The Influence of Weathering on the Reduction of Ilmenite with Carbon

SURESH K. GUPTA, V. RAJAKUMAR, and PAUL GRIEVESON

The reduction of synthetic ilmenite and three ilmenite concentrates (Westralian Sands Limited (WSL), Western Mineral Sands (WMS) and Florida) with coal at 1000 °C to 1100 °C was studied using thermogravimetry and X-ray diffraction, optical microscopy, and electron probe microanalysis of the products. The rate of reduction and the size of the iron particles decrease with increasing degree of weathering of the concentrate. Stoichiometric ilmenite reduces faster than pseudorutile ($Fe_2O_3 \cdot 3TiO_2$), which is a product of weathering. The addition of $FeCl_3$, which promoted the nucleation of iron, increased the rate of reduction, and significant coarsening of the iron was obtained at 1000 °C. In general, the products of reaction are iron, rutile, reduced rutiles, unreduced ilmenite or α-oxide, and pseudobrookite solid solution. A small amount of manganese (1.2 to 1.6 pct MnO) present in the concentrates stabilizes a pseudobrookite phase which retains a significant amount of iron. The manganese also forms an α-oxide phase, $(Fe,Mn)TiO_3$, which is mainly a manganese titanate and concentrates toward the center of the reducing particles.

I. INTRODUCTION

THE mineral ilmenite ($FeTiO_3$) is found in nature in an extensive series of compounds, solid solutions, and alteration products. A major proportion of the mined ilmenite is the raw material for the production of rutile, which is used to produce pigment grade TiO_2 and titanium metal. Many methods have been proposed[1,2] for upgrading ilmenite to a rutile substitute by selective removal of iron. These include smelting, direct acid leaching, selective chlorination, and reduction processes. The solid-state reduction of ilmenite, in which ilmenite is reduced to metallic iron and rutile which are subsequently separated by leaching, has received a great deal of attention in the recent past.

The reduction of synthetic as well as naturally occurring ilmenite has been studied extensively.[1-4] The reaction sequence,[5-11] the kinetics of reduction,[12-20] and the role of preoxidation[20-26] have also been studied. In the reduction with carbon, it has been concluded[13,15] that the reaction proceeds through carbon monoxide as a gaseous intermediate at temperatures above 1000 °C. The majority of published work, however, is restricted to temperatures of 1200 °C and above. It has also been shown[19] that it is difficult to nucleate iron in the reduction of synthetic ilmenite with carbon, which can be overcome by the addition of a catalyst such as ferric chloride. The influence of weathering of the ore on the rate of reduction and morphology of the iron, however, has not been examined. The present investigation is concerned with the reduction of three ilmenite concentrates: Westralian Sands Limited (WSL), Western Mineral Sands (WMS), and Florida, which differ significantly in the degree of weathering. Western Mineral Sands concentrate was the least and Florida concentrate was the most weathered, while WSL concentrate exhibited an intermediate degree of weathering. The isothermal reduction of these concentrates with coal at 1000 °C to 1100 °C was investigated. If satisfactory separation of the iron could be obtained following reduction at these temperatures, significant savings in energy and costs would be achieved. Synthetic ilmenite (chemically pure $FeTiO_3$) was also reduced with coal in order to obtain results for comparison with those for the concentrates. The role of ferric chloride additions in the reduction of the concentrates with coal is examined in detail with a view toward establishing the coarsening characteristics of the iron formed. A combination of several techniques including thermogravimetry, optical microscopy, X-ray diffraction (XRD), and electron probe microanalysis (EPMA) was used to obtain a detailed understanding of the mechanism of reduction.

II. EXPERIMENTAL

A. *Materials*

The three concentrates were reduced with Collie coal. The WMS and WSL concentrates and coal were from Australia, while the Florida concentrate was from the United States. The chemical analyses of these materials, given in Table I, were provided by Ti-Oxide International Ltd, United Kingdom. X-ray diffraction results showed that the least weathered WMS concentrate was essentially a single-phase ilmenite. Pseudorutile was the major phase in the highly weathered Florida concentrate, while ilmenite and pseudorutile were present in WSL concentrate, which had been subjected to an intermediate degree of weathering. The unmilled concentrates were sieved, and the size fraction 104 to 152 × 10^{-6} m, which accounted for ~70 pct of the material,

---

SURESH K. GUPTA, formerly with the Imperial College, London, is National Research Fellow, G.K. Williams Laboratory for Extractive Metallurgy Research, Department of Chemical Engineering, Melbourne University, Parkville, Victoria 3052, Australia. V. RAJAKUMAR, formerly with the Imperial College, London, is Principal Research Scientist, CSIRO, Division of Mineral and Process Engineering, Clayton, Victoria 3168, Australia. PAUL GRIEVESON, Professor of Applied Metallurgy, is with the Department of Materials, Imperial College of Science and Technology, London SW7 2BP, United Kingdom.

Manuscript submitted June 9, 1988.

Table I. Chemical Analyses of Ilmenite Ores and Collie Coal in Weight Percent

	Ilmenite Ores		
Oxide	WMS	WSL	Florida
TiO_2	54.2	56.5	64.9
Fe_2O_3	18.0	29.8	27.9
FeO	24.0	10.3	2.2
MgO	0.16	0.21	0.24
MnO	1.6	1.2	1.3
SiO_2	0.4	0.28	0.24
Al_2O_3	0.85	0.53	1.0
P_2O_5	0.02	0.01	0.12
Cr_2O_3	0.03	0.04	0.09
V_2O_5	0.13	0.16	0.12
CaO	0.01	0.03	0.06
Nb_2O_5	—	0.19	0.13
ZrO_2	—	—	0.13

Collie Coal	
Total carbon	59.50
Fixed carbon	48.40
Hydrogen	3.60
Sulfur	0.34
Ash	2.65
Loss at 105 °C	23.30

was used for the experiments. The Collie coal was crushed, and the particles of the same size range were used.

Synthetic ilmenite was prepared from a stoichiometric mixture of high-purity iron, ferric oxide, and rutile powders. Five grams of the mixture were compacted in a closed die of 12.5 mm in diameter at a pressure of 392.4 MPa. The compact was placed in a silica tube which was flushed with high-purity argon ($p_{O_2} \leqq 4$ Pa) and evacuated to a pressure of 5 Pa and sealed. The capsules were heated slowly to 1100 °C, held at this temperature for 25 hours, cooled slowly to 800 °C, and then quenched in water. The XRD pattern confirmed that the synthesized material was pure ilmenite. The ilmenite was melted at 1500 °C in a platinum crucible held in a furnace in high-purity argon gas flowing at 5×10^{-5} m^3/s. X-ray diffraction confirmed that the product was ilmenite with a small amount of pseudobrookite, which could have formed as a result of minor oxidation by the air entrapped in the pores of ilmenite particles. The premelted material was crushed, and particles of 104 to 152 $\times$ 10^{-6} m size were used for the reduction experiments.

In experiments with ferric chloride addition, 5 and 10 pct $FeCl_3$ in the form of $FeCl_3 \cdot 6H_2O$ was thoroughly mixed with the ilmenite-coal mixtures.

B. *Apparatus and Procedure*

A mixture of weighed amounts of ilmenite and coal was pressed in a die, 6.25 mm in diameter, at a pressure of 196.2 MPa. Pellets 0.8 g in weight and 10 mm in height were prepared. The concentrate-coal mixture was adjusted such that the molar ratio of carbon to oxygen (N_C/N_{O_2}) was 2, which corresponds to the maximum carbon requirement for the removal of all the oxygen in the ilmenite sample as carbon monoxide.

The experiments were carried out using a thermogravimetric apparatus,[19] in flowing high-purity argon, dried by passing through a column of magnesium perchlorate. The gas flow rate was 1×10^{-6} m^3/s. The pellet was supported on a platinum pan suspended in the constant temperature zone of the reactor which was purged with argon for 45 minutes before the hot furnace, at about 1150 °C, was raised around it. The weight of the sample and the temperature adjacent to it were continuously recorded. The temperature was maintained constant to within ±5 °C. At the end of the experiment, the furnace was lowered, and the reduced sample was cooled to ambient temperature in flowing argon.

The samples, which were quite porous after reduction, were carefully removed and prepared for XRD, optical microscopy, and EPMA. The XRD patterns were obtained using a Guinier focusing camera with monochromatized cobalt K_α radiation. For optical microscopy, samples mounted in "Metset" mounting plastic were ground on silicon carbide papers to 800 grade and polished successively with 6, 3, and 1 μm "Hyprez" diamond lapping compound. The EPMA was done using a JEOL JXA-3A Electron Probe Microanalyzer. Quantitative distributions of iron, titanium, manganese, and magnesium were obtained at selected points within the grains.

III. RESULTS

The reduction paths are presented in terms of the percent weight loss against time:

$$\text{percent weight loss} = \frac{W_0 - W_t}{W_0} \times 100$$

where W_t = weight of sample at time t; and
W_0 = starting weight of the sample after the removal of moisture and volatile matter from the coal.

