Mechanically Activated Carbothermic Reduction of Ilmenite

Y. CHEN, T. HWANG, M. MARSH, and J.S. WILLIAMS

A systematic study of the effect of milling conditions on the low-temperature carbothermic reduction of the mineral ilmenite has been carried out. It was found that after ball milling of an ilmenite-carbon mixture at room temperature, the ilmenite was reduced to rutile and metallic iron during subsequent low-temperature annealing (760 °C for 30 minutes). A longer milling time results in a lower reduction temperature and a higher reduction rate. Higher milling intensity also leads to a lower reduction temperature. This enhanced reduction reaction induced by ball milling mainly results from the intimate mixing and large contact area between milled ilmenite and carbon particles.
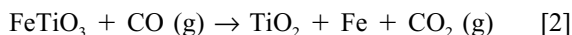
I. INTRODUCTION

THE mineral ilmenite is a naturally occurring iron titanate (nominally $FeTiO_3$) and is abundant in nature. The commercial grades of ilmenite contain 45 to 658 pct TiO_2[1] and are regarded as a huge resource to the production of rutile (TiO_2), which can be used directly as pigment or for the manufacture of titanium. However, extraction of the iron from the ilmenite has been, and still is, an expensive undertaking. Metallurgical processing involves high-temperature processing and often hot acid leaching, with associated environmental problems.[2,3] Therefore, the search for an environmentally friendly, cost-effective extraction method remains a strong industrial imperative. In a commonly used extraction process (''Becher process''),[4,5] ilmenite is reacted with coal in an iron reduction kiln at 1100 °C. This carbothermic reaction reduces the iron in the ilmenite to the metallic form. After cooling the products of the reaction, the iron can be rusted out in slurry form with ammonium chloride acting as a catalyst for rusting. The remaining iron compounds are removed by leaching with sulfuric acid.

In order to increase the efficiency of the preceding reduction process, the carbothermic reactions have been extensively investigated.[6–10] The chemical reactions that occur during the reduction process can be conveniently separated into a solid-state reduction (typically from 860 °C to 1000 °C):
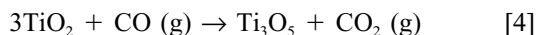
$$FeTiO_3 + C \rightarrow Fe + TiO_2 + CO \text{ (g)} \quad [1]$$

a gaseous reduction (typically above 1000 °C):

$$FeTiO_3 + CO \text{ (g)} \rightarrow TiO_2 + Fe + CO_2 \text{ (g)} \quad [2]$$

with CO generation (the Boudouard reaction):

$$C + CO_2 \rightarrow 2CO \quad [3]$$

and a reduction of rutile (typically above 1200 °C):

$$3TiO_2 + CO \text{ (g)} \rightarrow Ti_3O_5 + CO_2 \text{ (g)} \quad [4]$$

The kinetics of these reactions can be illustrated by thermogravimetric curves obtained by heating a mixture of ilmenite and graphite in a thermogravimetric analyzer. A schematic example illustrating typical behavior is shown in Figure 1. The decrease in sample weight in the low-temperature range is relatively slow and corresponds to the solid-state reduction (Reaction [1]) in which oxygen diffusion to the surfaces of ilmenite particles is thought to be the rate limiting step. The rapid weight loss in the high-temperature range corresponds to gaseous reduction reactions (Reactions [2], [3], and [4]). For prolonged, complete reduction at higher temperatures than that in Figure 1, the final stable phase is titanium carbide (TiC).

In an attempt to increase the rate of reduction, catalysts, such as alkali metal carbonates, have been used during the reduction process. As a consequence, the reduction temperature can be reduced by about 200 °C.[11] Recently, it was found that chemical reactions, which normally take place only at very high temperatures, are often realized by controlled, high energy ball milling at room temperature.[12,13,14] Thus, the ball milling technique is used in an attempt to realize carbothermic reduction at room temperature. The preliminary results[15] showed that although carbothermic reduction did not occur during milling, the reduction took place during a subsequent low-temperature annealing (760 °C). In this present work, a systematic study of the mechanical activation effect of high energy ball milling on the carbothermic reduction of ilmenite was carried out. A lowering of the reduction temperature for producing rutile (TiO_2) and the dependence of the reaction rate on milling conditions such as milling time, intensity, and atmosphere were reported. The influence of structural changes and atomic mixing occurring during ball milling on the subsequent reduction is discussed.

