Effective Extraction of Titanium from Rutile by a Low-Temperature Chloride Process

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The carbochlorination of rutile is carried out at high temperatures (800−1,500°C) in the commercial chloride processes of the pigment industry. Chlorination at high temperatures results in high energy consumption, rapid corrosion of the equipment, pipeline and control system, and agglomeration of solid reactants in the reactor. In a typical chloride process, rutile is used as a primary reactant, Cl_2 as a chlorinating agent, and carbon as a reductant. The thermodynamic equilibrium simulation of the reaction system shows that a complete conversion of rutile is feasible at a temperature as low as 200°C. Kinetic and diffusion barriers, however, make the reaction practically impossible at low temperatures. In the study, these barriers were removed by intensifying the rutile-carbon solid−solid contact. In the low-temperature chloride process developed, reaction temperatures are reduced to 350−450°C. The conversion rate of the rutile at 385°C is 30% higher than that at 1,000°C. A fluidized-bed reactor was used for the chlorination process. It was concluded that the formation of an activated TiO_2-C-Cl complex on the TiO_2/C interface accounts for the gas−solid−solid reaction mechanism.

Introduction

Titanium dioxide pigments are produced by two different processes: the older sulfate process, and the modern chloride process. Today, titanium white (TiO_2) is increasingly produced by the chloride process because it is simple, economic, and environmentally friendly. It also gives better pigment quality. In a typical chloride process, TiO_2 concentrates, such as rutile, are chlorinated by chlorine with carbon as a reductant at 800−1,500°C. Titanium tetrachloride ($TiCl_4$) is formed as a major chloride product. The volatile chlorides are collected by condensation and $TiCl_4$ is separated from other chlorides by distillation. The $TiCl_4$ is burnt in a plasma or a flame at temperatures of 900−1,400°C to form extremely pure TiO_2 pigment.

Intensive study on the carbochlorination of TiO_2-containing materials has been made in the past. Several papers or patents appear each year discussing kinetic aspects of this reaction system. However, all the papers or patents focus their attention on a high-temperature domain. The high-temperature (800−1,500°C) chlorination process has been well accepted by researchers and engineers. For example, the temperatures for the chlorination used by Dunn (1961), Bergholm (1961), Morris and Jensen (1976), and Vijay et al. (1976) were in the range of 600 to 1,100°C. They all concluded that the rate of reaction increased with temperature. The temperatures used for the chlorination process, claimed by the patentees, were Robinson (1979), 1,500°C; Bonsack (1982), 800−1,200°C; and Crosby and Robinson (1983), 950−1,170°C.

It is well known that a high-temperature chlorination process results in the following problems:

1. High-energy consumption from operating the reactor at high temperatures and from heating the reactants and cooling the products.
2. Rapid corrosion on the process equipment, the pipelines, and the control system caused by the chlorine or chlorides.
3. The chlorides of minor constituents, such as $MgCl_2$ [melting point (m.p.) 714°C], $CaCl_2$ (m.p. 782°C), and $MnCl_2$ (m.p. 650°C), exist in liquid state at high temperatures. They accumulate in the fluidized-bed reactor and cause bed agglomeration and cessation of the process.

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A chloride process operating at low temperatures will certainly avoid many of these problems. The objective of this work is to investigate the possibility of reducing the reaction temperature and of developing a low-temperature chloride process.

Thermodynamic Simulation

Reaction system

The reactants in the reaction system are TiO_2 (rutile, <5 micron, 99.9%), Cl_2, and carbon black (MN 1100, 14 nm, Cabot Corporation). The ratio of TiO_2/C is 3 by weight.

Thermodynamic calculations

Chemical equilibrium calculations of the $TiO_2/C/Cl_2$ reaction system were performed by the NASA CEA program (McBride and Gorden, 1996). This program is based on the minimization of free energy.

