Phase Development in Carbothermal Reduction of Ilmenite Concentrates and Synthetic Rutile

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The phase development in the course of carbothermal reduction of ilmenite concentrates and synthetic rutile was studied in temperature programmed reduction (350–1 600°C) and isothermal reduction at 1 100°C in hydrogen and 1 300°C in argon and helium. Ilmenites and synthetic rutile were reduced in a tube reactor with continuously flowing gas. The rate and extent of reduction were monitored by online off-gas analysis. Samples reduced to different extent were subjected to XRD and SEM/BSE analyses. Pseudorutile and ilmenite were the main phases in ilmenite concentrates; rutile was the main phase in synthetic rutile. The phase changes in the course of reduction followed the same sequence in both hydrogen and inert gases. Pseudorutile was converted to ilmenite and titania; iron oxides in ilmenite were quickly reduced to metallic iron. Titania was reduced to titanium suboxides and further to titanium oxycarbide. Reduction of ilmenites and synthetic rutile in hydrogen was much faster than in inert atmosphere. The rate of conversion of titanium oxides to oxycarbide was affected by iron content in the ilmenites. The reduction of lower grade ilmenite with high iron content was faster in hydrogen; but slower in an inert gas. The latter was attributed to the higher porosity of highly weathered ilmenite and synthetic rutile.

KEY WORDS: titanium oxycarbide; ilmenite; carbothermal reduction; hydrogen; argon; helium.

1. Introduction

Ilmenite ore, a major raw material for titania pigment and titanium metal production, has a complex mineralogy, which has a significant effect on the ore processing. Chemistry and mineralogy of the ore are important in selecting a suitable separation process that produced a high grade concentrate. Conventional processing of the ilmenite concentrate in the Becher process includes reduction of iron oxides by coal and separation of metallic iron with production of synthetic rutile. Titania in the synthetic rutile is converted to titanium tetrachloride which is processed further to titania pigment or titanium metal.¹⁾

Under strong reducing conditions at 1 200–1 300°C, titanium oxides in the ilmenite concentrate are reduced to titanium oxycarbide.²⁾ Titanium oxycarbide is chlorinated at much lower temperature than titania³⁾; complete reduction of iron and manganese oxides will facilitate their removal, what is important in processing of ilmenites with high Mn content, such as Eucla Basin ilmenite concentrate.⁴⁾

Carbothermal reduction of ilmenites was examined in.^{5–9)} Authors of this paper studied reduction of pure titania (rutile), ilmenites of different grade and synthetic rutile in different gas atmosphere.^{2,10,11)} In their studies, titanium oxides were reduced to titanium oxycarbide, while iron and manganese oxides were reduced to the metallic state. It was shown that carbothermal reduction of ilmenite concentrates strongly depends on temperature, gas composition and con-

centrate grade. Synthesis of titanium oxycarbide was much faster in hydrogen than in argon or helium. The rate of reduction of titanium oxides to oxycarbide was affected by the iron content; it was higher for ilmenite of lower grade with higher iron concentration.

This paper reports phase development in reduction of ilmenites and synthetic rutile in different gas atmospheres.

2. Experimental

The chemical analysis of ilmenite concentrates and synthetic rutile is presented in **Table 1**. XRD analysis showed

Table 1. Chemical composition of ilmenite concentrates (wt%).

Composition	Primary Ilmenite	Secondary Ilmenite	HYTI 70	Synthetic Rutile
TiO ₂	53.90	58.20	71.50	92.50 ^a
Ti ₂ O ₃				12.10 ^b
Total Fe (Fe+Mn)	30.50	25.90	14.50	2.80
FeO	18.00	11.20	1.20	-
Fe ₂ O ₃	23.60	24.50	19.40	-
MnO	1.63	1.15	0.71	0.86
SiO ₂	0.27	0.75	0.78	0.91
ZrO ₂	0.09	0.16	0.16	0.09
P ₂ O ₅	0.01	0.03	0.09	0.02
Al ₂ O ₃	0.40	0.51	1.70	0.97
S	0.004	0.005	0.05	0.63
Nb ₂ O ₅	0.10	0.14	0.32	0.23
Cr ₂ O ₃	0.047	0.05	0.100	0.07
CaO	<0.01	<0.01	0.04	0.02
MgO	0.18	0.22	0.10	0.36
V ₂ O ₅	0.17	0.18	0.29	0.28
Ti/Fe	1.24:1	1.57:1	2.49:1	26.46:1