II. EXPERIMENTAL DETAIL

In these experiments, ilmenite powder ($\sim$300 μm) was supplied by Westralian Sands Ltd. (Capel, Western Australia). The chemical composition is listed in Table I. A granular activated carbon powder (purity >99 pct) was used as reducing agent. The weight ratio of ilmenite to carbon was 4:1, which was found previously[15] to provide sufficient carbon for full reduction of ilmenite to rutile. Ball milling was performed using a specially designed ball mill (Uni-Ball-Mill),[16] which consisted of a horizontal rotating stain-
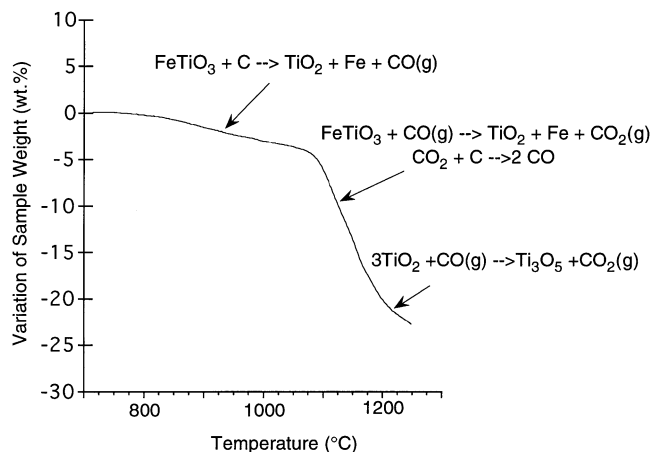
Fig. 1—Reduction of the sample weight as a function of temperature obtained from TG analysis, indicating the reaction sequence of the carbothermic reduction of ilmenite without premilling.

Table I. Chemical Composition of Ilmenite Ore (Weight Percent)

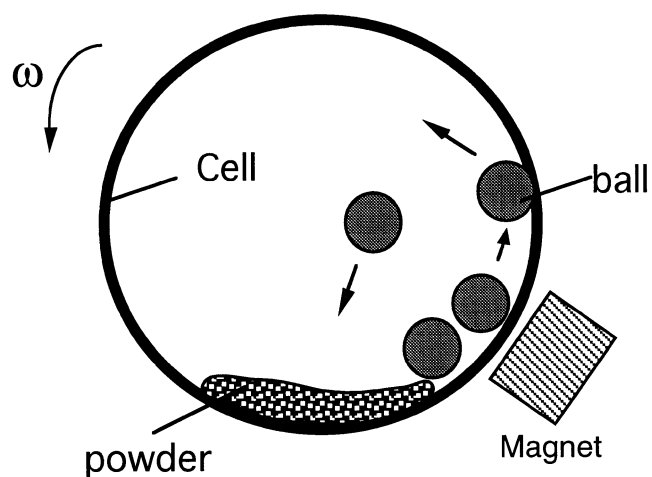| FeO	Fe_2O_3	TiO_2	MnO	SiO_2	ZrO_2	Others
20.8	20.0	53.6	1.54	1.27	0.61	<2

Fig. 2—A schematic illustration of the milling device. ω: the rotation speed.

less steel cell with several hardened steel balls. The cell was sealed using a TEFLON* O-ring so that milling

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TEFLON is a trademark of E.I. Du Pont de Nemours & Co., Inc., Wilmington, DE.

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could be carried out in an atmosphere of a static vacuum (10^{-2} kPa) or gas (such as nitrogen, argon, or air). The ball movement inside the cell was controlled by adjusting the rotation speed of the cell and the position of an external magnet. A schematic representation of the milling device is shown in Figure 2. The milling arrangement used in our experiments provided higher energy impact milling rather than abrasive milling, as indicated by the motion in Figure 2. Milling intensity (impact intensity) can be changed using balls of different sizes and/or magnets of different strengths (pulling forces). Three relative levels of milling intensity were tested: Int. 1, 20 small balls (diameter = 8.6 mm) and
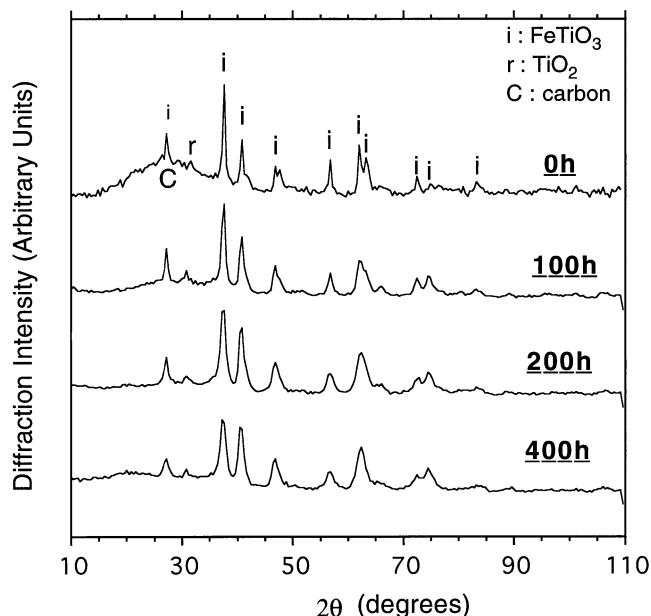

Fig. 3—XRD patterns taken from the mixtures of ilmenite and activated carbon milled under milling intensity of Int. 2 for various times.