For experiments with ferric chloride addition, the starting weight was corrected for the removal of water and chlorine according to the reaction:

$$2(FeCl_3 \cdot 6H_2O) = Fe_2O_3 + 6HCl_{(g)} + 9H_2O_{(g)}$$

In analyzing the results in terms of the percent weight loss, an almost direct correlation between total weight loss and oxygen loss can be assumed since the analysis of the gas produced during the reduction showed it to consist of >99 pct CO. The effects of temperature and the additive on the reduction path, the products, and their structure are discussed below.

A. *Effect of Temperature*

Figures 1 and 2 for WSL and WMS ilmenite, respectively, reacted with coal at 1000 °C, 1050 °C, and 1100 °C show that the initial and overall rates of reduction increase significantly with temperature. The time required to obtain the percent weight loss corresponding to "100 pct iron metallization," when all of the iron oxide component in the starting material is expected to be reduced to metallic iron, is given in Table II for all of the experiments. Although in practice the reduction to iron is generally not complete and some reduction of rutile to reduced rutiles (Ti_nO_{2n-1}, where $n = 4 - 10$) would occur at

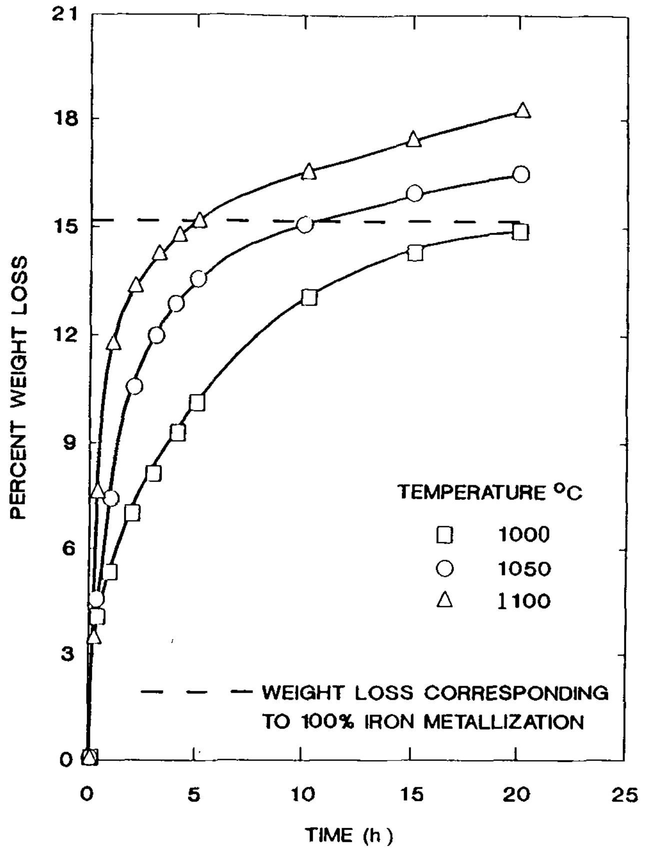

Fig. 1—The effect of temperature on reduction of WSL ilmenite.

this stage, the time at which this weight loss is obtained is very useful for assessing the influence of experimental conditions on the reduction.

With WMS concentrate, the time for 100 pct iron metallization is approximately halved when the temperature is increased from 1000 °C to 1050 °C and is reduced to a third between 1000 °C and 1100 °C. For the more weathered WSL concentrate, 100 pct iron metallization was not obtained even after 20 hours at 1000 °C, and the time required was halved when the temperature was increased from 1050 °C to 1100 °C.

B. *Effect of Ferric Chloride*

A typical set of results is shown for WSL concentrate in Figure 3 for reduction at 1000 °C. It is evident that

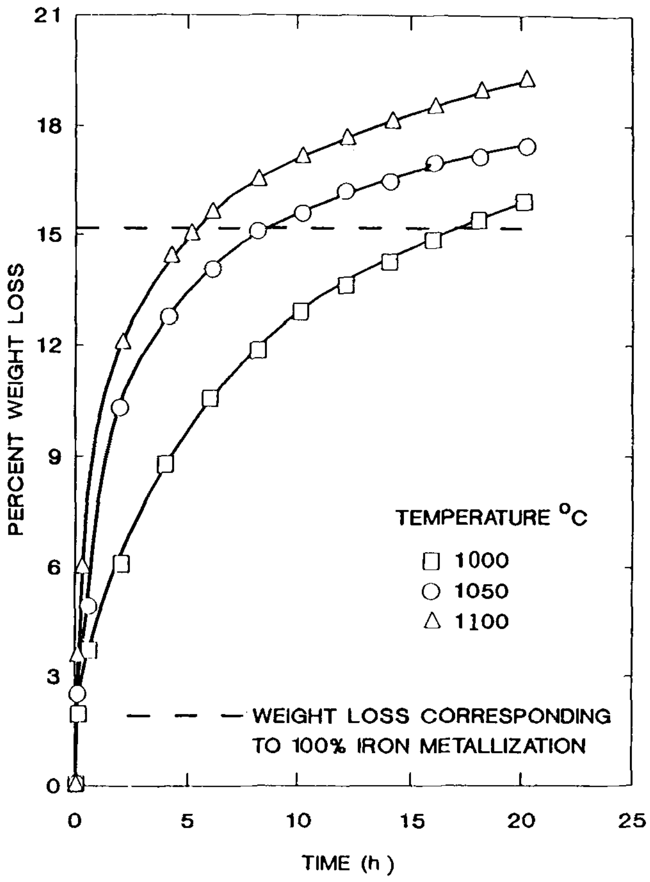

Fig. 2—The effect of temperature on reduction of WMS ilmenite.

the addition increases the reaction rate significantly. At 1000 °C, the effect is much more pronounced than at the higher temperatures. At 1050 °C and 1100 °C, the time for 100 pct iron metallization was halved by the addition of 5 pct ferric chloride. The effect of the amount of additive on the rate is not simple. At 1000 °C, addition of 5 pct was more effective than one of 10 pct. At 1100 °C, the rate was almost identical with 5 and 10 pct additions up to 100 pct iron metallization, beyond which the sample with the 10 pct addition reduced at a faster rate than that with the 5 pct addition.

Figures 3 through 6 show the effect of the additive on the reduction at 1000 °C of WSL, WMS and Florida concentrates, and synthetic ilmenite, respectively. The

Table II. Time Required for Weight Loss Corresponding to 100 Percent Iron Metallization

Temperature (°C)	$FeCl_3$ Addition (Pct)	Time Required for Weight Loss Corresponding to 100 Pct Iron Metallization (Hours)			
		WSL	WMS	Florida	Synthetic
1000	0	not even in 20 h	16	not even in 20 h	13
	5	8.25	8	5.5	8
	10	14	10	5	12
1050	0	10	8	—	—
	5	5	2.25	—	—
	10	6	3.75	—	—
1100	0	5	5	—	—
	5	2.5	1.75	—	—
	10	2.5	2	—	—

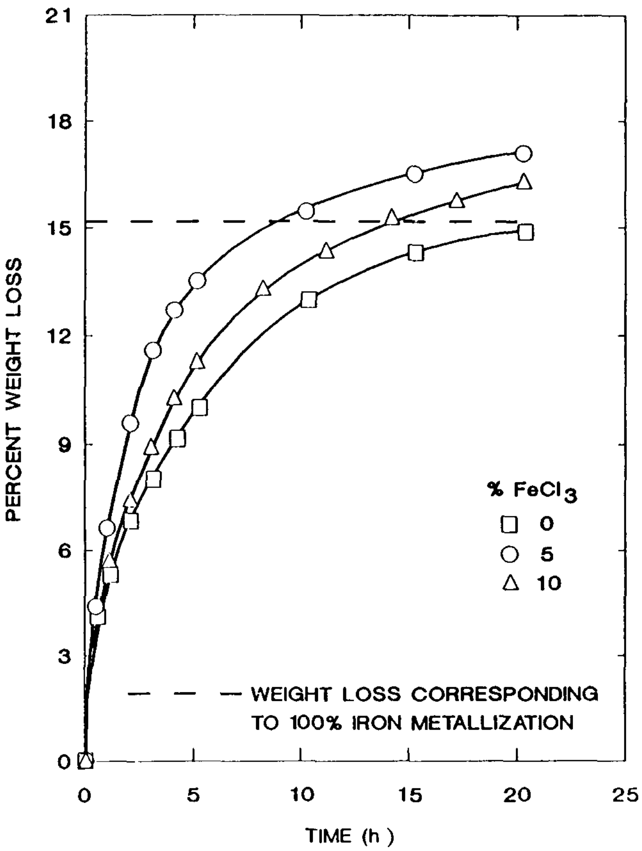

Fig. 3—The effect of ferric chloride addition on reduction of WSL ilmenite at 1000 °C.