The following reaction conditions were used: $P_{\text{total}} = 102.1$ kPa and $T = 200-1{,}600°C$. The initial ratio of reactants was $TiO_2:C:Cl_2 = 1:2.22:6$ (in moles). This ratio represents a real process in which the carbon is in excess and a sufficient amount of chlorine passes through the solid bed. The ratio of $TiO_2:C = 1:2.22$ (in moles or 3:1 by weight), used in simulation, is the same as in our experiments. From the results shown in Figure 1, it is clear that a complete conversion of TiO_2 can be achieved at all temperatures considered. The equilibrium products are $TiCl_4$, CCl_4, $COCl_2$, CO, and CO_2. The formation of CCl_4 starts when the temperature is lower than 600°C. The carbon tetrachloride, CCl_4, has a very high concentration below 400°C. The carbon monoxide, CO, is the only oxide of carbon existing above 800°C. However, CO_2 becomes dominant below 400°C. The concentration of $COCl_2$ is very low in the entire temperature region considered.

From the thermodynamic point of view, the major reactions occurring in the system are as follows:

$$TiO_2\ (s) + 2C\ (s) + 2Cl_2\ (g) = TiCl_4\ (g) + 2CO\ (g) \quad (1)$$

$$TiO_2\ (s) + C\ (s) + 2Cl_2\ (g) = TiCl_4\ (g) + CO_2(g). \quad (2)$$

Below 600°C, the following reactions may also happen:

$$C + 2Cl_2 = CCl_4 \quad (3)$$

$$CCl_4 + TiO_2 = TiCl_4 + CO_2 \quad (4)$$

$$TiO_2 + 2C + 4Cl_2 = 2COCl_2 + TiCl_4. \quad (5)$$

Kinetics

Role of gas–solid–solid contact

Results in the preceding subsection proved that a low-temperature chlorination process is thermodynamically feasible. The problem is how to overcome the kinetic barrier.

The carbochlorination of TiO_2 by chlorine and carbon is a gas–solid–solid reaction. In this reaction system, the reactions take place on the gas–solid–solid interface; therefore, the contact among the reactants, especially the solid–solid (TiO_2–C) contact, is critical for the reaction to proceed. The effect of the TiO_2–C contact on the reactivity was investigated by Barin and Schuler (1980). They found that the rate of reaction is the highest for the TiO_2–C contact and decreases with increasing TiO_2–C initial separation.

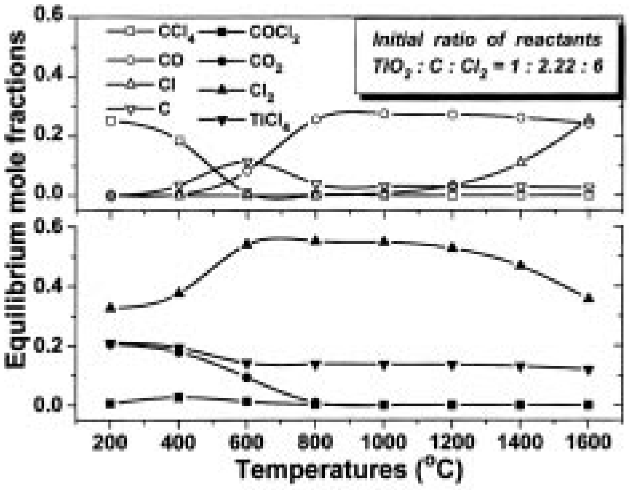

Figure 1. Chemical equilibrium in $TiO_2 + C + Cl_2$ reaction system.

Intensification of the solid–solid contact

To intensify the TiO_2–C contact, the following measures were taken:

Fine Particle Sizes. Solid reactants of fine particle sizes (TiO_2, rutile, <5 micron; carbon black, 14 nm) were used to provide a sufficient surface contact area.

Sufficient Mixing. The TiO_2 powder was mixed with 25% carbon black, which is in excess of stoichiometry to facilitate a complete conversion of TiO_2. A Turbula Shaker-Mixer (Type T2C, Impandex Inc., NJ) was used. The container attached to the mixer contained 50 g of the solid mixture and 50 g of ceramic milling balls ($d = 4$ mm). It was shaken and rotated for 2 h to thoroughly mix the solids.