a magnet of low strength to provide a low impact energy; Int. 2, four large balls (diameter = 25.4 mm) and a magnet of low strength; and Int. 3, five large balls (diameter = 25.4 mm) and a magnet of high strength to provide a high impact energy. The intensity order was: Int. 1 < Int. 2 < Int. 3. For each milling, the mill was charged with 7.5 g of a powder mixture and pumped to a vacuum of typically 10^{-1} kPa prior to milling. After ball milling, thermal analysis was carried out using a laboratory thermogravimetric (TG) analyzer (Shimadzu TA 50I)[17]. A sample weighing 40 mg was heated at a rate of 20 K/min and under constant Ar flow (80 mL/min). The furnace chamber of the TG apparatus was purged by Ar flow for at least 10 minutes before heating. The structure of products was characterized by X-ray diffraction (XRD) analysis using Co K_α radiation (λ = 1.789 Å) at room temperature. The specific external surface area (not including micropore internal surfaces) of powders was determined using a Gemini surface area analyzer with N_2 gas at liquid nitrogen temperature, where the sample is degassed at 200 °C under vacuum for 1 hour before the measurement. A Hitachi (S-2250N) scanning electron microscope (SEM) was employed to study the powder morphology.

III. EXPERIMENTAL RESULTS

A. Behavior during Ball Milling

1. Structural development during milling

Under the middle milling intensity (Int. 2), samples were ball milled at room temperature under vacuum for different periods: 100, 200, and 400 hours. The XRD patterns of the milled samples and the starting mixture are shown in Figure 3. The XRD pattern of the starting mixture shows that the ilmenite has a crystalline structure (rhombohedral) and the activated carbon has an amorphous structure that is represented by a broadened peak (peak C at 25 deg). A very
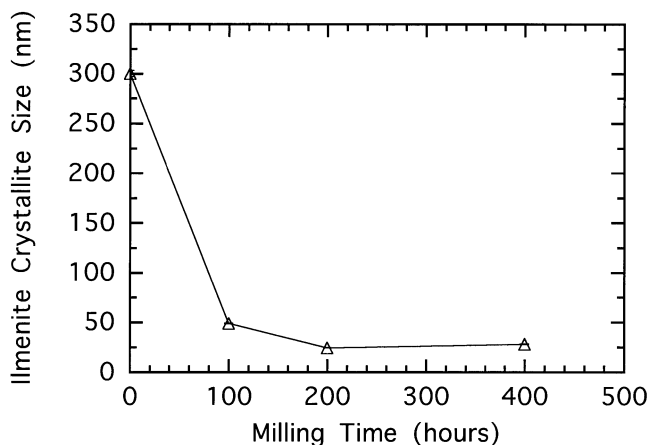
Fig. 4—Size reduction of the ilmenite crystallite as a function of the milling time under Int. 2.
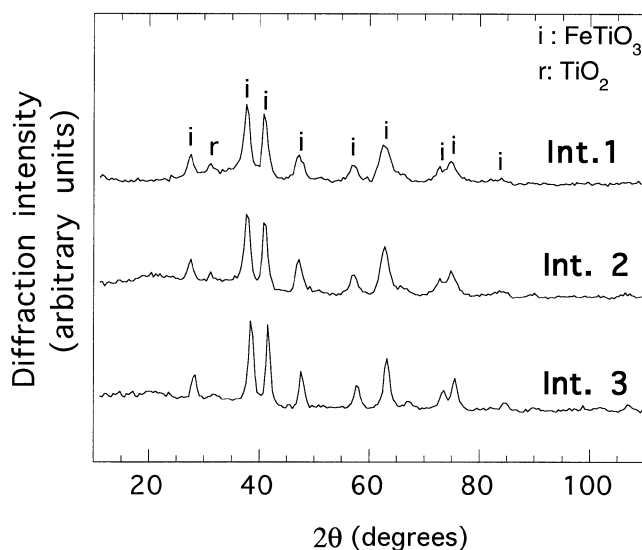

Fig. 5—XRD patterns taken from the mixtures of the ilmenite and the activated carbon milled for 400 h under Int. 1 and Int. 2 and 200 h under Int. 3 (Int. 1 < Int. 2 < Int. 3).

small fraction of TiO_2 (rutile) was found (peaks indicated by symbol r) in the supplied ilmenite powder. The amorphous carbon was not detected by XRD beyond 100 hours of milling, but the ilmenite structure remained stable during continued milling up to 400 hours. In addition, no new diffraction peaks were found in these XRD patterns. This suggests that no significant chemical reduction reaction took place during the entire milling process. However, the disappearance of the amorphous carbon peak after 100 hours of milling is interesting, possibly indicating that carbon was mixed with or incorporated into the near surface of ilmenite particles, an aspect which will be addressed later. Also, the diffraction peaks of the ilmenite phase became broadened during milling, consistent with a size reduction of the ilmenite crystallites. The average size of the crystallites was estimated from diffraction peak broadening using the Sherrer formula,[18] and the results are shown in Figure 4 as a function of milling time. The crystallite size is reduced to below 50 nm after 100 hours of milling and remains a similar size for further milling up to 400 hours. This suggests that nanometer sized crystallites of ilmenite

were produced at the early stages of milling. Thus, a high fraction of the boundary region is expected to exist between nanometer-sized ilmenite crystallites, and these boundaries have a highly disordered structure. A higher background scattering level observed in milled samples compared with the unmilled samples is indicative of such structure.