^a Based on total titanium content. ^b Equivalent content of all titanium suboxides.

that primary ilmenite contains mainly ilmenite FeTiO_3 and pseudorutile $\text{Fe}_2\text{Ti}_3\text{O}_9$ phases, while secondary and HYTI70 ilmenites also contain rutile. Titania (TiO_2) was the major phase in the synthetic rutile. Chemical analysis showed that synthetic rutile contained titanium suboxides equivalent to 12.1 wt% Ti_2O_3 .

As received ilmenite concentrates and synthetic graphite (99.5% purity, $<20\mu\text{m}$ in particle size) were wet mixed and pressed into cylindrical pellets. The ilmenite-graphite mixture contained 10 mol% extra graphite to the stoichiometric amount of carbon necessary to reduce oxides of titanium, iron and manganese present in the ilmenite. The contents of other oxides were low, and they were considered to be unreducible under given experimental conditions. The pellets of about 2 g in weight were 8 mm in diameter and about 12 mm high.

Reduction of ilmenite concentrates and synthetic rutile by graphite in hydrogen, argon and helium gases was studied in a laboratory fixed bed reactor in a vertical tube electric furnace. Experimental set-up and procedure were presented elsewhere.¹²⁾ The stages and phase development during reduction of different grade of ilmenites in various atmospheres were studied by temperature programmed reduction experiments by ramping furnace temperature from 350 to 1 600°C at 3°C/min. The reduction was stopped at different stages and the phase composition of samples analysed by XRD. Further investigation was done by isothermal reduction, at 1 100°C in hydrogen and at 1 300°C in argon. The outlet gas was analysed online by an infrared $\text{CO}/\text{CO}_2/\text{CH}_4$ analyser (Advanced Optima AO2020, ABB, Ladenburgh, Germany). The total gas flow rate was maintained at 1.00 NL/min.

The reduced pellets were analysed by XRD with Philips X'Pert-Pro MPD diffractometer (PANalytical, Lelyweg, Netherlands) with $\text{Cu K}\alpha$ radiation. Back Scattered Electron (BSE) images of samples were taken by Hitachi S3400 (Hitachi, Mito Japan) using 60 kV accelerating voltage and elemental analysis of the samples were conducted with Energy dispersive X-ray spectroscopy (EDS, Noran, Waltham, US).

3. Results

3.1. Temperature Programmed Reduction

Temperature-programmed carbothermal reduction experiments were carried out in hydrogen, argon and helium in the temperature range of 350–1 600°C with a ramping rate of 3°C/min.

Carbothermal reduction reactions in inert atmosphere produced CO, while in the course of reduction in hydrogen, H_2O was also evolved. Rates of evolution of H_2O and CO in reduction experiments in different gas atmospheres for secondary ilmenite, HYTI70 and synthetic rutile are presented in Fig. 1.

The reduction curves for primary,²⁾ secondary (Fig. 1(a)) and HYTI70 (Fig. 1(b)) ilmenites had similar shapes. Reduction in hydrogen started with conversion of pseudorutile to ilmenite and titania, followed by reduction of FeO from ilmenite to metallic iron and partial reduction of titania to titanium suboxides. In the process of reduction in hydrogen, CO started to evolve in the reduction of secondary ilmenite

Fig. 1. H_2O and CO evolution rates in temperature programmed reduction of ilmenite concentrates and synthetic rutile in different gas atmospheres. The furnace temperature was ramped from 350 to 1 600°C at 3°C/min.

at 780°C and in the reduction of HYTI70 at 835°C. In both cases, the main CO peak corresponded to about 1 200°C.

Figure 2 presents XRD patterns of secondary ilmenite in the progress of reduction in hydrogen. The XRD analysis of the sample heated to 510°C when the first water evolution peak terminated detected titania and unreduced ilmenite with negligible amount of metallic iron. At this temperature, pseudorutile was completely reduced to ilmenite and titania by Reaction (1):

At 750°C ilmenite was mostly converted to titania and metallic iron:

When the reduction was stopped at 1 010°C, titanium was mainly in the form of Ti_3O_5 , although Ti_2O_3 was also detected in a small amount. Reduction of titania to Ti_3O_5 (Re-

Fig. 2. XRD patterns of secondary ilmenite in the progress of temperature programmed reduction in hydrogen. Furnace temperature was ramped at 3°C/min.

action (3)) was reflected in a shoulder peak prior to the main CO peak.