Pelletizing with a Volatile Binder. The well-mixed mixture was pelletized to disks that had a diameter of 29 mm and a thickness of 5 mm. The pellets of the mixture were produced in a press (Laboratory Press, Fred S. Carver Inc.) and a force of 2 metric ton was applied. 1-Butanol was used as a binder, as it wets both TiO_2 and carbon and it also can be easily removed (boiling point = 117.7°C). A volatile binder avoids undesirable reactions during the chlorination process.

Sintering. The sample disks were dried at room temperature for 3 h and then at 100°C for 2 h to slowly remove the binder. The dried disks were sintered at 800°C for 1.5 h in an argon stream. After cooling to room temperature, the disks were crushed and sieved to get small granules. The granules were strong enough to withstand chlorination at high temperatures in a fluidized bed.

Fluidization Characteristics

Classification of fluidization

For a gas–solid bed, the fluidization behavior depends on a combination of mean particle size, particle density, presence of fines, and type of gas used (Zhao et al., 1994).

A classification of powder fluidization has been suggested by Geldart (1973). The granules of pelletized TiO_2/C mixture fall into the Geldart's Group B.

Fluidization of the granules

The fluidization of the granules of $d_p = 0.25–0.42$ mm, $d_p = 0.15–0.25$ mm, and $d_p = 0.044–0.15$ mm was carried out in a transparent quartz tube (diameter = 28 mm, length = 650 mm). The gas distributor was represented by two 4-mm-thick ceramic porous disks placed together. Dried air was used as the fluidizing gas. The granules were well fluidized. Little entrainment was observed during the fluidization and the fluidized bed behaved regularly. The pressure drop and expansion of bed height as a function of the superficial gas velocities were measured. The results were shown in Figures 2a to 2c. From the measurements, minimum fluidization velocities were determined: $U_{mf} = 7.0$ cm/s for $d_p = 0.25–0.42$ mm, $U_{mf} = 2.4$ cm/s for $d_p = 0.15–0.25$ mm, and $U_{mf} = 0.40$ cm/s for $d_p = 0.044–0.15$ mm.

Carbochlorination Reaction

Experimental setup

A quartz tube ($L = 760$ mm, ID = 28 mm, wall thickness = 2.5 mm) was used as the reactor tube. It was positioned vertically inside a Lindberg tube furnace (1,200°C, HTF 55322A) equipped with a temperature controller. Two ceramic porous discs (thickness 4 mm) fixed inside the tube acted as the gas distributor. Another disc was placed close to the top end of the tube to prevent particle entrainment. A thermocouple was installed on the outside wall of the reactor tube to avoid rapid damage due to direct contact with the corrosive media. The temperature inside the reactor tube was determined indirectly through calibration by measuring the local axial temperature profile inside the tube with an inert gas. Chlorine

