore and raw iron sand, although the initial surface area of the preoxidized iron sand was much lower than that of raw iron sand. It is because the first stage of the reduction of TTH involves the structural transformation from rhombohedral to spinel cubic (TTM),
which results in the volume increase about 25% and open-up the structure, facilitating the subsequent reduction stages. Reduction rate of preoxidized ironsand up to 85% of reduction was close to that of hematite iron ore. However, at the late stage (extent of reduction above 85%), reduction of preoxidized ironsand slowed down in comparison with reduction of hematite iron ore. At this stage, iron was formed by ilmenite reduction, which was apparently slower than the reduction of hematite.

The slow reduction of raw ironsand in comparison with hematite and magnetite iron ores was attributed to two major factors: 1) the dense spinel cubic structure of TTM, which makes the reduction of magnetite slower than of hematite, and 2) the thermodynamic stability of TTM, which makes the reduction of ironsand slower than the reduction of magnetite ore.

On the basis of results obtained in this paper it can be concluded that the major factor was the dense spinel cubic structure of ironsand. The transformation of TTM to TTH made the rate of ironsand reduction very close to the reduction of hematite ore.

4. Conclusion

In the preoxidation of ironsand, TTM is transformed to TTH and further to PSB. In non-isothermal preoxidation, TTM started to oxidize above 873 K. In the temperature interval 873–1073 K, TTM was oxidized to titanium-containing cubic maghemite phase, and then to TTH. At high temperatures above 1 273 K, TTM was oxidized to TTH directly. TTH was oxidized further to PSB, although oxidation of TTH to PSB was not completed.

Examination of the isothermal preoxidation of the ironsand at 1 273 K showed, that PSB was formed in the core of the TTH with decrease in the Fe/Ti ratio of surrounding TTH. The formation of PSB can be described by reaction:

\[
\begin{align*}
\text{Fe}_{2 - \frac{2}{3}} \text{Ti}_{\frac{2}{3}} \text{O}_3 & \rightarrow \frac{1}{6} \left( \frac{2x - 3\delta}{2 - 3\delta} \right) \text{O}_2 = 2 \left( \frac{1 - x}{2 - 3\delta} \right) \text{Fe}_{2 - \delta} \text{Ti}_\delta \text{O}_3 \\
& + \frac{2}{3} \left( \frac{2x - 3\delta}{2 - 3\delta} \right) \text{Fe}_2 \text{TiO}_4 \\
\end{align*}
\]

Preoxidation of the ironsand increases its reducibility, what is attributed to the structural transformation of spinel cubic TTM to rhombohedral TTH in the preoxidation process. In the reduction of preoxidized ironsand, the volume increase during the transformation of TTH to TTM accelerates reduction reactions. In the isothermal reduction by 75vol%CO–Ar gas mixture at 1 373 K, the preoxidized ironsand was reduced as fast as hematite iron ore.

In the non-isothermal reduction of preoxidized ironsand by carbon monoxide, which started at 673 K, iron carbide was formed. It was not observed in the non-isothermal reduction of raw ironsand, which started at 1 073 K or isothermal reduction of both, raw and preoxidized ores at 1 273–1 373 K.

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