Formation of Cementite from Titanomagnetite Ore

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(Received on November 11, 2005; accepted on January 28, 2006)

This paper examines the formation of cementite in reduction of titanomagnetite ore by methane-containing gas. The reduction of titanomagnetite ore (New Zealand ironsand) by hydrogen–methane–argon gas mixtures was investigated from 600 to 1100°C. Iron oxides were reduced by hydrogen to metallic iron, which was carburised by methane to form cementite. The reduction rate increased with increasing hydrogen content in the reducing gas, while the methane content had no effect on the reduction process. Preoxidation of the titanomagnetite accelerated its reduction. Reduced iron in titanomagnetite was converted to cementite more slowly than in hematite.

KEY WORDS: titanomagnetite; cementite; direct reduced iron; reduction; carburisation.

1. Introduction

Titanium-containing magnetite ore (titanomagnetite ore or ironsand) is used as a source of iron in ironmaking. Reduction behaviour of titanomagnetite ore attracts attention from the viewpoint of its commercial processing and is extremely interesting from the viewpoint of the effect of the ore chemistry and morphology on reduction mechanisms and kinetics.

Ironsand is found in many volcanic areas around the world. Its mineralogy has been studied extensively by geologists. It is mainly composed of homogeneous titanomagnetite particles.1–3) Titanomagnetite is a solid solution of magnetite and ulvospinel, with spinel cubic structure. The ulvospinel fraction x in the solid magnetite–ulvospinel solution (Fe3O4)1−x(Fe2TiO4)x in the New Zealand ironsand, which was studied in this work, was 0.27±0.2.4)

The cation (Fe2+, Fe3+ and Ti4+) distribution in a titanomagnetite lattice depends on the composition and temperature.5–9) There are two kinds of phase separation in titanomagnetite: 1) phase separation caused by the miscibility gap between magnetite and ulvospinel9,10) and 2) phase separation caused by partial oxidation of titanomagnetite.1,2,11–13) The latter case is called exsolution, which is due to low solubility of rhombohedral phase in a cubic phase.2)

Chemistry and morphology of titanomagnetite ore have a profound effect on its reduction behaviour. It was well-established that carbothermal reduction of titanomagnetite ore, which is a major industrial technology for the ore processing, is slower than of hematite ore.3,14,15) A similar situation was observed in the gaseous reduction by carbon monoxide3,14,16) and hydrogen.17)

The reduction of titanomagnetite by carbon monoxide can be presented by the following reaction16):

\[ \text{Fe}_{3−x}\text{Ti}_x\text{O}_4 + (4−2x)\text{CO} = (3−x)\text{Fe} + x\text{TiO}_2 + (4−2x)\text{CO}_2 \]

It proceeds with formation of intermediate wüstite and ulvospinel phases. The reduction of titanomagnetite to wüstite was the slowest step, while wüstite transformed to metallic iron quickly.16)

Preoxidation of ironsand accelerated its reduction, which was attributed to the structural transformation of spinel cubic titanomagnetite to rhombohedral titanohematite during the oxidation. In the reduction of preoxidised ironsand, the volume increase during the transformation of titanohematite to titanomagnetite accelerates and facilitates further reduction reactions.

Reduction behaviour of titanomagnetite was also found to be different from that of magnetite iron ore, although both minerals have the same crystal structure. Titanium in titanomagnetite stabilises the spinel structure and changes the thermodynamics of reduction.

The slow reduction of ironsand in comparison with hematite and magnetite iron ores is due to two factors; 1) the spinel cubic structure of titanomagnetite and 2) the stability of titanomagnetite.16,17)

These features in reduction behaviour of titanomagnetite ore stimulate further interest in its study, particularly using the methane-containing gas, which has not been reported in literature. The aim of this study was to obtain data on reduction behaviour of titanomagnetite by methane-containing gas, stability of cementite formed in the reduction of titanomagnetite and elucidation of mechanisms of cementite decomposition. This paper presents results of a study of reduction behaviour and formation of cementite. Cementite decomposition will be discussed in another paper.
2. Experimental

The composition of the titanomagnetite ore (New Zealand ironsand) studied in this paper is given in Table 1. The reduction behaviour of the Mt Whaleback hematite ore was examined for a comparison. Its composition is also given in Table 1. The ore was sized, with only the 150 to 255 μm fraction being used in this study. The titanomagnetite ore was pre-oxidised in a muffle furnace at 1 000°C under air for 4 d.

Reduction and cementation of iron ores by CH₄–H₂–Ar gas mixtures was studied using a lab-scale fixed bed reactor in a vertical tube electric furnace. The experimental set-up has been described elsewhere. The gas flow rate was maintained at 1 L·min⁻¹, which was sufficient to neglect the external mass transfer resistance in the gas phase.

A nominally 1 g sample of iron ore was lowered into the hot zone of the furnace under argon. When the sample reached the experimental temperature a reducing/carburising gas of varying composition was passed through the reactor. A summary of the experimental conditions is presented in Table 2.

The sample was quenched after the experiment under argon.

The specific surface area of samples was measured by a single-point BET method.