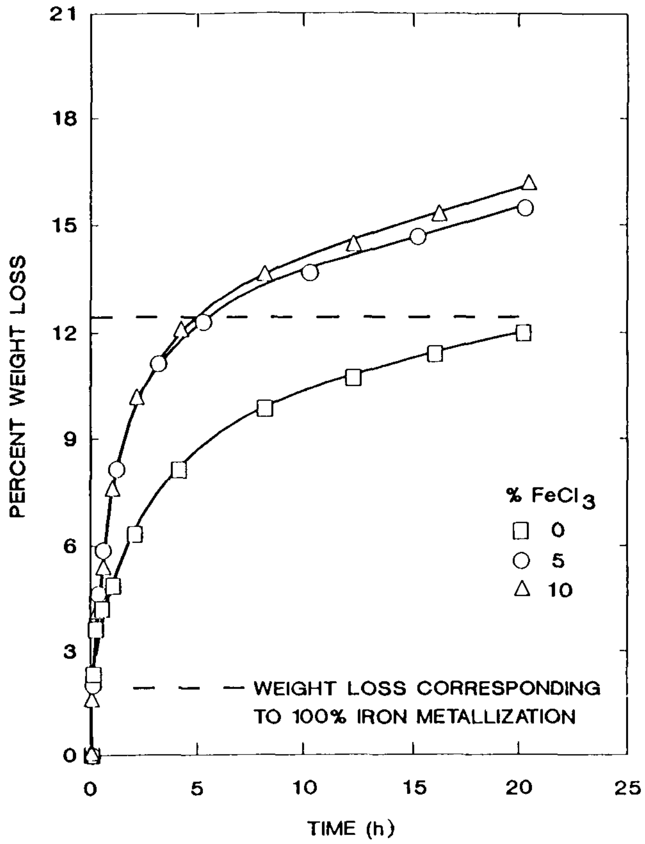

Fig. 5—The effect of ferric chloride addition on reduction of Florida ilmenite at 1000 °C.

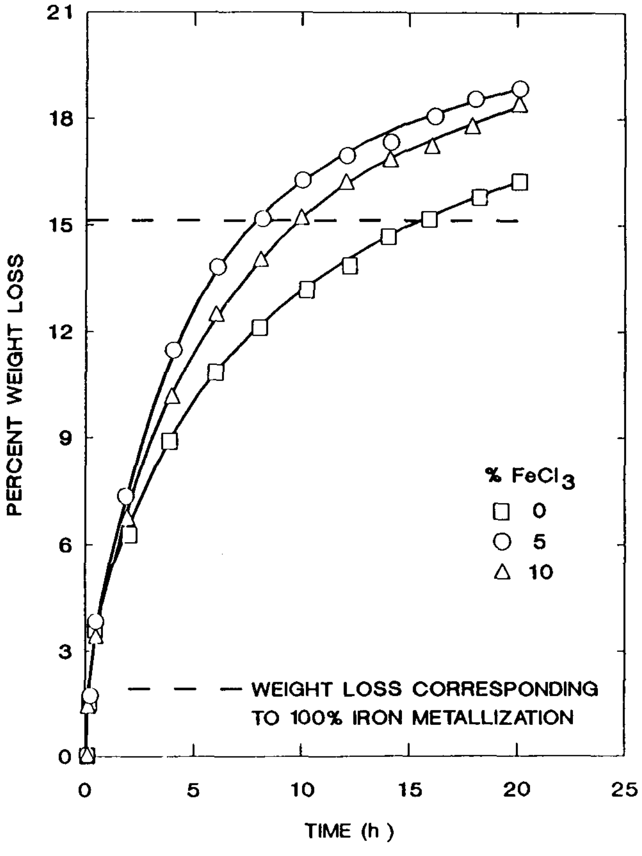

Fig. 4—The effect of ferric chloride addition on reduction of WMS ilmenite at 1000 °C.

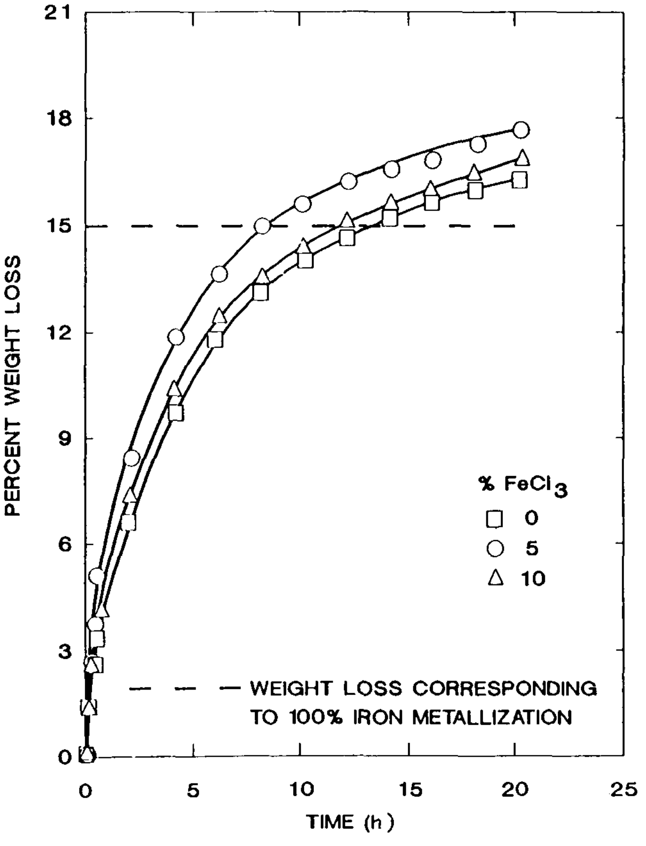

Fig. 6—The effect of ferric chloride addition on reduction of synthetic ilmenite at 1000 °C.

speeding up of the reduction in the presence of the additive is evident for all materials. The addition was more effective in the highly weathered WSL and Florida concentrates; in the absence of the addition, the weight loss corresponding to 100 pct iron metallization was not obtained even after 20 hours in these concentrates. The effect is most pronounced for the Florida concentrate, which is essentially a pseudorutile with minor concentrations of rutile and ilmenite, the time being decreased to about 5 hours in the presence of ferric chloride.

C. *Phases Present after Reduction*

The XRD results of the reduced samples are summarized in Table III. As expected, iron, rutile, and reduced rutiles were observed in all cases, together with other phases depending on the starting material. The addition of ferric chloride does not significantly alter the phases observed in the product. The specific results for each material are summarized below.

1. *Synthetic ilmenite*

The unreduced material consisted of ilmenite and a trace of pseudobrookite solid solution, which was not present in the synthetic ilmenite powder used for its preparation. The pseudobrookite probably resulted from the oxidation of a minor amount of ilmenite with the air trapped in its pores.

After 20 hours of reduction at 1000 °C, the phases present were metallic iron, unreduced ilmenite, rutile, and reduced rutiles. No pseudobrookite was detected.

2. *WMS concentrate*

The samples reduced at 1000 °C contained the same phases as the reduced synthetic ilmenite together with a trace of pseudobrookite solid solution. The addition of ferric chloride decreased the concentration of ilmenite and increased those of iron, rutile, and reduced rutiles. It is interesting to note that the ilmenite phase was present at 1050 °C, an α-oxide (M_2O_3) or $(Fe,Mn,Ti)_2O_3$ was present at 1100 °C, and a trace of the pseudobrookite phase was present even at 1100 °C in spite of the higher weight loss obtained after 20 hours.

3. *WSL concentrate*

At 1000 °C, iron, ilmenite, rutile, reduced rutiles, and a trace of pseudobrookite solid solution were observed, similar to the results obtained for WMS concentrate. However, the ilmenite phase disappeared, and a pseudobrookite solid solution appeared at 1050 °C and 1100 °C. In contrast, the unreduced M_2O_3 or $(Fe,Mn,Ti)_2O_3$ phase persisted in the WMS samples reduced at the same temperatures.

4. *Florida concentrate*

This concentrate is essentially made up of pseudorutile with some rutile and a minor amount of ilmenite. After reduction at 1000 °C, the phases present were iron, ilmenite, rutile, reduced rutile, and a pseudobrookite solid solution. The addition of ferric chloride decreased the concentrations of ilmenite and rutile and increased those of iron and reduced rutile in the reacted samples.

D. *Optical Microscopy and EPMA*

Preliminary examination revealed that the particles in each of the starting concentrates varied widely in their shape, size, pore structure, and mineralogy. A detailed study showed that the concentrates exhibit two major types of particles. In the first type (Type 1), the particles are highly weathered with numerous, well-distributed pores. The largest particles in Figures 7(a) and (b) are typical examples. In the second type (Type 2), the particles, as shown in Figure 7(c), are less weathered and denser.