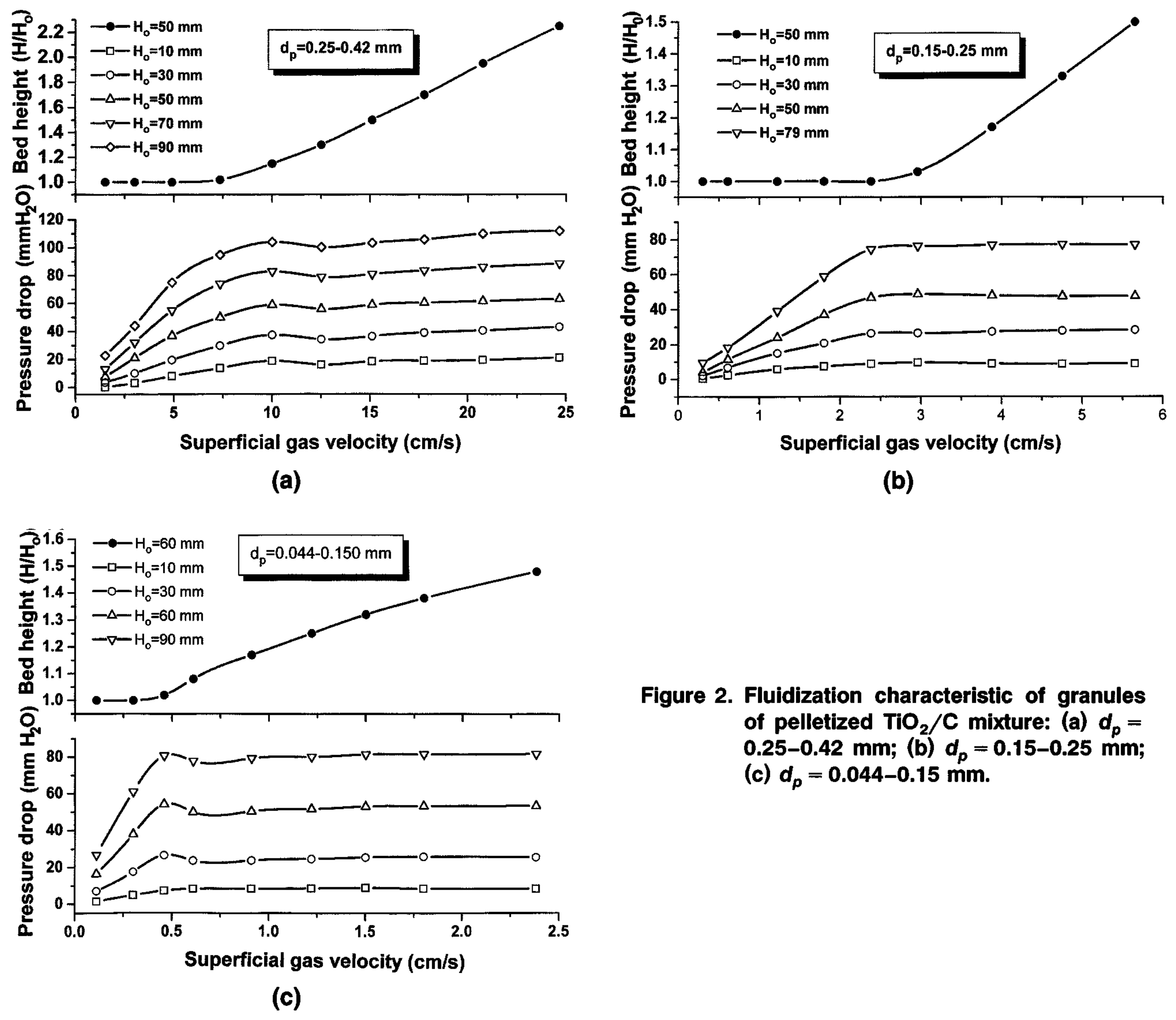

Figure 2. Fluidization characteristic of granules of pelletized TiO_2/C mixture: (a) $d_p = 0.25–0.42$ mm; (b) $d_p = 0.15–0.25$ mm; (c) $d_p = 0.044–0.15$ mm.

and argon were stored in cylinders and were introduced to the reactor through plastic tubing. Mass flowmeters (Type 1259B, MKS Instruments Inc.) and metering valves were used to control the flow rate. The exit gas was neutralized in the two-stage scrubbers by a 5% caustic soda solution and then discharged to the atmosphere.

Reaction procedures

The granules of $d_p = 0.044–0.15$ mm were chosen for the chlorination experiments. To verify the minimum fluidization velocities at actual reaction conditions, a direct observation of the fluidized bed through a small opening of the furnace was done with the reactant gas (Cl_2) at 400, 600, 800, and 1,000°C. It was observed that the minimum fluidization velocities at actual reaction conditions were virtually the same with the ones from the cold-gas test.