The degree of reduction was defined as a fraction of oxygen removed in the reduction of iron oxides on the basis of the on-line mass-spectrometric analysis of off-gas composition.

Cementite formation was analysed using quantitative XRD analysis, which was conducted using a copper Kα source. The scans were done at a rate of 1°/min with a step size of 0.2° 2θ. The morphology of samples was examined by both optical microscopy and SEM. Etching of the optical microscopy samples in a basic sodium picrate solution allowed differentiation between cementite and metallic iron.

3. Results

3.1. Reduction of Titanomagnetite Ore at Different Temperatures and Gas Compositions

The effect of temperature on titanomagnetite reduction was studied in the temperature range 600 to 1 100°C using gas containing 25 vol% H₂, 5 vol% CH₄ and 70 vol% Ar. The change in the degree of reduction with time at different temperatures is shown in Fig. 1.

Increasing the temperature from 600 to 1 000°C increased the rate of reduction, which is expected as the reduction rate constant increases with temperature. Further increasing the temperature from 1 000 to 1 100°C had little effect on the rate and extent of reduction. This is due to sintering and the subsequent reduction in the surface area of the ore at high temperatures, shown in Fig. 2. The amount of carbon deposited within the sample increased as the temperature increased.

The effect of the methane content of the reducing gas on the reduction of titanomagnetite ore was studied by varying the methane content of the gas from 0 to 20 vol%, with a fixed hydrogen content of 50 vol% at 900°C. The change in the degree of reduction with time for the reduction of ti-
tanomagnetite ore with different methane contents is shown in Fig. 3. The methane content of the reducing gas did not have a significant effect on the reduction behaviour. The effect of the hydrogen content of the reducing gas on the reduction of titanomagnetite ore was studied by varying hydrogen content from 0 to 70 vol% with a fixed methane content of 5 vol% at 900°C. The change in the extent of reduction with time for the reaction of titanomagnetite ore with reducing gases of different hydrogen contents is shown in Fig. 4.

It can be seen that when there was no hydrogen in the reducing gas, reduction by methane only was very slow. The rate of reduction increased with increasing hydrogen content to around 30 vol%. Further increase in the hydrogen content had no significant effect on the reduction rate.

### 3.2. Comparison of Reduction Behaviour of Raw Titanomagnetite, Preoxidised Titanomagnetite and Hematite Ores

In the preoxidation of titanomagnetite ore, titanomagnetite was partially oxidised to titanohematite. Change in the ore morphology and its effect on reduction behaviour using CO gas was studied in Ref. 16). It was shown that preoxidation increased the rate of reduction of titanomagnetite, approaching the reduction rate of hematite ore. Cementite formed in the reduction of hematite ore is unstable at temperatures above 900°C. To compare reduction behaviour of raw and preoxidised titanomagnetite ores with hematite ore by methane-containing gas, the reduction temperature was lowered down to 750°C.

Reduction curves for the raw titanomagnetite, preoxidised titanomagnetite and hematite ores by gas containing 35 vol% CH₄, 55 vol% H₂ and 10 vol% Ar are shown in Fig. 5. As in the reduction by carbon monoxide, preoxidation of titanomagnetite to titanohematite sped up the reduction. The reduction curve for pre-oxidised titanomagnetite ore is close to the hematite ore.

The further studies into the carburisation of the titanomagnetite ore were mainly conducted on the pre-oxidised ore.

### 3.3. Cementite Formation in Reduction of Titanomagnetite and Hematite Ores

Cementite formation was studied in the reduction/carburising experiments with hematite iron ore and preoxidised titanomagnetite ore at 750°C and 925°C, using gas containing 35 vol% methane, 55% hydrogen and 10% argon at a total gas flow rate of 1 L/min.

The formation of cementite from pre-oxidised titanomagnetite at 750°C is shown in Fig. 6. The mass fraction of iron-containing phases with time during the formation of cementite from pre-oxidised titanomagnetite ore using a gas mixture containing 35 vol% CH₄, 55 vol% H₂ and 10 vol% Ar for at 750°C.
magnetite was, practically, instant. Conversion reactions of magnetite to wüstite and wüstite to metallic iron occurred in parallel, while cementation reaction started in 5–10 min after appearance of metallic iron.

While the reduction of the two ores occurs at a similar rate, the rate of formation of cementite from the two ores was quite different. The formation of cementite from the pre-oxidised iron-sand was significantly slower than for the hematite ore at 750°C, taking around 30 min for full conversion to cementite, as opposed to around 12 min for hematite (Fig. 7).

At 925°C, cementite started to form much faster, as shown in Fig. 8. At this temperature, conversion of iron to cementite was not complete as a result of cementite decomposition. It should be mentioned that in the reduction/carburisation of hematite ore at 925°C, conversion of iron to cementite had a much lower degree because of rapid cementite decomposition.

Photomicrographs of pre-oxidised titanomagnetite ore after reduction/cementation at 750°C for 30 min are shown in Fig. 9. Although XRD analysis showed that conversion of iron to cementite at this temperature is close to completion in 30 min., a few iron grains (Fig. 9(b)) and segments of iron rim on particle edges are clearly seen in these photomicrographs (Fig. 9(c)). Particles have porous structure formed in reduction of titanomagnetite.