Electron probe microanalysis slow scans for iron and titanium were made across typical, highly weathered (Type 1) and less weathered (Type 2) particles. The element concentrations plotted in Figure 8 show that, in general, regions enriched in titanium are depleted in iron and *vice versa*. Figure 8(a) shows a uniform distribution of titanium and iron in a typical, highly weathered, Type 1 particle. The average iron and titanium contents are about 26 and 33 pct, respectively, which are close to those in pseudorutile (28 pct Fe, 36 pct Ti). In the less weathered Type 2 particle, the iron concentration varies in the range of 25 to 34 pct, and titanium is in the range of 28 to 33 pct, as shown in Figure 8(b). The maximum concentration of iron occurs in the regions of virtually unaltered ilmenite with a molar ratio of Fe/Ti = 1.03, which is close to that of pure ilmenite. The corresponding molar ratio for the weathered regions of minimum iron content is 0.63, which is almost equal to that for pseudorutile, $Fe_2O_3 \cdot 3TiO_2$ (Fe/Ti = 2/3 = 0.67).

Table III. X-Ray Diffraction Analyses of Reduced Samples

		WSL		WMS		Florida		Synthetic	
Temp. (°C)	$FeCl_3$ (Pct)	Wt Loss (Pct)	Phases Observed	Wt Loss (Pct)	Phases Observed	Wt Loss (Pct)	Phases Observed	Wt Loss (Pct)	Phases Observed
1000	0	14.91	Fe, I, R, RR, PB(*t*)	15.96	Fe, I, R, RR, PB(*t*)	12	Fe, I, R, RR, PB	16.27	Fe, I, R, RR
	5	17.11	Fe, I, R, RR, PB(*t*)	18.60	Fe, I, R, RR, PB(*t*)	15.6	Fe, I, R, RR, PB	17.61	Fe, I, R, RR
	10	16.23	Fe, I, R, RR, PB(*t*)	18.06	Fe, I, R, RR, PB(*t*)	16.0	Fe, I, R, RR, PB	16.85	Fe, I, R, RR
1050	0	16.43	Fe, R, RR, PB	17.52	Fe, I, R, RR, PB	—	—	—	—
	5	17.98	Fe, R, RR, PB	21.61	Fe, I, R, RR, PB	—	—	—	—
	10	17.85	Fe, R, RR, PB	20.71	Fe, I, R, RR, PB	—	—	—	—
1100	0	18.34	Fe, R, RR, PB	19.21	Fe, M(*t*), R, RR, PB	—	—	—	—
	5	19.27	Fe, R, RR, PB	23.28	Fe, M(*t*), R, RR, PB	—	—	—	—
	10	19.94	Fe, R, RR, PB	22.87	Fe, M(*t*), R, RR, PB	—	—	—	—

Fe—metallic iron; I—ilmenite; R—rutile; RR—reduced rutiles; PB—pseudobrookite; M—α-oxide (M_2O_3) or $(Fe,Mn,Ti)_2O_3$; and (*t*)—trace.

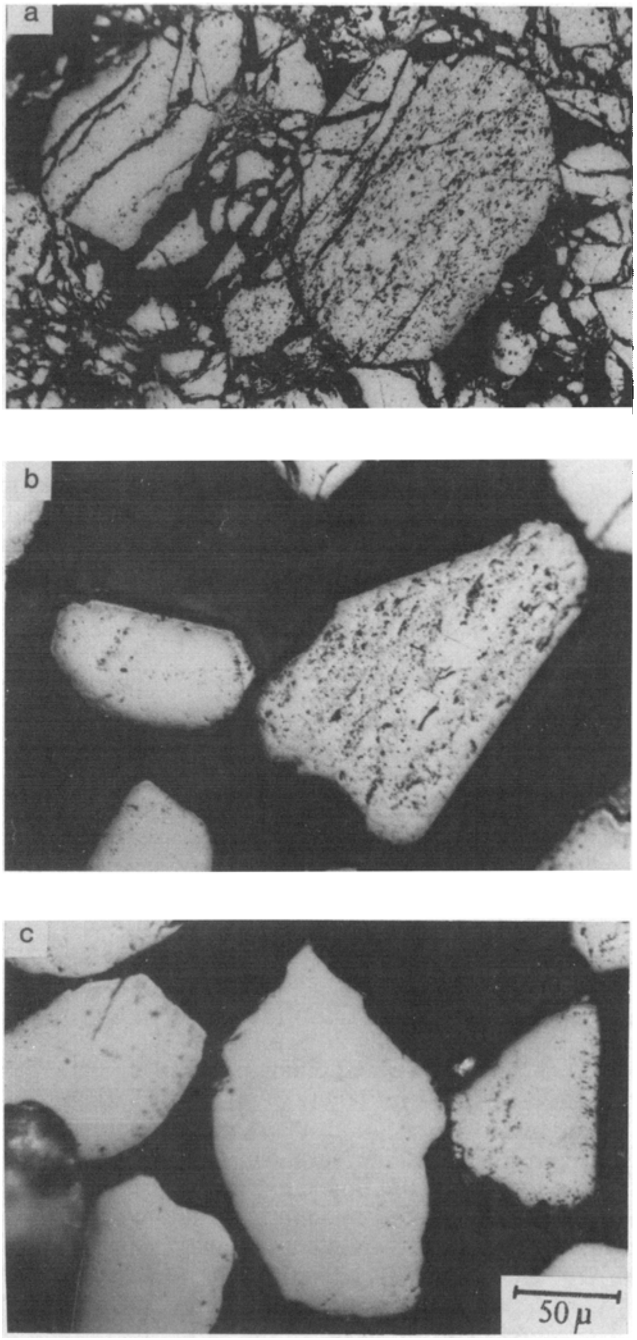

Fig. 7—Photomicrographs of unreduced ilmenite particles: (*a*) WSL, (*b*) and (*c*) WMS. Light gray areas within particles are unweathered, and dark gray areas are weathered ilmenite. Cracks and pores (black) are also visible.

The pattern of growth of the iron and the effect of ferric chloride addition on the microstructure of reduced samples are very different in the two types of particles. The differences are evident at all temperatures; consequently, typical structures are shown in Figure 9 for both types of particles of WSL concentrate reduced at 1000 °C.

In the absence of $FeCl_3$ addition, Type 1 particles (Figure 9(a)) yield finely distributed iron, while in Type 2 particles (Figure 9(b)), coarse growths are obtained. The effect of temperature is also significant. The iron in Type 1 particles coarsened, while that in Type 2 particles became finer at the higher temperature.

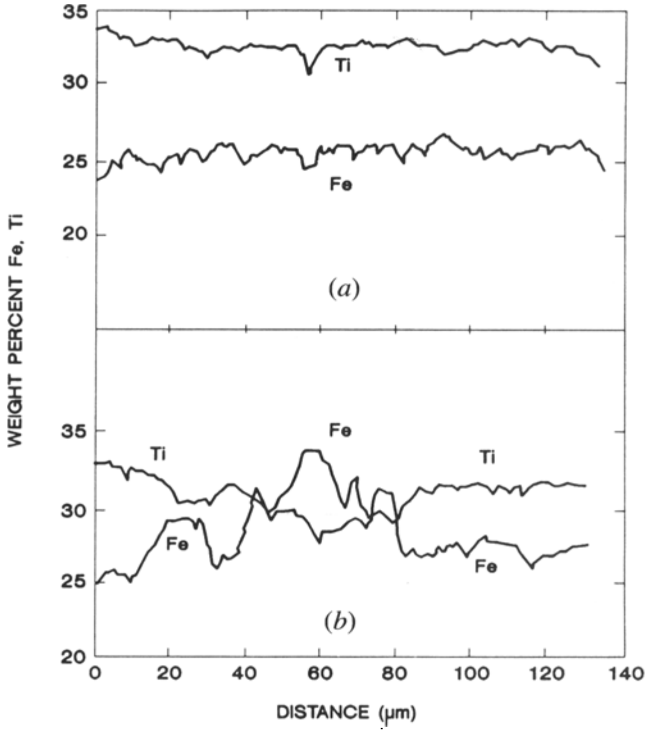

Fig. 8—Concentration profiles of iron and titanium across two unreduced WSL ilmenite particles: (*a*) Type 1 and (*b*) Type 2.

The addition of ferric chloride coarsens the iron in Type 1 particles, but it remains quite uniformly distributed in the matrix. The effect of the additive on Type 2 particles is important, particularly at 1000 °C (Figures 9(b) and (d)), where a significant coarsening of the iron is observed. Therefore, it would be advantageous to carry out the reduction at 1000 °C in the presence of the additive, which speeds the reaction and improves the possibility of physical separation of a significant amount of the coarse iron.