2. *Milling under different conditions*

The same mixtures of ilmenite and activated carbon were ball milled for 400 hours under Int. 1 and Int. 2 and 200 hours under Int. 3. The XRD patterns for the three milled samples are essentially similar, as shown in Figure 5. Crystalline ilmenite is the dominant structure in these three samples. Also, no chemical reaction occurred during milling, even under the highest milling intensity (Int. 3). Similar XRD patterns were also obtained after milling under different atmospheres of vacuum, N_2, Ar, and air. Indeed, apart from broadening of ilmenite peaks, milling under different conditions (time, intensity, and atmosphere) appeared to produce as-milled powders with identical X-ray diffraction patterns. As indicated later, the similarity of such X-ray data following milling is misleading and does not predict large differences in the subsequent annealing behavior.

3. *Powder morphology*

The SEM pictures taken from the original ilmenite powder and typical milled mixtures (ilmenite + activated carbon) are shown in Figure 6. Figure 6(a) shows that the ilmenite particles have a regular shape and a relatively homogeneous size of 200 to 300 μm. Figure 6(b) shows that the 100 hour as-milled sample consists of both small individual (diameter < 0.5 μm) particles and large clusters (diameter = several μm) composed of a high number of the small particles. Figures 6(c) (200 hour milled sample) and (d) (400 hour milled sample) show that the size of the small individual particles was stabilized during further milling. But, more large clusters formed. The structure of a typical large cluster is shown in Figure 6(d). These results suggest that ilmenite and carbon powders were first reduced to a submicron size by ball milling. During prolonged milling, the agglomeration process to form larger clusters will be equilibrium with fracturing and size reduction. It can be suggested that an intimate mixing between ilmenite and carbon particles will be achieved during this process.

Variation of specific particle surface area of the samples milled under Int. 2 for different times is shown in Figure 7. The specific surface area increased from 4.4 to 14.1 m^2/g during the first 100 hours of milling and then remained stable during further milling. This is consistent with the constant size of the small individual particles during further milling. The specific surface areas for the powders milled under Int. 1 for 400 hours and Int. 3 for 200 hours were 12.0 and 15.4 m^2/g, respectively, indicating that high intensity milling slightly increased the particle surface area. The increase in the external surface area of ilmenite and carbon particles produced by ball milling presumably increases the contact area between ilmenite and carbon particles.

B. *Thermal Annealing*

Figure 8 shows typical TG curves (variation of sample weight as a function of temperature during a continuous heating of 20 K/min) taken from an as-mixed and a sample
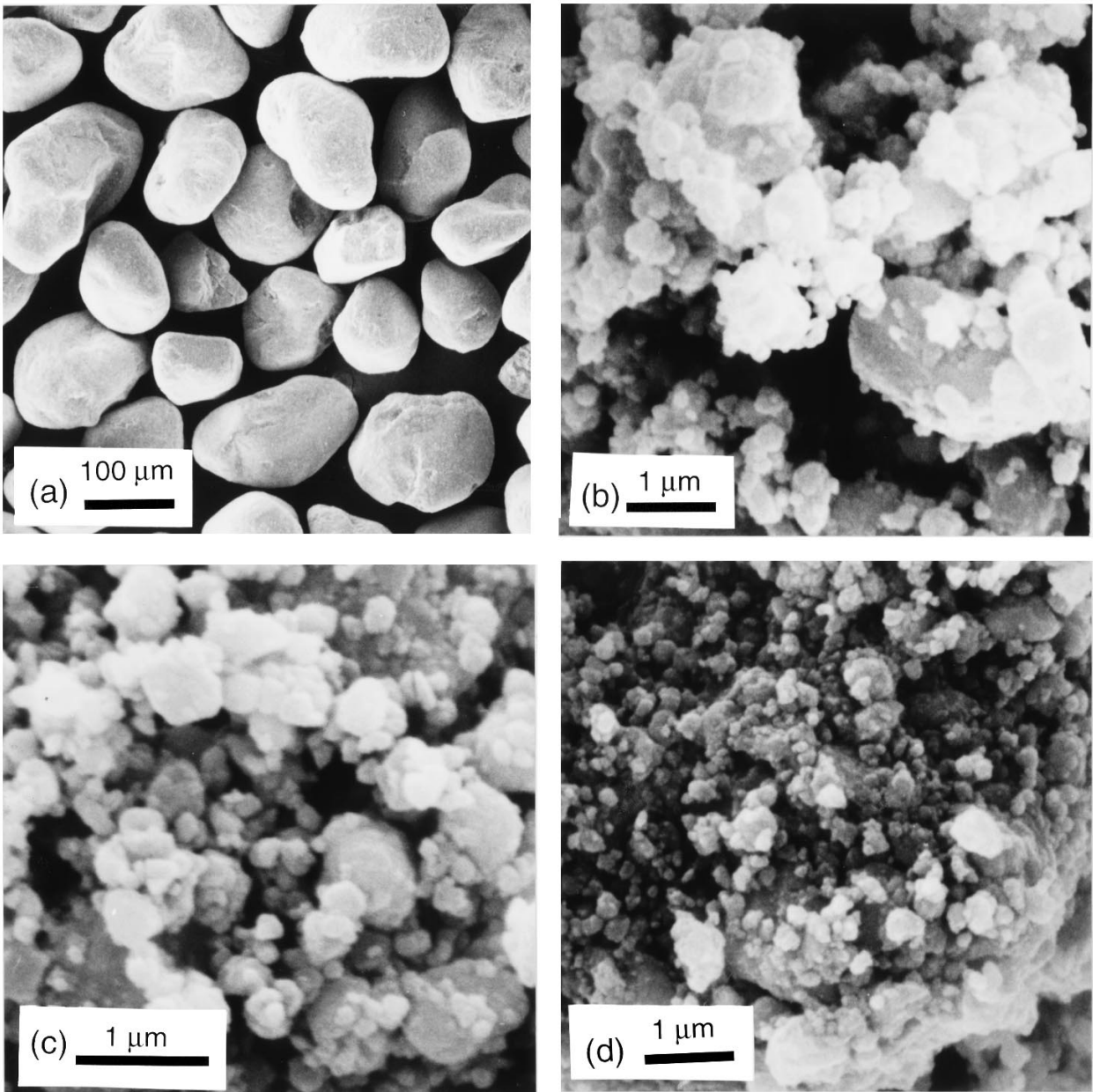
Fig. 6—Scanning electron micrographs for (*a*) starting ilmenite powder and powders of ilmenite-carbon mixtures after milling under Int. 2 for different times: (*b*) 100 h, (*c*) 200 h, and (*d*) 400 h.