4. Discussion

4.1. Cementite Formation

Cementite formation in the process of reduction of hematite ore by methane–hydrogen gas includes the following stages:

1. Reduction of iron oxides to metallic iron by hydrogen.
2. Adsorption of methane on the surface of reduced iron and its decomposition with the formation of highly-active adsorbed carbon and hydrogen, which is catalysed by metallic iron.
3. Dissolution of adsorbed carbon into the metal, and diffusion of dissolved carbon into metallic iron.
4. Reaction between iron and dissolved carbon to form cementite (the activity of dissolved carbon is higher than unity relative to graphite).

The overall chemical reaction on the surface of the iron is given by:

\[
\text{CH}_4 = \text{C} + 2\text{H}_2
\]

Where C is carbon dissolved within the metallic iron.

For the hematite ore, the rate of iron cementation is controlled by the chemical reaction of methane adsorption and decomposition on the iron surface. This was supported by the fact that surface-active sulphur slowed down the rate of cementation.

It was suggested that the rate of the reaction (1) is proportional to the iron surface area \(A\), the fraction of the iron surface area available for adsorption \(1 - \theta\), and is a function of the partial pressures of methane and hydrogen,
The mechanism of cementite formation from the titanomagnetite ore is similar to that from hematite. Therefore, specific surface area and fraction of the iron surface area available for adsorption are important factors in cementite formation. The two ores have significantly different surface properties in their original states. The specific surface area of the hematite ore was found to be \(3.6 \text{ m}^2 \text{ g}^{-1}\) and \(0.08 \text{ m}^2 \text{ g}^{-1}\) for the pre-oxidised titanomagnetite ore. However, in samples reduced in a 25vol%H\(_2\)-Ar gas mixture, the specific surface area was found to be around \(4.8 \text{ m}^2 \text{ g}^{-1}\) for the hematite ore\(^{22}\) and \(7.1 \text{ m}^2 \text{ g}^{-1}\) for the ironsand.\(^{23}\) Thus, the difference in the surface area of the reduced iron is not likely to have caused the decrease in the rate of cementite formation for the pre-oxidised titanomagnetite ore.

SEM images of samples obtained in reduction/cementation at 750°C of pre-oxidised titanomagnetite for 30 min and hematite ore for 15 min for hematite are shown in Fig. 10. Samples produced from both ores have a porous structure. In the sample obtained from the titanomagnetite ore, whiskers are clearly observed. Particles consist of porous cementite grains and unreduced oxides. These were identified by EDS to contain largely unreduced titanium oxides, CaO, MgO and other impurities. During pre-oxidisation, the uniform titanomagnetite present in the original ore was transformed into titanohematite. This was confirmed by XRD in the present study, as well as by Park.\(^{23}\) In the core of the titanohematite, pseudobrookite was observed, which is enriched with titanium in comparison with the bulk material.\(^{16}\) After reduction, titanium was present mainly in the form of oxides dispersed through the metallic iron.\(^{17}\) Titanium was also detected in the cementite phase.

Oxides in the iron ore affect the formation of cementite from iron ore. Egashira et al.\(^{24}\) studied the effect of adding different gangue materials to iron oxide pellets on the formation of cementite. They found that CaO within the ore suppressed cementite formation. The hematite studied in this work contained 0.016 wt% CaO, while the ironsand apart from titanium oxides contained 0.67 wt% CaO as well as 2.94 wt% MgO. These oxides remain unreduced in the reaction of the titanomagnetite ore with methane–hydrogen gas mixture. Oxygen, which is present in the system, is a surface active element and decreases a fraction of the iron surface area available for adsorption of methane, slowing the formation of cementite.

5. Conclusion

Reduction of titanomagnetite ore and hematite ore by hydrogen–methane–argon gas mixtures was investigated in the range of 600 to 1100°C. Iron oxides were reduced by hydrogen to metallic iron, which was carburised by methane with the formation of cementite. Increasing the temperature from 600 to 1000°C increased the rate of reduction, while further a increase to 1100°C had little effect. Increasing the hydrogen content of the reducing gas up to 30 vol% increased the reduction rate; above this level, the effect of hydrogen on the reduction rate was quite slight. The methane content of the reducing gas had no effect on the rate of reduction, but increased the deposition of free carbon.

The hematite ore was reduced much more quickly than the titanomagnetite ore. However, preoxidation of the ironsand, in which the original titanomagnetite solid solution was transformed to titanohematite, increased the rate of reduction to a level close to that of the hematite ore.

Iron oxide in the titanomagnetite ore was converted to cementite slower than in the hematite ore, despite having similar reduction rates. At 750°C, iron formed in the reduction of hematite ore was transformed to cementite in 12 min, while taking 30 min for the pre-oxidised titanomagnetite. This was due to the chemical differences be-
tween the ores, namely the high concentration of titanium, calcium and magnesium oxides in titanomagnetite ore. The presence of oxygen due to unreduced oxides may decrease the fraction of surface area of iron available for adsorption of methane which slowed the process of conversion of iron to cementite.

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