In WMS concentrate, which is less weathered than WSL, a larger proportion of Type 2 particles was observed. In the more weathered Type 1 particles, finer iron growths occur after reduction (Figure 10(a)) at 1000 °C. In the denser Type 2 particles (Figure 10(b)), much coarser iron was obtained. The effect of ferric chloride on the morphology of iron was similar to that for WSL concentrate. Typical microstructures of WMS samples reduced at 1050 °C and 1100 °C with 10 pct $FeCl_3$ addition are shown in Figures 10(c) and (d).

In the highly weathered Florida concentrate, Type 1 particles were predominant. The bulk of the particles is altered beyond the pseudorutile composition and yields fine iron growths during reduction. Some coarsening of the iron is observed in Type 2 particles, but significant amounts of finer growths were present.

A typical microstructure of unreacted synthetic ilmenite particle is shown in Figure 11(a). The particles are dense. As seen in Figures 11(b) and (c), the bulk of the reduced particles shows coarse iron growths more typical of Type 2 particles in the concentrates. Furthermore, the addition of ferric chloride coarsens the iron significantly, and physical separation of the iron could be quite successfully achieved.

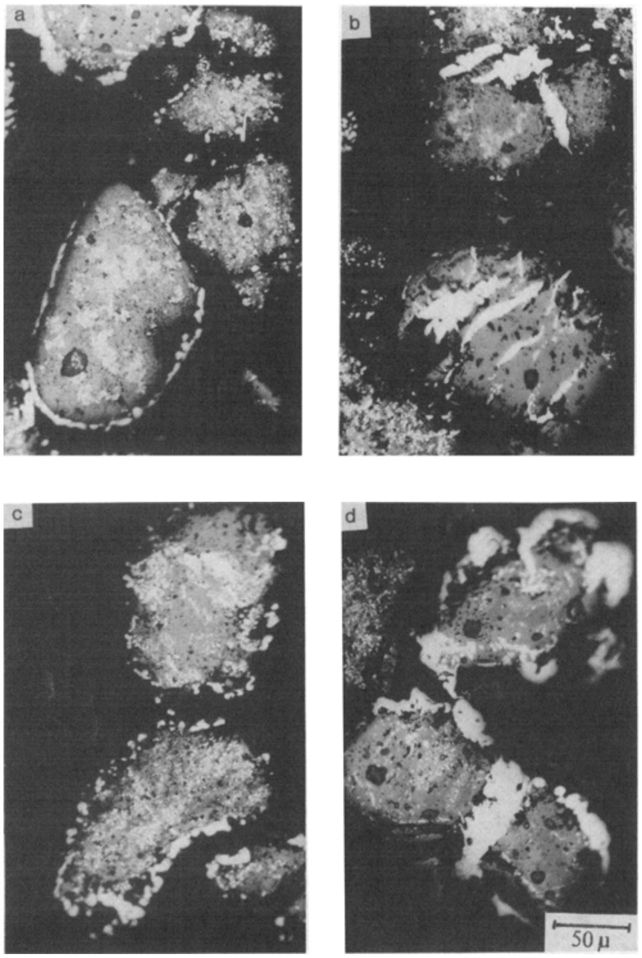

Fig. 9 — Photomicrographs of WSL ilmenite particles reduced at 1000 °C: (*a*) and (*b*) without $FeCl_3$; (*c*) and (*d*) with 10 pct $FeCl_3$ addition, showing iron (white), titanium oxides (gray), and voids (black).

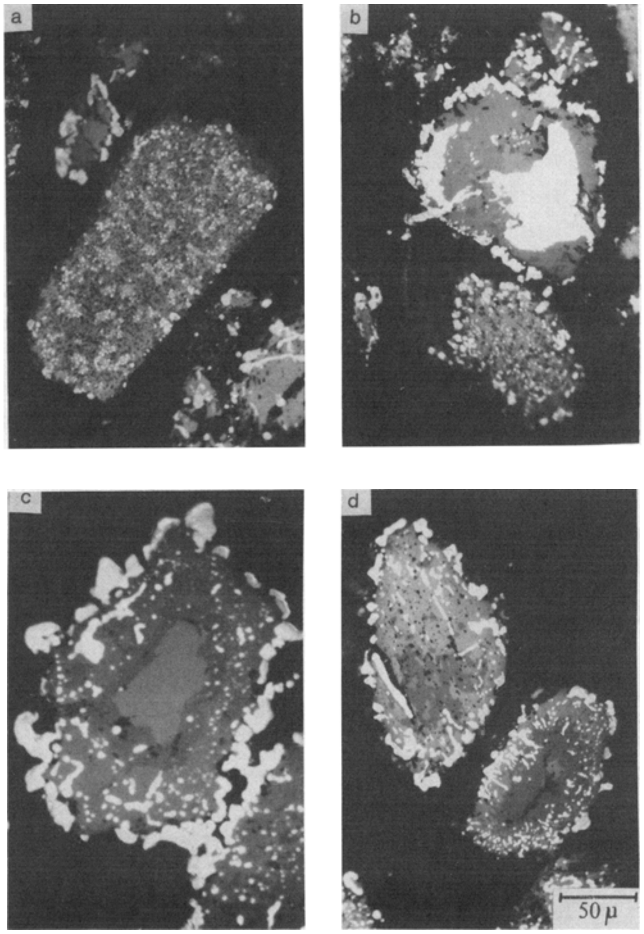

Fig. 10 — Photomicrographs of reduced WMS ilmenite particles: (*a*) and (*b*) at 1000 °C without $FeCl_3$; (*c*) at 1050 °C with 10 pct $FeCl_3$; and (*d*) at 1100 °C with 10 pct $FeCl_3$ addition, showing iron (white), titanium oxides (light gray), α-oxide or M_2O_3 (medium gray), pseudobrookite (dark gray), and voids (black).

E. *Effect of Manganese*

A detailed examination of reduced particles in the three concentrates revealed that manganese, even at small concentration levels, plays an important role in the formation of phases during reduction. Typical photomicrographs of WMS particles reduced at 1000 °C without and with a 10 pct ferric chloride addition are shown in Figures 12 and 13. Apart from iron (white) and titanium oxides (light gray), medium and dark gray phases are also visible. The EPMA displays for Fe, Ti, and Mn for particle I in Figure 12(a) are given in Figures 12(b), (c), and (d), respectively. Quantitative EPMA showed that there is no manganese in the light gray titanium-oxide phase, and its concentration in the medium and dark gray phases is approximately 10.6 and 1.4 pct, while that of iron is 1.25 and 12.5 pct, respectively. The medium gray phase is, therefore, an α-oxide (M_2O_3), and the dark gray phase is pseudobrookite.

The EPMA displays for Fe and Ti for the particle shown in Figure 13(a) are given in Figures 13(b) and (c), respectively; however, no manganese display could be obtained because of its very low concentration. The particle marked with an (×) in Figure 13(a) has large iron growths on the periphery with an inner light gray phase containing uniformly distributed iron particles. The central dark gray region does not contain metallic iron. The analysis at the point marked with the (×) in this region is 1.7 pct Mn, 15 pct Fe, and 31 pct Ti, which corresponds to a pseudobrookite phase. It is concluded that a small amount of manganese stabilizes a pseudobrookite phase at 1000 °C, and a significant amount of iron is retained in this phase.

During reduction at 1000 °C, manganese diffuses ahead of the advancing reaction interface to form a narrow enrichment zone in which the Fe^{2+} in the ilmenite is replaced by Mn^{2+}. This phase, M_2O_3 (α-oxide), is usually surrounded by M_3O_5 (pseudobrookite) in which the manganese, despite its low concentration, ties up a large amount of iron, which remains unreduced.

IV. DISCUSSION

A. *Effect of Weathering*

The results show that the reaction kinetics and the morphology of the iron are strongly dependent on the phases formed during the weathering of the ilmenite concentrates. The weathering process decreases the concentration of ferrous ion and increases the concentrations of