The superficial gas (Cl_2) velocity used for all chlorination runs was $U_f = 1.03$ cm/s, which is 2.7 times the U_{mf} (0.40 cm/s for $d_p = 0.044–0.15$ mm). For each run, the solid sample of 6 g was loaded into the fluidized-bed reactor. The entrainment was restricted by the top disc and therefore was negligible. Argon was introduced to purge the bed for 5 minutes at a flow rate of 250 mL/min, and then heating was started. As the desired temperature was reached and was maintained for 15 minutes for stabilization, the argon stream was shut off and chlorine was fed into the reactor at $U_f = 1.03$ cm/s. After specified reaction time, chlorine was replaced by argon again to purge the system. Heating was maintained for 5 minutes to ensure a complete removal of the volatile chlorides produced. Afterward, the power was switched off and the furnace body was opened for quick cooling. The sample was removed after being cooled to room temperature. The reacted sample was weighed and unreacted carbon was oxidized in TGA (Model ST-736, 20–1,600°C, Harrop Industries, Columbus, OH). Conversion of TiO_2 can be easily calculated based on the data given earlier.

Experimental results

Conversion at Different Temperatures. The carbochlorination reaction is a complex system of consecutive and parallel reactions (see Eqs. 1–5), with different rates and activation energies. For metallurgical purposes we are mainly interested in the efficiency of converting solid TiO_2 to a volatile $TiCl_4$. All products of the chlorination process are volatile chlorides of titanium and carbon, $COCl_2$, CO, and CO_2.

We can easily measure the global conversion, TiO_2 conversion, and carbon conversion. The global conversion is the total weight change during the reaction related to the initial sample weight. It can be easily measured by weighing the initial sample and the sample removed from the reactor.

The carbon conversion represents the weight change of carbon during the reaction. The unreacted carbon in the sample can be quantitatively measured by burning it in the air in a TGA unit.

The conversion of TiO_2 can be easily calculated from the global conversion and carbon conversion values.

The chlorination reaction was carried out in the fluidized-bed reactor at temperatures from 300 to 1,000°C. The reaction time was 10 minutes. Conversions at different temperatures are shown in Figure 3. From the measurement it is evident that a rather complex picture results. The highest conversion of TiO_2 lies in the low-temperature domain from 350 to 450°C. The conversion rate of TiO_2 at 385°C is about 30% higher than that at the high temperature regime of 800 to 1,000°C.

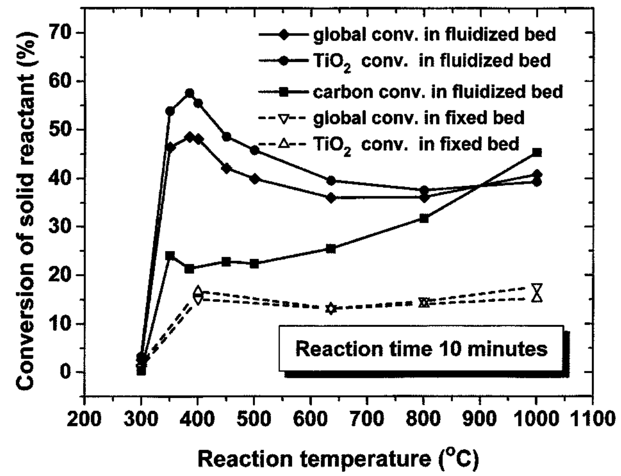

Figure 3. Conversion of TiO_2 or $TiO_2 + C$ at different temperatures.

At low temperatures, the conversion of C is much lower than that of TiO_2, but becomes higher as the temperature increases. This result indicates that the balance between Eqs. 1 and 2, varies with the reaction temperature. This observation is in agreement with the results of thermodynamic calculations presented in the subsection on thermodynamic calculations. Obviously, a low-temperature chlorination process can reduce the carbon consumption substantially.