milled for 200 hours under Int. 2. For the as-mixed sample which was not milled, a significant weight loss is observed only above 800 °C (curve 1). In this case, only 4.0 wt pct of the starting sample weight was lost during heating to 1100 °C, and the corresponding XRD pattern shows that only a small fraction of ilmenite was reduced to rutile and metallic iron, as is shown in Figure 9(e). This result is consistent with that reported by Gupta *et al.*[6] for carbothermic reduction of ilmenite without premilling. By contrast, for the sample in which the ilmenite-carbon mixture was milled for 200 hours (curve 2) prior to heating, the first weight loss is observed during the temperature range from 100 °C to 850 °C and the second sharp decrease in weight occurs above 850 °C. A total of 21.5 wt pct was lost. The XRD patterns of this sample after heating (20 K/min) to temperatures 760 °C, 900 °C, and 1100 °C (as indicated in Figure

8 by (a) through (c)), corresponding to various stages of the weight loss, are shown in Figure 9 (Figures 9(a) through (c), respectively). The XRD patterns indicate that after heating to 760 °C, together with a large quantity of unreacted ilmenite, measurable quantities of TiO_2 and α-Fe and γ-Fe(C) phases were present in the sample (Figure 9(a)). Some γ-Fe(C) may come from debris of the milling cell and ball materials (stainless steel) or from reaction of C with Fe on heating. Presumably, the detection of γ-Fe(C), the austenite phase observed during X-ray analysis at room temperature, suggests that the cooling rate is fast enough to suppress formation of iron carbide. The presence of the TiO_2, α-Fe, and γ-Fe(C) phases in the annealed sample suggests that a carbothermic reduction (presumably a solid-state reaction) had commenced during heating in which a small fraction of the ilmenite was reduced to rutile and
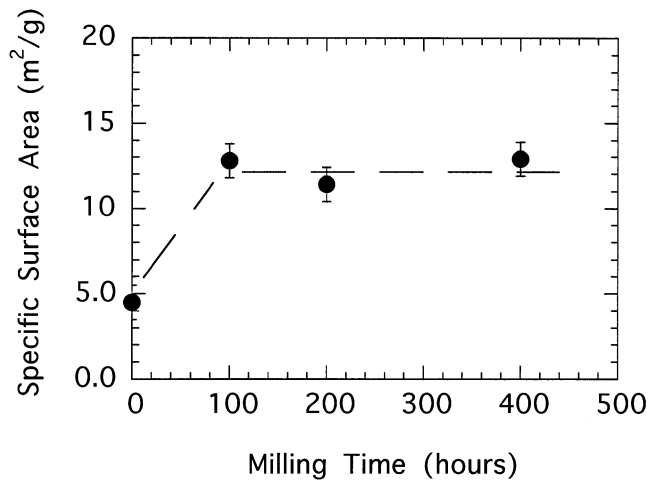
Fig. 7—Variation of the specific surface area of the ilmenite-carbon mixtures as a function of milling time under milling intensity Int. 2.
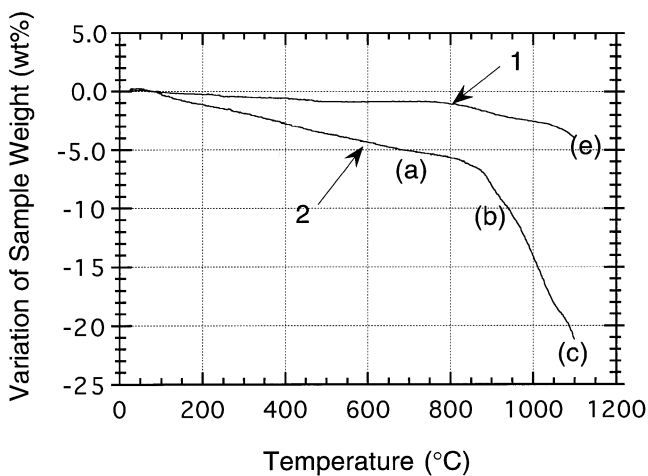