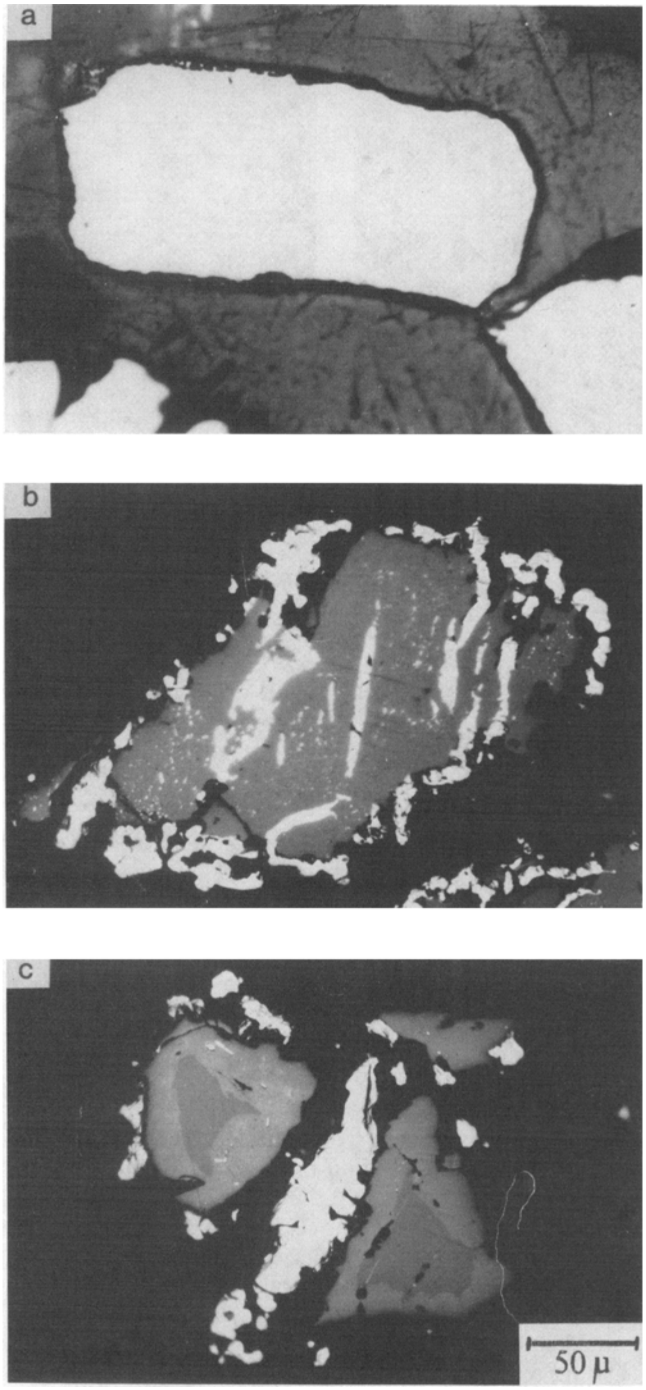

Fig. 11—Photomicrographs of synthetic ilmenite particles: (*a*) unreduced; and (*b*) and (*c*) reduced at 1000 °C without and with a 10 pct $FeCl_3$ addition, respectively. The phases present are iron (white) and titanium oxides (gray). The unreduced ilmenite is also visible as dark gray in (c).

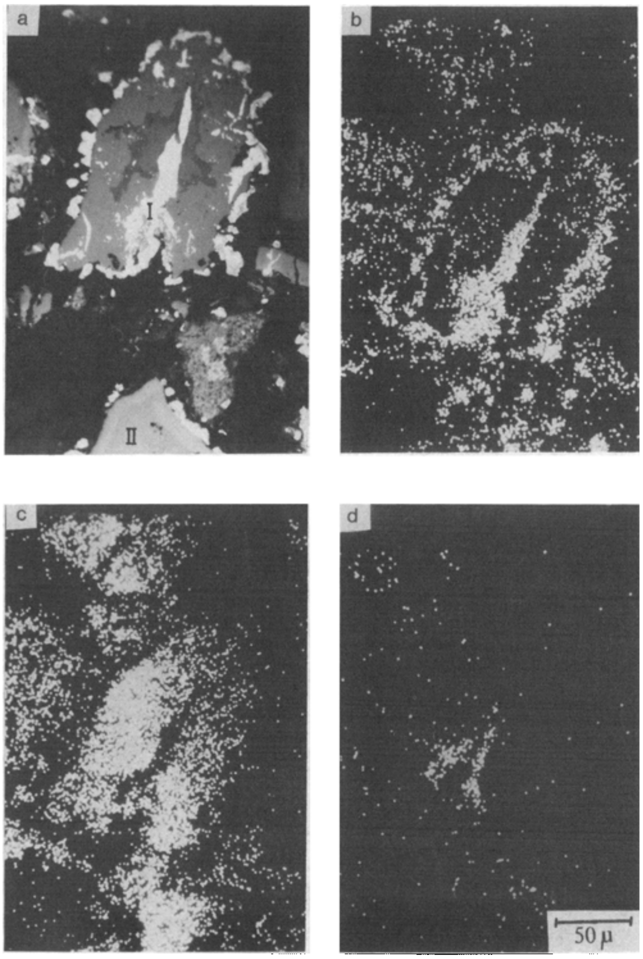

Fig. 12—(*a*) Photomicrograph of WMS ilmenite particles reduced at 1000 °C. Iron (white), titanium oxides (light gray), α-oxide or M_2O_3 (medium gray), pseudobrookite (dark gray), and voids (black). EPMA displays of (*b*) iron, (*c*) titanium, and (*d*) manganese in particle I in (a).

ferric ion and titanium, resulting in the formation of pseudorutile[27] and iron, which is progressively removed by leaching. Western Mineral Sands concentrate is the least altered and consists principally of an ilmenite phase; WSL concentrate has undergone significant alteration and consists of ilmenite and pseudorutile; and Florida concentrate is highly altered and consists mainly of pseudorutile. In view of the wide variation between the starting materials, it is difficult to compare the reduction paths, particularly in the initial stages of reduction, based on the results presented in Figures 1 through 6. In order to obtain a more relevant comparison, the results were recalculated in terms of the fraction reacted, F, where:

$$F = \frac{\text{percent weight loss at time } t}{\begin{array}{c}\text{percent weight loss corresponding} \\ \text{to 100 pct iron metallization}\end{array}}$$

Although, as discussed above, all of the iron oxide in the concentrate is not reduced to metallic iron at the weight loss corresponding to 100 pct iron metallization, a useful picture emerges when the results are normalized in this manner.

The reduction paths at 1000 °C are presented in terms of the fraction reacted against time for the three concentrates and synthetic ilmenite in Figure 14. A careful examination of these curves shows that Florida concentrate was reduced at the highest rate during the initial stage, but the rate was the lowest at the later stage. Furthermore, the rate of the initial stage decreased in the sequence Florida–WSL–WMS–synthetic ilmenite, while this trend was reversed in the later stages of reduction. The overall rate was highest for synthetic ilmenite

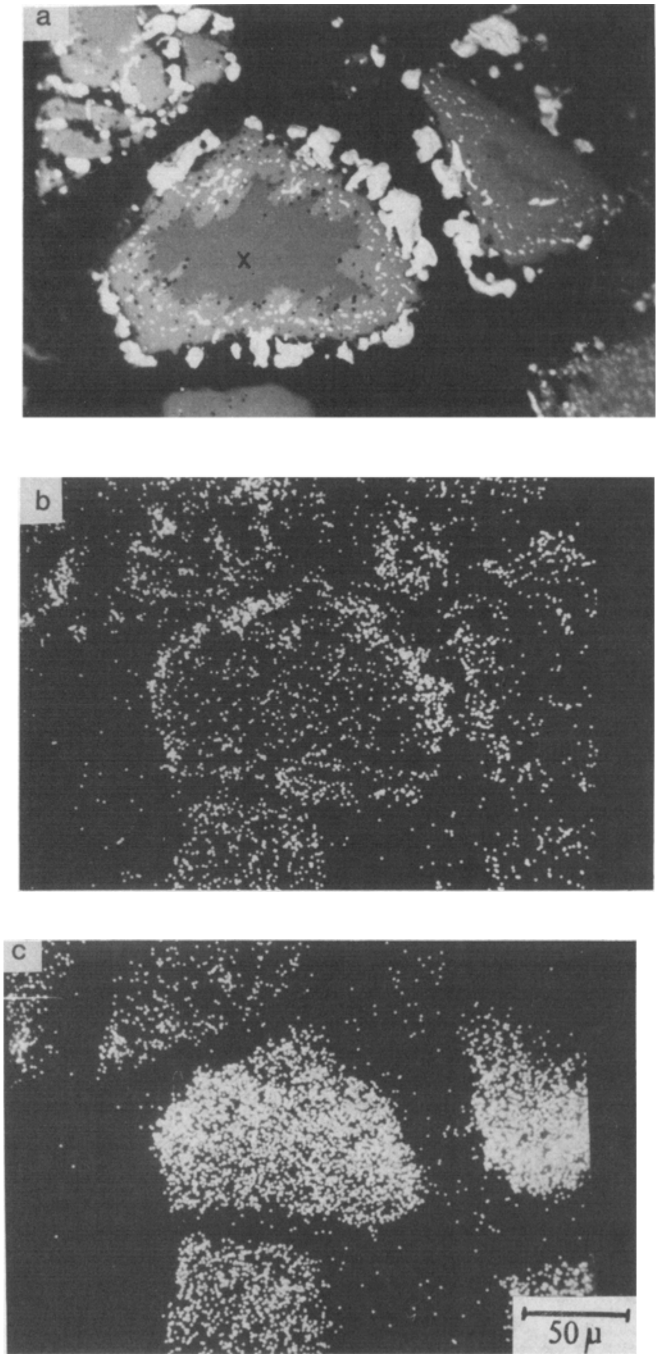

Fig. 13—(*a*) Photomicrograph of WMS ilmenite particles reduced at 1000 °C with a 10 pct $FeCl_3$ addition shows iron (white), titanium oxides (light gray), pseudobrookite (dark gray), and voids (black). EPMA displays of (*b*) iron and (*c*) titanium.

followed by WMS, WSL, and Florida concentrates. It is concluded that (a) the initial rate of reduction increases with the amount of ferric iron in the concentrate; (b) the rate at the later stage decreases as the pseudorutile content increases; and (c) the highest overall rate is obtained for concentrates with compositions approaching that of stoichiometric ilmenite.