Effect of Reaction Time. The highest TiO_2 conversion rate was obtained approximately at 400°C. The conversions of TiO_2 for different reaction times were determined experimentally in the fluidized-bed reactor at 400°C. The results in the form $(1 - X_{TiO_2})^{1/3} = f(t)$ are shown in Figure 4. The lin-

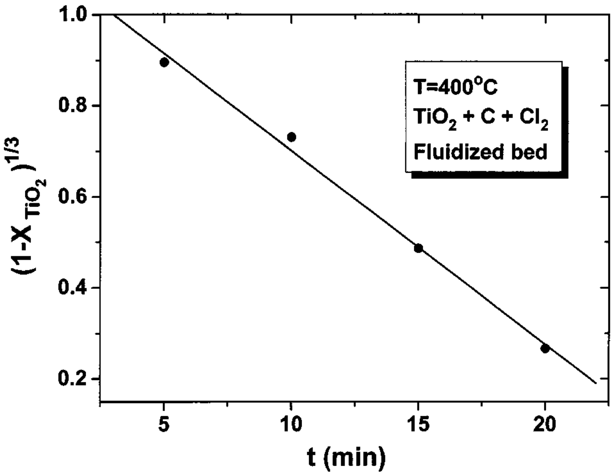

Figure 4. Plot of $(1 - X_{TiO_2})^{1/3}$ vs. reaction time ($T = 400°C$).

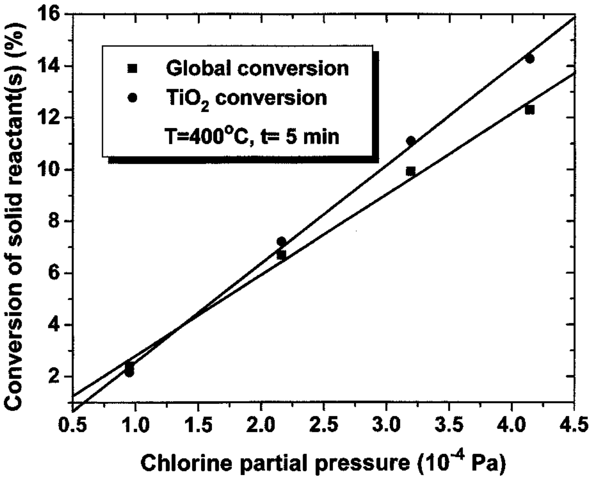

Figure 5. Conversion vs. chlorine partial pressure (T = 400°C).

ear relation between $(1-X_{TiO_2})^{1/3}$ and the reaction time illustrates the fact that the experimental data fit the shrinking model with chemical reaction as the controlling step (Levenspiel, 1972; Yang and Hlavacek, 1998, 1999). The conversion of TiO_2 is completed in 20 minutes at 400°C.

Fluidized Bed vs. Fixed Bed. The chlorination of the mixture "$TiO_2 + C$"was also performed in a fixed bed. The same sample and the same experimental setup were used. The following changes were made: (a) the gas (Cl_2) flow rate was set just below U_{mf}, and (b) the top porous disk was placed right on top of the solid sample bed to prevent the particles from fluidizing. The reaction time was 10 minutes.

Conversions of solid reactants in the fixed bed are also recorded in Figure 3. At 400°C, the conversion of TiO_2 in the fluidized bed is 2.6 times higher than that in the fixed bed. Obviously, the rate of reaction was highly enhanced by the fluidization process.

Effect of Chlorine Partial Pressure. Experiments were done in the horizontally placed reactor tube. The sample was placed in a ceramic boat (length 50 mm, width 12 mm, and depth 9 mm), which was held in the middle of the reactor tube. To eliminate the mass-transfer resistance, a flow rate of 600 mL/min was used with argon as a dilute gas. The sample (granules, $d_p = 0.044-0.15$ mm) amount was 1.6 g. The reaction temperature was 400°C and the reaction time was 5 minutes. The conversion of TiO_2 and the global conversion are plotted in Figure 5. The results indicate that at 400°C the conversion of TiO_2 and the global conversion depend linearly on the chlorine partial pressure.

Table 1. Equilibrium Mole Fractions (%) of Reaction System with Initial Reactants

Temp. (°C)	300	400	600	800	1,000	1,200
Cl	0	0	0.003	0.071	0.637	3.130
ClO	0	0	0	0	0.002	0.011
Cl_2*	66.667	66.667	66.650	66.472	65.505	62.222
O_2	0	0	0.01	0.102	0.471	1.368
$TiCl_4$	**0**	**0**	**0.01**	**0.102**	**0.472**	**1.374**
TiO_2**	33.333	33.333	33.326	33.254	32.912	31.896

*Cl_2 = 2 mol.
**TiO_2 = 1 mol.