Fig. 8—TG curves for two different ilmenite-carbon mixtures: (1) without premilling and (2) after 200 h of milling under Int. 2. Additional annealing (continuous heating with the rate of 20 K/min) was carried out on these samples to the temperatures indicated by (a), (b), (c), and (e). The corresponding XRD patterns of as-annealed samples are represented in Fig. 9.
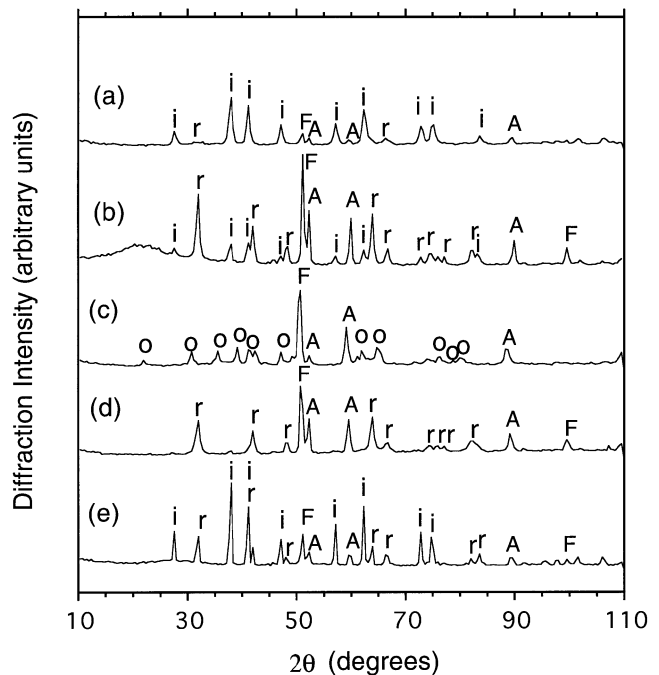

Fig. 9—XRD patterns for the 200 h milled sample (under Int. 2) continuously heated at a constant rate of 20 K/min to different temperatures: (a) 760 °C, (b) 900 °C, (c) 1100 °C, (d) after an isothermal annealing at 760 °C for 30 min, and (e) for an as-mixed sample heated continuously up to 1100 °C without premilling. i: $FeTiO_3$, r: TiO_2, F: α-Fe, A: γ-Fe(C) (austenite), and o: Ti_3O_5.

metallic iron. When the temperature reached 900 °C, the dominant phases of the as-annealed sample were TiO_2 and Fe(C), where Fe(C) is essentially the mixture of α-Fe and austenite phases. Indeed, most of the ilmenite has been reduced (Figure 9(b)) in such cases, as indicated by the weak ilmenite peaks. After further heating to a higher temperature (1100 °C), new reduction products appeared, such as γ-Ti_3O_5, together with α-Fe and γ-Fe(C), indicating the further reduction reaction of rutile (Reaction [4]), and the ilmenite structure had disappeared completely (Figure 9(c)). As shown in Figure 9(d), an apparent full reduction of ilmenite to rutile was also achieved by annealing the same milled sample at a lower temperature (760 °C) for a short time (30 minutes). These results confirm that a series of carbothermic reactions occurred during the subsequent annealing and the end products depended on annealing conditions (temperature and time). Indeed, the observed reaction sequence (based on the shape of TG curves and XRD patterns) is similar to that (the reaction sequence of Reactions [1] through [4] in Figure 1) reported in the lit-

erature[6,8,9,10] for unmilled ilmenite-carbon mixtures. However, the annealing temperatures at which the reactions occurred were much lower than those without a premilling treatment. In conclusion, the major effect of ball milling treatment prior to annealing is a dramatic lowering of the annealing temperature required for the carbothermic reduction of ilmenite.

To investigate the milling effect in detail, samples milled under different conditions were analyzed in a TG apparatus under the same annealing conditions. The TG curves for the 100, 200, and 400 hour milled samples under Int. 2 and for a mixed sample (0 hour milling) of the same ratio of ilmenite to activated carbon (4:1) are shown in Figure 10. This figure shows that a longer milling time leads to a higher rate of weight loss in the low-temperature range (the solid-state reaction) and a lower temperature onset of the second stage, indicated by a sharp weight loss in the high-temperature range (presumably the gaseous phase reaction). The onset temperatures of the second stage reduction for samples milled for 100, 200, and 400 hours are approximately 900 °C, 850 °C, and 750 °C, respectively. The weight losses during continuous heating to 1100 °C are 17.5, 21.5, and 24 wt pct, respectively. Therefore, the longer a sample is milled, the more rapidly it exhibits weight loss during annealing. As has been previously mentioned (cf. Figure 1), the weight loss profile during annealing is indicative of the various stages of carbothermic reaction. Hence, a longer milling time leads to a faster solid-state reduction and a lower temperature for the onset of a gaseous reduction.