B. *Role of Ferric Chloride in the Reduction*

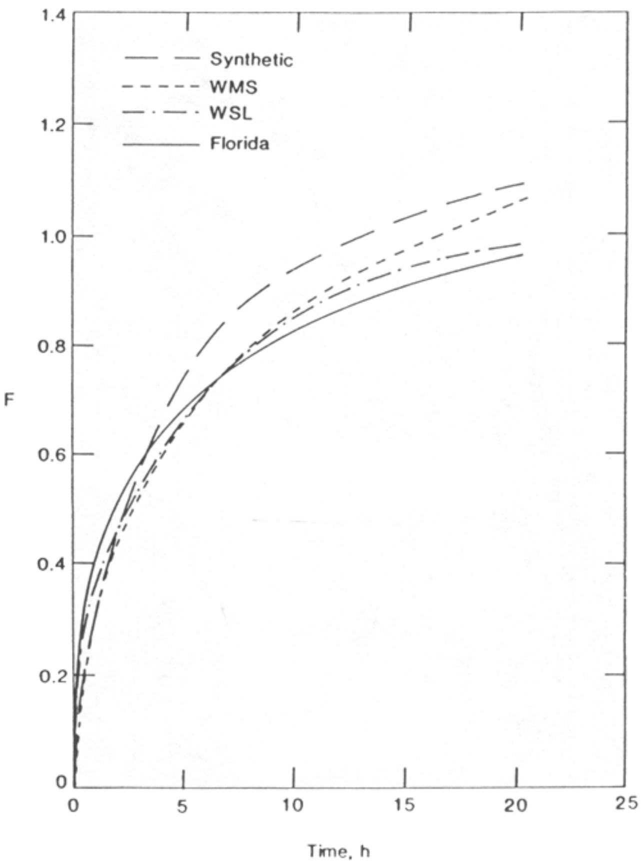

Fig. 14—Fraction reacted (*F*) *vs* time at 1000 °C for synthetic, WMS, WSL, and Florida ilmenites.

The addition of $FeCl_3$ significantly increases the rate of reaction of concentrates as well as synthetic ilmenite with coal. The effect of the quantity of addition is complex, but, in general, the difference in the rate with 5 and 10 pct additions decreases as the temperature increases.

It is clear that despite the use of a reactive coal, there is some difficulty in nucleating the reduced phases, iron and rutile, according to the following reaction:

$$FeTiO_3 + C = Fe + TiO_2 + CO$$

In previous work,[19] it was shown that the reaction between synthetic ilmenite and graphite could not be initiated at 1000 °C in the absence of a catalyst. The addition of ferric chloride enhances the reduction significantly by providing iron nuclei and speeding up the regeneration of carbon monoxide by the reaction:

$$CO_2 + C = 2CO$$

Although the reactivity of natural ilmenites (WSL and Florida) and coal mixtures is much higher than that of the synthetic material, the results clearly demonstrate that the provision of iron through an additive significantly enhances the initial and overall rates of reaction.

Ferric chloride is more effective in the presence of ferric than ferrous iron in the ilmenite. The effect of the addition on the reduction paths of Florida concentrate and synthetic ilmenite is compared in Figure 15. The initial and overall rates of reduction of Florida concentrates are higher than those of synthetic ilmenite. However, for reasons which are unclear, the results for WSL and WMS

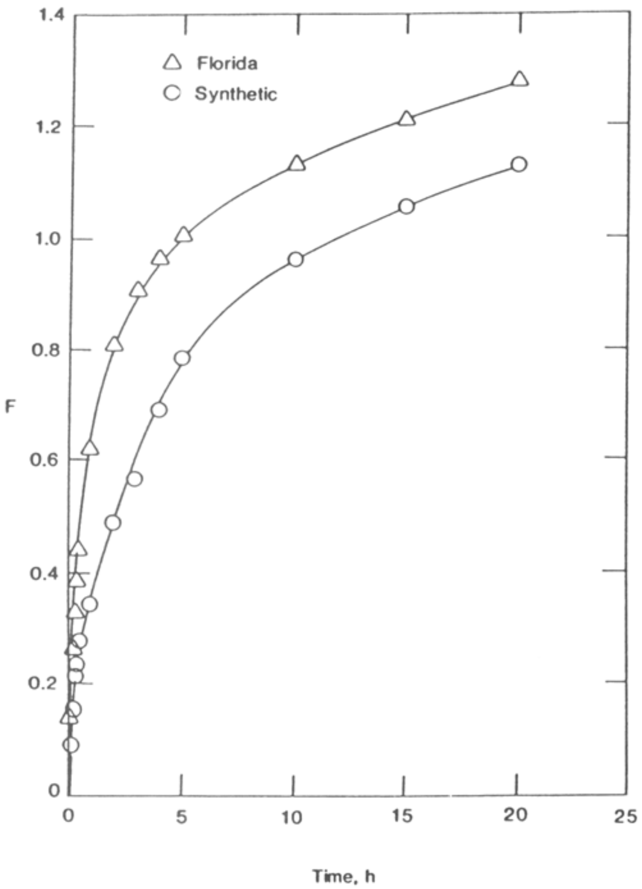

Fig. 15—The comparison of reduction data, fraction reacted (F) *vs* time, of Florida and synthetic ilmenites at 1000 °C with a 10 pct $FeCl_3$ addition.

concentrates did not fit the pattern. The differences in the levels of impurities and the physical properties of the particles may have a bearing in this regard.

C. *Products of Reduction*

The products of reduction of synthetic ilmenite and concentrates in the range of 1000 °C to 1100 °C lie in the Fe-FeO-Ti_3O_5-TiO_2 region of the Fe-Ti-O phase diagram if minor impurities are neglected. Thermodynamic data at 1050 °C and 1100 °C are very limited, but according to the phase diagram at 1000 °C,[28] the first phases which form on reduction of stoichiometric ilmenite are iron and rutile. On further reduction, the ilmenite phase disappears, and iron and reduced rutile form. The composition of the reduced rutiles depends upon the oxygen potential of the system. In the present investigation, when stoichiometric ilmenite was reduced with coal, the phases observed were iron, rutile, and reduced rutiles. Some ilmenite was also present even after 20 hours of reduction and 16.3 to 17.6 pct weight loss, while the weight loss corresponding to 100 pct iron metallization is 14.92 pct. The evidence, therefore, points to a sluggish reaction at these temperatures. The same phases were observed after the reduction of WMS, WSL, and Florida concentrates, but a small quantity of pseudobrookite solid solution was also present. Although pure ferrous pseudobrookite, $FeTi_2O_5$, is not stable below 1140 °C,[29] the pseudobrookite structure based on the solid solution $FeTi_2O_5$-$MnTi_2O_5$-Ti_3O_5 can be stabilized by manganese at temperatures considerably lower than 1140 °C.[11,19,30] When synthetic ilmenite containing a trace of pseudobrookite was reduced, the latter phase disappeared, and iron, rutile, reduced rutiles, and a small quantity of ilmenite were obtained. The pseudobrookite was not stabilized in the absence of manganese or magnesium.

D. *Morphology of Iron*

The morphology of iron produced depends on many factors, the most important being the degree of weathering of the concentrate. The formation of pseudorutile from ilmenite during weathering causes a volume reduction of about 6 pct,[31] which would produce elastic stress in the oxygen lattice leading to considerable microcracking and porosity.