Table 2. Equilibrium Mole Fractions (%) of Reaction System with Initial Reactants

Temp. (°C)	300	400	600	800	1,000	1,200
Ar*	50.00	50.00	50.00	50.125	57.143	56.865
CO	0	0	0	0.083	4.757	11.785
CO_2	0	0	0	0	0.003	0.002
C**	33.333	33.333	33.333	33.333	33.336	22.841
TiC	**0**	**0**	**0**	**0**	**0**	**3.282**
TiO_2†	16.667	16.667	16.667	16.376	0	0
Ti_3O_5	0	0	0	0	0	5.224
Ti_4O_7	0	0	0	0.083	4.762	0

Note: Ar was added into the reactants for convergence purpose.
*C = 2 mol.
**TiO_2 = 1 mol.
†Ar = 3 mol.

Reaction Mechanism

Two solid reactants and one or more gaseous reactants are involved in the carbochlorination process. The mechanism of this reaction system is a complicated one. Such questions as the initiation of the chlorination process and transport mechanism of the species in the solid–solid reactant system have puzzled researchers for a long time. Bergholm (1961) assumed that the formation of an unstable intermediate compound or the atomic chlorine and radicals could explain the characteristics of the $Cl_2/C/TiO_2$ reaction. He also pointed out that the gaseous diffusion is not a rate-controlling step. Dunn (1979) suggested that a gaseous titanium oxychloride species transported the titanium from the titania particle surface to the carbon surface, where it gives up its oxygen and receives chlorine to become titanium tetrachloride and to form carbon oxide.

From the results of our experiments it can be inferred that at temperatures in the range of 200 to 1,000°C, any binary reaction in the $TiO_2/C/Cl_2$ ternary component system does not take place, or takes place only with an extremely low conversion. Our thermodynamic calculations (cf. Tables 1–3) support this experimental observation. These facts lead to the following conclusions:

1. Formation of $TiCl_4$ by a direct reaction of Cl_2 with TiO_2 does not take place.

2. Direct reduction of the TiO_2 by carbon does not occur at the temperatures studied here. It is known that the reduc-

Table 3. Equilibrium Mole Fractions (%) of Reaction System with Initial Reactants

Temp. (°C)	300	400	600	800	1,000	1,200
CCl_3	0	0	0	0	0.001	0.003
CCl_4	**74.098**	**32.716**	**1.902**	**0.198**	**0.042**	**0.013**
C_2Cl_2	0	0	0	0	0	0.001
C_2Cl_6	0.014	0.005	0	0	0	0
Cl	0	0	0.003	0.071	0.639	3.154
Cl_2*	17.263	44.854	65.396	66.475	66.106	64.029
C**	8.625	22.424	32.698	33.255	33.212	32.801

*Cl_2 = 2 mol.
**C = 1 mol.

tion of TiO_2 by carbon yields the corresponding carbides; however, this is only possible when the temperature is above 6,000°C (cf. Ullmann, 1985). Therefore, chlorination at these temperatures cannot be achieved via $TiO_2 + C \rightarrow TiC$ followed by $TiC + Cl_2 \rightarrow TiCl_4$.

3. The route of $C + Cl_2 \rightarrow CCl_4$ followed by $CCl_4 + TiO_2 \rightarrow TiCl_4$ also can be neglected, since carbon reacts with chlorine extremely slowly (cf. Mellor, 1945).

The solid–solid diffusion between carbon and oxide may occur. However, since the diffusivity is of the order of magnitude of 10^{-10} to 10^{-15} cm^2/s, the diffusion process does not represent any significant mass flux and cannot be responsible for a relatively fast rate of reaction.