The TG curves of the samples milled for 400 hours at the lowest intensity (Int. 1) and 200 hours at the highest intensity (Int. 3) are shown in Figure 11. The total weight
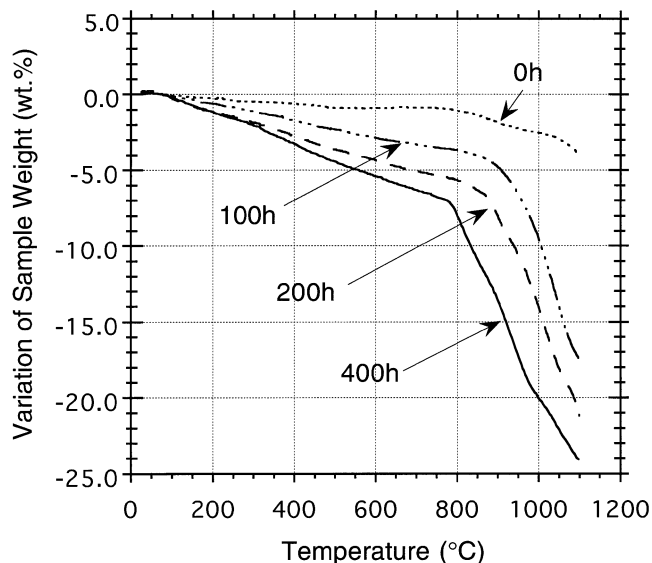
Fig. 10—Thermogravimetric curves of the ilmenite-carbon mixtures milled for different periods under Int. 2.
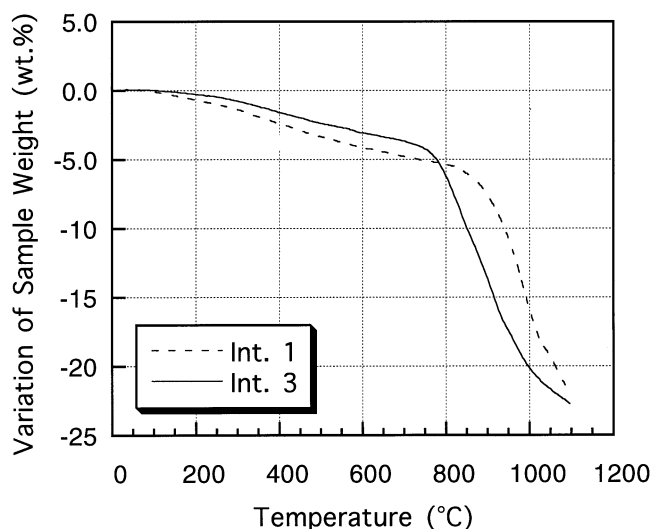

Fig. 11—Thermogravimetric curves of the ilmenite-carbon mixtures milled under different intensities (400 h under Int. 1 and 200 h under Int. 3).

losses after heating to 1100 °C were 22.1 and 24.5 wt pct, respectively. This figure shows that higher intensities result in faster and more extensive weight loss during annealing in the high-temperature range corresponding to gaseous reduction. Moreover, the onset temperature of gaseous reduction for Int. 3 is lower than that of Int. 1 by about 100 K. Therefore, high milling intensity leads to a lower onset temperature for gaseous reduction to rutile, despite the fact that the apparent ''structure'' after milling is relatively insensitive to the milling conditions. In the low-temperature range, the rate of the solid-state reaction for Int. 1 is slightly higher than the rate for Int. 3. The difference between the two rates may be due to measurement error.

Little difference was observed (XRD analysis) during annealing for samples milled under different atmospheres such as vacuum, Ar, and N_2. By contrast, for a sample milled in air, XRD analysis indicates that the solid-state reaction took place at a considerably higher temperature

(900 °C). It is suggested that oxygen is an unfavorable atmosphere for the milling treatment (suggesting an additional source of oxygen for potential reaction with carbon) and must be avoided during the milling process.

IV. DISCUSSION

No evidence of a chemical reaction was obtained during the milling process for ilmenite-carbon mixtures, but rather, a series of reduction reactions occurred during the subsequent annealing process. However, the temperatures during which the various reaction stages occurred are much lower than those without a milling treatment or for ilmenite premilled and then mixed with carbon before annealing.[15] For example, from TG analysis, the solid-state reaction (Reaction [1]) began at about 100 °C in the milled sample, as indicated by the onset of weight reduction, but the initial weight loss is at 800 °C for a sample without premilling (Figure 8). The gaseous reduction to rutile (cf. Reactions [2] and [3]) occurred at typically 800 °C for the milled sample compared with about 1100 °C for the sample without premilling. The further reduction of rutile (Reaction [4]) is normally realized above 1200 °C,[7] whereas the reaction appeared to be completed at 1000 °C for the milled sample. In addition, complete reduction of ilmenite to rutile and metallic iron (or austenite) was achieved by an isothermal annealing at 760 °C for 30 minutes. In contrast, annealing at 1100 °C for several hours is typically required in the Becher process to completely reduce ilmenite,[5] but in such cases, the product contains a high proportion of reduced TiO_{2-x} oxides in addition to rutile.[19] Furthermore, the reaction rate, especially for solid-state reduction at low temperatures, is substantially increased by ball milling treatment. Thus, compared with the standard reduction reactions, premilling of an ilmenite-carbon mixture provides a large measure of selectivity for the various reaction stages. Indeed, it is possible with milled samples to terminate the annealing stage when essentially all the ilmenite has been reduced to rutile with little evidence for further reduction (Figure 9(d)).