With increasing temperature Ti_3O_5 was further reduced to Ti_2O_3 :

Actually, TiO_2 and Ti_3O_5 were reduced by H_2 . Water formed by the reduction was consumed by carbon gasification reaction. As a result, CO was observed as a reduction product.

The amount of Ti_2O_3 achieved the maximum at 1200°C, which corresponded to the maximum CO evolution rate. The sample also contained significant amount of titanium oxycarbide, which was the major phase in the sample quenched at 1300°C. TiO_xC_y is the solid TiO–TiC solution which was formed by the reduction Reactions (5) and (6):

In Reactions (5) and (6), methane was involved as a reaction intermediate.²⁾

The amount of water evolved in temperature programmed reduction of synthetic rutile was negligible, as shown by the reduction curve of synthetic rutile in hydrogen (Fig. 1(c)) in which the water peaks are almost invisible. These peaks are related to reduction of iron oxides, which concentration in the synthetic rutile was very low. In the reduction of synthetic rutile, CO started to evolve at about the same temperature as in reduction of ilmenites of lower grade. However, the CO peak corresponded to a temperature by 80–100°C higher and it was lower and wider compared with other ilmenite concentrates.

The reduction curves in helium and argon for all il-

Fig. 3. XRD patterns of HYTI70 ilmenite in the progress of temperature programmed reduction in argon. Furnace temperature was ramped at 3°C/min.

menites and synthetic rutile included two overlapped CO peaks at higher temperature range than that in hydrogen. Reduction in helium was slightly faster than in argon.

XRD analysis of HYTI70 in the progress of reduction in argon is presented in **Fig. 3**. The relative intensity of the iron peak in the XRD spectra of samples heated to 1310°C and above practically did not change with the sample temperature, meaning that reduction of iron oxides was completed at 1310°C. A sample, heated to 1310°C also contained Ti_2O_3 (the main titanium containing phase), Ti_3O_5 and TiO_xC_y . Further ramping temperature resulted in waning Ti_3O_5 and Ti_2O_3 peaks, with corresponding rising TiO_xC_y peaks. In the quenched sample heated to 1400°C, the main titanium-containing phases were Ti_2O_3 and TiO_xC_y , with a small amount of Ti_3O_5 . The same phases but Ti_3O_5 were identified by XRD in the sample quenched at 1485°C (the main CO evolution peak); TiO_xC_y was the major titanium-containing phase. The sample heated to 1600°C contained TiO_xC_y , metallic iron and unreacted carbon.

Unlike reduction in hydrogen with separated reduction stages, steps of ilmenite reduction in inert gas occurred with significant overlapping. Reduction of iron oxides proceeded simultaneously with reduction of titania to Ti_3O_5 and further to Ti_2O_3 (first CO peak). Titanium oxycarbide started to evolve before completion of Ti_3O_5 converting to Ti_2O_3 (the second CO peak). First peaks of reduction of synthetic rutile with low iron oxide content in inert gases were significantly smaller than those of ilmenite concentrates.

3.2. Phase Development in Isothermal Reduction of Ilmenite Concentrates

The XRD patterns of samples of secondary ilmenite in the progress of reduction in hydrogen at 1100°C are presented in **Fig. 4**. Main phases in the original secondary il-

Fig. 4. XRD patterns of secondary ilmenite in progress of reduction in hydrogen at 1100°C.