Owing to the facts just listed, it is reasonable to assume the following mechanism: the gaseous Cl_2 diffuses into the TiO_2/C solid–solid interface and an activated TiO_2–C–Cl complex is apparently formed. This active complex is very unstable and is instantaneously decomposed into CO and $TiCl_4$. Therefore, the concentration of the complex is very low.

The rate of formation of this active complex is the controlling step. It is affected by (a) the surface area of the TiO_2 particle, which is in contact with both carbon and chlorine; (b) the chemisorption of Cl_2 on carbon surface; and (c) the reaction temperature.

Conclusions

1. Thermodynamic calculations reveal that a complete conversion of TiO_2 by C and Cl_2 is feasible at low temperatures (even as low as 200°C).

2. By intensifying the TiO_2–C solid–solid contact, the diffusion barrier is reduced. Therefore, the carbochlorination of TiO_2 can occur with a high conversion at low temperatures (350–450°C). The conversion of TiO_2 at 385°C is 30% higher than that in the high-temperature domain (800–1,000°C). The conversion of TiO_2 at 400°C is completed in less than 20 minutes.

3. The formation of an activated TiO_2–C–Cl complex on the TiO_2/C interface accounts for the gas–solid–solid reaction mechanism.

4. The fluidized-bed reactor improves mass and heat transfer and therefore highly enhances the reaction rate.

5. The low-temperature chlorination process reduces carbon consumption substantially.

Notation

H_o = bed height before onset of fluidization, mm
H = bed height in fluidized state, mm

Literature Cited

Bergholm, A., "Chlorination of Rutile," *AIME Trans.*, **221**, 1121 (1961).

Bonsack, J. P., "Entrained-Flow Chlorination of Fine Titaniferous Materials," U.S. Patent No. 4,343,775 (1982).

Barin, I., and W. Schuler, "On the Kinetics of the Chlorination of Titanium Dioxide in the Presence of Solid Carbon," *Metall. Trans. B*, **11B**, 199 (1980)

Crosby, A. D., and M. Robinson, "Production of Metal Chlorides," European Patent 0,096,241 A1 (1983).

Dunn, W. E., Jr., "High-Temperature Chlorination of TiO_2 Bearing Minerals," *AIME Trans.*, **218**, 6 (1960).

Dunn, W. E., Jr., "High Temperature Chlorination of Titanium Bearing Minerals: Part IV," *Metall. Trans. B*, **10B**, 271 (1979).

Geldart, D., "Types of Gas Fluidization," *Powder Technol.*, **7**, 285 (1973).

Hausner, H. H., and M. K. Mal, *Handbook of Powder Metallurgy*, 2nd ed., Chemical Publishing Co., New York, p. 185 (1982).

Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed., Wiley, New York (1972).

McBride, B. J., and S. Gorden, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications," NASA Reference Publication, 1311 (1996).

Mellor, J. W., ed., *Inorganic and Theoretical Chemistry*, Vol. V, Longmans, Green, London, p. 822 (1945).

Morris, A. J., and R. F. Jensen, "Fluidized-Bed Chlorination Rates of Australian Rutile," *Metall. Trans. B*, **7B**, 89 (1976).

Robinson, M., "Production of Titanium Chlorides," UK Patent GB 2,019,373 A (1979).

Ullmann's *Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A27, p. 102 (1985).

Vijay, P. L., C. Subramanian, and C. S. Rao, "Chlorination of Rutile in Fluidized Beds," *Trans. Indian Inst. Metals*, **29**(5), 355 (1976).

Yang, F., and V. Hlavacek, "Carbochlorination Kinetics of Titanium Dioxide with Carbon and Carbon Monoxide as Reductant," *Metall. Mat. Trans.*, **29B**, 1297 (1998).

Yang, F., and V. Hlavacek, "Carbochlorination of Tantalum and Niobium Oxides. Thermodynamic Simulation and Kinetic Modeling," *AIChE J.*, **45**, 581 (1999).

Zhao, G. Y., C. W. Zhu, and V. Hlavacek, "Fluidization of Micron-Size Ceramic Powders in a Small-Diameter Fluidized Bed," *Powder Technol.*, **79**, 227 (1994).

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