In exploring the mechanisms for the enhancing effect of ball milling on subsequent reduction during annealing, it is worth noting that the magnitude of the enhancement depends to a very large extent on the milling conditions (particularly time). However, the crystalline structure and particle size of the ilmenite phase appeared to stabilize during prolonged milling, as indicated by X-ray data which changed little between 100 and 400 hours of milling. Indeed, it has been observed that the particle size reduction stabilizes after times as short as 10 hours. Consistent with such particle and crystallite size reduction, there is a corresponding increase in surface area. Furthermore, intimate mixing of carbon with ilmenite particles (as suggested by the loss of carbon peaks in XRD patterns and the formation of clusters) also occurred during milling. It can be suggested that the intimate mixing of carbon with ilmenite occurs during early stages of milling, predominantly at the interface area of microsized ilmenite and carbon particles. During prolonged milling, intimate mixing of ilmenite and carbon can take place by repeated fracturing and welding events at the area of high fraction of boundaries of nanometer-sized ilmenite crystallites. Based on the measure-

ments, the milling process may be broadly divided into two stages: (1) during the initial stages of milling (for much shorter times than 50 hours), the particle/crystallite size decreased rapidly to generate defective nanocrystals of ilmenite, with a corresponding increase in the specific surface area; and (2) thereafter, the particle size and the surface area are stable or change only slowly with further milling. However, the degree and homogeneity of carbon mixing with ilmenite continue to increase with milling time, and this has the dominant effect on subsequent annealing behavior. It is also worth noting that the effect of milling atmosphere suggests that oxygen must be excluded from the milling process. It is probably that the oxygen absorbed in the powder during milling inhibits carbothermic reduction during annealing. Some oxygen is chemisorbed and bands to carbon during the milling process. This point needs to be further clarified.

During annealing, it is accepted that the solid-state reduction reaction occurs mainly at the contact points between ilmenite and carbon particles. The reaction kinetics are limited by the relative contact area.[11,20] With intimate carbon mixing at the large area of the ilmenite nanocrystal boundaries during prolonged milling, the solid-state reduction may occur at a lower temperature and with a higher rate. This presumably arises from the much reduced diffusion length of oxygen to carbon. Furthermore, the lower onset temperature of the gaseous reaction (typically about 800 °C) may arise mainly from the enhanced solid-state reaction which produces a larger quantity of CO gas at a lower temperature than in the conventional Becher process. Indeed, the onset of gaseous reduction relies on CO produced by the solid-state reduction. When the concentration of CO rises, the gaseous reaction is favored. The gaseous reduction rate may also be enhanced by small grain/particle size and mechanical disorder to ilmenite crystals, enabling complete ilmenite reduction to rutile to occur before appreciable further reduction to TiO_{2-x} (where $2 > x > 0$) occurs. This may account for the high selectivity of the reduction phase to rutile for premilled powders compared with the conventional Becher process. It is worth noting that the final, stable reduced state (requiring sufficient carbon, high temperatures, and long times) is TiC. In optimizing the reduction to rutile, controlled milling can enable full reduction to rutile before the (slower) further reduction steps take place. Hence, it is possible to preferentially enhance rutile production as an intermediate reduction state.

V. CONCLUSIONS

After ball milling of a carbon-ilmenite mixture at room temperature, ilmenite was reduced to rutile and metallic iron (or austenite) during subsequent low-temperature annealing. The reduction temperature and the reduction kinetics for production of this intermediate reduction state (TiO_2) depend critically on the milling conditions: (1) with increasing milling time, the reduction temperature decreases and the reaction rate increases; (2) high milling intensity also leads to a lowering of the annealing temperature for the main reduction step to rutile; and (3) oxygen should be excluded during the milling process. The enhanced reduction process in premilled samples is attributed mainly to intimate mixing of carbon with disordered ilmenite nanocrystallites during milling. This substantially reduces the diffusion length of oxygen to carbon in the solid-state reaction, thus increasing the rate of CO production for initiating the main gaseous reduction. Finally, the improved process leads to a high degree of selectivity for reduction to rutile without further reduction products, and the efficiency of the carbothermic reaction is greatly increased by ball milling treatment. However, this study has concentrated on the effect of ball milling on carbothermic reduction of ilmenite and not on the industrial potential of such a process. If scaling up of the simple ball milling process proves to be a simple and cost-effective method for extraction of rutile from ilmenite, then the process could have a substantial commercial potential.[21]

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