The most probable sites for the nucleation of iron are the interface between the matrix and the inclusions, lattice defects, and surface irregularities. The natural alteration of ilmenite produces numerous such sites; therefore, a large number of iron nuclei are formed in the weathered ilmenite particles, and they all grow simultaneously. The opportunity for coalescence is low because of the presence of titanium oxides and pores. This results in a large number of fine iron particles within the reduced ilmenite particles. The proportion of fine iron in the reduced sample increases with the degree of

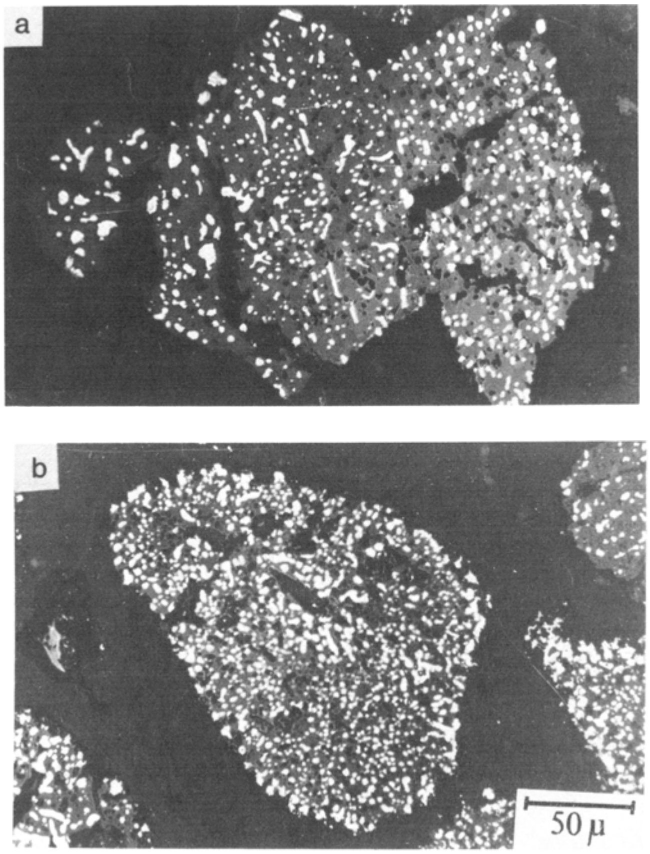

Fig. 16—Photomicrographs of ilmenite particles reduced at 1240 °C: (*a*) WMS and (*b*) WSL. Iron (white), titanium oxides (light gray), and pseudobrookite (dark gray).

weathering of the starting material. Florida concentrate yielded the largest proportion of fine iron growths.

On the other hand, with dense ilmenite particles, fewer nuclei of iron would form mainly on the surface, and their growth would result in large iron particles, as observed, for example, with the synthetic ilmenite (Figures 11(b) and (c)). The WMS and WSL concentrates exhibit behavior intermediate between these two extremes.

The second important factor which influences the morphology of iron is the temperature of reduction. At higher temperatures, a larger number of iron nuclei form and grow simultaneously to accommodate the higher rate of reduction. In order to check the hypothesis that high rates of reduction do not favor the coarsening of iron, WSL and WMS concentrates were reduced with coal at 1240 °C. It is evident from Figure 16 that the iron is much finer and uniformly distributed in the particles under these conditions.

The addition of ferric chloride enhances the rate of reduction, even when the conditions favor the formation of fine iron particles, but significant coarsening is not obtained. However, at a "low" temperature such as 1000 °C, the addition would be doubly advantageous, because it increases the rate of reduction while simultaneously aiding the production of coarse iron, which is more suitable for subsequent physical separation from the titanium oxides.

V. CONCLUSIONS

1. The degree of weathering of ilmenite has a great effect on the reduction kinetics and the morphology of the iron produced. The rate decreases, and finer iron particles are produced with an increased degree of weathering.
2. The rate of reduction increases significantly with temperatures in the range of 1000 °C to 1100 °C.
3. The addition of ferric chloride increases the rate of reduction by providing iron nuclei and by speeding up the regeneration of carbon monoxide.
4. The intrinsic reducibility of the pseudorutile phase is low. Stoichiometric ilmenite ($FeTiO_3$) reduces faster than pseudorutile ($Fe_2O_3 \cdot 3TiO_2$), which is a product of weathering, despite the numerous pores and cracks present in pseudorutile particles.
5. If the composition of the reacting particles is close to stoichiometric ilmenite and the temperature is low, coarse iron particles are produced. The addition of ferric chloride helps in the formation of coarse iron particles, which is advantageous from the physical separation point of view.
6. In general, the products of reaction are metallic iron, rutile, reduced rutiles, unreduced ilmenite or α-oxide, and pseudobrookite solid solution. Although ferrous pseudobrookite is not stable below 1140 °C, the presence of a small amount of manganese (1.2 to 1.6 pct MnO) stabilized this structure in all three concentrates reduced at 1000 °C to 1100 °C. The manganese also forms an α-oxide $(Mn,Fe,Ti)_2O_3$ which is mainly a manganese titanate. The manganese and, consequently, this phase concentrate toward the center of the particles. A significant amount of iron remains in the pseudobrookite phase, which has a low intrinsic reducibility.

ACKNOWLEDGMENT

The authors express their appreciation to Ti-Oxide International Ltd., United Kingdom, for providing financial support and the materials for this work.

REFERENCES

1. J.J. Henn and J.A. Barclay: *U.S. Bur. Mines Inf. Circ.*, no. 8450, 1970.
2. F.R. Hartley: 8th Commonwealth Min. Metall. Congr. Australia and New Zealand, 1965; *Australas. Inst. Min. Metall.*, 1967, vol. 6, pp. 1373-86.
3. W.B. Pings: *Colo. Sch. Mines Ind. Bull.*, 1972, vol. 15 (4), p. 13; (5), p. 17.
4. J.A. Milner: *U.S. Bur. Mines Inf. Circ.*, no. 7791, 1957.
5. R.H. Walsh, H.W. Hockin, D.R. Brandt, P.L. Dietz, and R.R. Girardot: *Trans. AIME*, 1960, vol. 218, pp. 994-1003.
6. M. Kamal Hussein and S.Z. El-Tawil: *Indian J. Tech.*, 1967, vol. 5, pp. 97-100.
7. M. Kamal Hussein, R. Kammel, and H. Winterhager: *Indian J. Tech.*, 1967, vol. 5, pp. 369-77.
8. I.E. Grey, D.G. Jones, and A.F. Reid: *Trans. Inst. Min. Metall., Sect. C*, 1973, vol. 82, pp. C151-52.
9. D.G. Jones: *Trans. Inst. Min. Metall., Sect. C*, 1973, vol. 82, pp. C186-92.
10. I.E. Grey and A.F. Reid: *Trans. Inst. Min. Metall., Sect. C*, 1974, vol. 83, pp. C39-46.
11. I.E. Grey, A.F. Reid, and D.G. Jones: *Trans. Inst. Min. Metall., Sect. C*, 1974, vol. 83, pp. C105-11.
12. A. Yamaguchi and J. Moriyama: *J. Mem. Fac. Eng.*, Kyoto University, Japan, 1966, vol. 28, pp. 389-403.
13. M.I. El-Guindy and W.G. Davenport: *Metall. Trans.*, 1970, vol. 1, pp. 1729-34.
14. D.G. Jones: *J. Appl. Chem. Biotechol.*, 1975, vol. 25, pp. 561-82.
15. T.O. Kang and J.K. Yoon: *J. Korean Inst. Met.*, 1978, vol. 16, pp. 80-89.
16. J.L. Fihey, F.J. Ajersch, and E.A. Dancy: *Can. Metall. Q.*, 1979, vol. 18, pp. 419-34.
17. G.A. Sucre, D. Ablitzer, and J.K. Brimacombe: *Int. Symp. Phys. Chem. Iron and Steelmaking*, Metall. Soc. CIM, Toronto, ON, Canada, 1982, pp. II16-25.
18. H.J. Wouterlood: *J. Appl. Chem. Biotechol.*, 1979, vol. 29, pp. 603-18.
19. S.K. Gupta, V. Rajakumar, and P. Grieveson: *Metall. Trans. B*, 1987, vol. 18B, pp. 713-18.
20. R.P. Donnelly, L.J. Brennan, W. McMullen, and A. Robillard: *Aust. Min.*, 1970, vol. 62, pp. 58-65.
21. G. Ostberg: *Jernkont. Ann.*, 1960, vol. 144, pp. 46-76.
22. R.G. Becher, R.G. Canning, B.A. Goodheart, and S. Uusna: *Proc. Australas. Inst. Min. Metall.*, 1965, no. 214, pp. 21-44.
23. V.B. Fetisov, L.I. Leonyer, B.Z. Kudinov, and S.V. Ivanova: *Russ. Metall.*, 1968, no. 2, pp. 35-37.
24. E.V. Snopova and N.I. Rotkov: *Sov. Metall.*, 1936, vol. 12, pp. 11-20.
25. G. Nakazawa: *J. Min. Inst. Jpn.*, 1957, vol. 73, pp. 833-36.
26. E.M. Khairy, M. Kamal Hussein, and S.Z. El-Tawil: *NML Tech. J.*, 1966, vol. 8 (2), pp. 10-14.
27. G. Teufer and A.K. Temple: *Nature*, 1966, vol. 211, pp. 179-81.
28. R.R. Merritt and A.G. Turnbull: *J. Solid State Chem.*, 1974, vol. 10, pp. 252-59.
29. S.E. Haggerty and D.H. Lindsley: *Carnegie Inst. Yearbook*, 1970, vol. 68, pp. 247-49.
30. D.G. Jones: *Trans. Inst. Min. Metall., Sect. C*, 1974, vol. 83, pp. C1-9.
31. I.E. Grey and A.F. Reid: *Am. Mineral.*, 1975, vol. 60, pp. 898-906.