Fig. 5. XRD patterns of HYTI70 ilmenite in progress of reduction in hydrogen at 1100°C.

menite were pseudorutile and ilmenite. $\text{Fe}_2\text{Ti}_3\text{O}_9$ was undetectable after 5 min reduction; the sample contained TiO_2 , FeTiO_3 and metallic iron. In 15 min, TiO_2 and FeTiO_3 phases disappeared; the XRD spectrum showed a significant amount of Ti_3O_5 , Ti_2O_3 and metallic iron. It should be noted that it took about 15–20 min for the sample temperature to reach the experimental value since the sample was placed in the maximum heated zone in the reduction furnace, so the reaction within the first 15–20 min occurred at temperatures below 1100°C. Conversion of Ti_3O_5 to Ti_2O_3 was completed after 30 min. TiO_xC_y phase was first observed after 30 min reaction, which content consistently increased with reduction time, with corresponding waning of Ti_2O_3 peaks. After 300 min reduction, the sample consisted of metallic Fe, TiO_xC_y , residual carbon, and a very small amount of uncarburised Ti_2O_3 .

Reduction of secondary ilmenite in hydrogen was similar to that of primary ilmenite.²⁾ Progress of reduction of HYTI70 in hydrogen (Fig. 5) also followed the same sequence, but with a slower development of titanium oxycarbide phase. Traces of TiO_xC_y were observed in 30 min; the amount of this phase slowly increased with increasing reduction time. After 120 min, Ti_2O_3 still was the major titanium containing phase. The amount of Ti_2O_3 decreased to a very low level after 300 min reduction.

The phase development in the course of reduction of ilmenite concentrates in argon and helium was studied at 1300°C. The XRD patterns of secondary ilmenite and HYTI70 reduced in argon are presented in Figs. 6 and 7, respectively. XRD spectra of samples reduced in helium were similar to those obtained in argon.

Carbothermal reduction in inert gases followed the same sequence as in hydrogen, but progressed slower although the temperature was raised to 1300°C. Compared to secondary ilmenite, reduction of HYTI70 was slightly slower. After 5 min reduction, the main phases in both ilmenite

Fig. 6. XRD patterns of secondary ilmenite in progress of reduction in argon at 1300°C.

concentrates were ilmenite and TiO_2 ; $\text{Fe}_2\text{Ti}_3\text{O}_9$ and metallic iron were not observed. Trace of Ti_3O_5 was also detected in the reduced secondary ilmenite. After 15 min reduction, metallic Fe was detected in a significant amount. Extending reduction to 30 min completed reduction of ilmenite. Conversion of Ti_3O_5 to Ti_2O_3 was not completed until 60 min in secondary ilmenite, and lasted longer in HYTI70. Further conversion of Ti_2O_3 to titanium oxycarbide did not complete after 300 min; the reduced samples contained metallic iron, TiO_xC_y , residual Ti_2O_3 and graphite.

Fig. 7. XRD patterns of HYT170 ilmenite in progress of reduction in argon at 1300°C.

3.3. Phase Development in Reduction of Synthetic Rutile

Synthetic rutile contained very little iron (2.8 wt% total Fe) and high titanium content, equivalent to 92.5% of TiO_2 . It also contained partially reduced suboxides, mainly in the form of Ti_3O_5 as shown by XRD analysis.

The XRD spectra of synthetic rutile in progress of reduction in hydrogen at 1100°C and in argon at 1300°C are presented in Figs. 8 and 9, respectively. After reduction for 5 min in hydrogen (Fig. 8), iron oxides were reduced to metallic iron. Reduction of TiO_2 to Ti_3O_5 was completed within the first 15 min. In the sample reduced for 30 min, titanium oxycarbide was observed; its amount slowly increased, although in the sample reduced for 120 min Ti_2O_3 was the main component. After 300 min reduction, the reduced sample contained metallic iron, TiO_xC_y , graphite and significant amount of residual Ti_2O_3 . Compared to ilmenite concentrates, the reduction of synthetic rutile and formation of titanium oxycarbide in hydrogen were slower.

Reduction of synthetic rutile in argon at 1300°C (Fig. 9) was faster than in hydrogen at 1100°C, which was opposite to what was observed in reduction of ilmenite concentrates. After 5 min of reduction, the main identified phases were TiO_2 , Ti_3O_5 and reduced iron. Significant amount of Ti_2O_3 was produced in a sample reduced for 15 min in argon, although it was hardly detectable in reduction in hydrogen at 1100°C. TiO_xC_y was observed in samples reduced in argon after 30 min reduction, while Ti_2O_3 was the main component. The residual Ti_2O_3 content in the sample reduced for 300 min was much lower than in the sample reduced in hydrogen.

4. Discussion

Main phases in ilmenite concentrates were ilmenite and pseudorutile. Reduction of ilmenites started with conver-

Fig. 8. XRD patterns of synthetic rutile in progress of reduction in hydrogen at 1100°C.

Fig. 9. XRD patterns of synthetic rutile in progress of reduction in argon at 1300°C.

sion of pseudorutile to ilmenite and titania, followed by further reduction of ilmenite to metallic iron and titania. Titania was reduced to sub-oxides and further to titanium oxycarbide. The reduction sequence, which follows from the analysis of phase development, can be presented as:

Carbothermal reduction of metal oxides proceeds through the gas phase. Gas atmosphere had a strong effect on the rate and extent of carbothermal reduction of ilmenite concentrate and synthetic rutile. Reduction of ilmenites of all grades in hydrogen was faster than in inert atmosphere under otherwise the same conditions. This was discussed

Fig. 10. Optical images of original ilmenite concentrates and synthetic rutile. (a) Primary ilmenite; (b) secondary ilmenite; (c) HYTI70; (d) synthetic rutile.

in.^{2,11)} In the process of carbothermal reduction in H_2 , hydrogen reduced iron oxides to metallic iron and titania to titanium sub-oxides, up to Ti_2O_3 . Reacting with carbon, hydrogen formed methane, which reduced Ti_2O_3 to titanium oxycarbide.

Figure 10 presents optical images of original ilmenite concentrates and synthetic rutile. The degree of weathering and particle porosity increased with increasing concentrate grade and was the highest for synthetic rutile. Metallic iron was also observed in some synthetic rutile particles.

The morphology of ilmenite concentrates changed in the process of reduction; this change depended on the concentrate grade and the gas atmosphere. BSE images of primary ilmenite concentrate in progress of reduction in hydrogen at 1 100°C and in helium at 1 300°C are shown in **Fig. 11**. Reduction of iron oxides from ilmenite concentrates by hydrogen was very fast; fine iron grains were formed and a porous structure within the titanium oxide matrix was developed. Reduction of ilmenites in inert gases resulted in formation of coarse grains of metallic iron with a denser particle structure in comparison with reduction in hydrogen. Originally most dense structure of primary ilmenite with the highest concentration of iron oxides, after reduction of iron oxides by hydrogen converted to the least dense structure. This positively affected the rate of conversion of titania to oxycarbide. Reduction of synthetic rutile with a small amount of iron oxides was not affected. The higher was a content of iron oxide in the ilmenite concentrate, the higher was the rate of reduction in hydrogen.

Reduction of iron oxides from ilmenites in argon or helium was relatively slow and proceeded at higher temperatures, producing coarse iron grains. In this case, the change in the particle structure was not significant; the original particle porosity was the major factor defining the conversion of ilmenite to iron and titanium oxycarbide. This conversion was the fastest in the case of synthetic rutile which had the highest porosity.

5. Conclusions

Development of different phases was examined in progress of carbothermal reduction of ilmenite concentrates

Fig. 11. SEM/BSE images of primary ilmenite at different stages of reduction in hydrogen at 1 100°C and helium at 1 300°C; (a, e) 30 min, (b, f) 60 min, (c, g) 180 min, (d, h) 300 min.

and synthetic rutile in temperature programmed reduction and isothermal experiments in different gas atmospheres. The main conclusions are summarised as follows.

(1) Carbothermal reduction of ilmenite concentrates proceeded in two main stages. In the first stage, ilmenite concentrates were reduced to metallic iron and titania. Second stage involved the reduction of titania to titanium oxycarbide.

(2) Pseudorutile was first reduced to ilmenite and titania, followed by reduction of ilmenite to metallic iron and titania. Titania was reduced to Ti_3O_5 , and then Ti_2O_3 , which was converted to titanium oxycarbide.

(3) Reduction of ilmenite concentrates in hydrogen significantly changed the ilmenite structure; it produced fine grains of metallic iron and titanium suboxides, which facilitated conversion of titanium oxide to oxycarbide. The higher the iron oxide content, the faster the reduction and carburization rate.

(4) The change of particles morphology in the reduction in inert gases was not significant. The highest reduction/carburization rate in argon and helium was observed for synthetic rutile which had the highest porosity.

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