Recycling Titanium from Ti-Waste by a Low-Temperature Extraction Process

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In the commercial chloride process, titanium is extracted from Ti concentrates at high temperatures (800–1,500°C), and the high-purity rutile is the primary raw material. Chlorination at high temperatures results in high-energy consumption, rapid corrosion of equipment, pipelines and control system, and agglomeration of the solid bed by the liquid byproducts. The high-purity rutile is expensive and its natural deposit is being depleted. Therefore, a low-temperature Ti extraction process using Ti-waste as the primary raw material is highly desirable. Thermodynamic equilibrium simulation of the reaction system shows that the extraction of Ti from Ti waste is feasible at a temperature as low as 200°C. In this study, a simple technology was used to remove diffusion barriers, and a low-temperature chloride process was developed. The chlorination reaction operates at 300–350°C, and Ti-waste can be used to replace the expensive rutile. Up to 80% of the titanium can be recycled in 5 min at 350°C. The extraction of other components has a relatively low extent, so a selective extraction of Ti can be achieved. A fluidized-bed reactor was used for the chlorination process. 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 occurs primarily in the minerals anatase, brookite, ilmenite, leucoxene, perovskite, rutile, and sphene. Of these minerals, only ilmenite, leucoxene, and rutile have significant economic importance. As a metal, titanium is well known for corrosion resistance and for its high strength-to-weight ratio. Approximately 95% of titanium is consumed in the form of titanium dioxide (TiO_2), a white pigment in paints, paper, and plastics. This pigment is characterized by its purity, refractive index, particle size, and surface properties. To develop optimum pigment properties, the particle size is controlled within the range of about 0.2 to 0.4 μm. The superiority of TiO_2 as a white pigment is due mainly to its high refractive index and resulting light-scattering ability, which impart excellent hiding power and brightness (Gambogi, 1998).

In the pigment industry, extraction of titanium is increasingly carried out by the chloride process. The chloride process mainly consists of reacting the natural rutile or synthetic rutile with chlorine to form titanium tetrachloride at high temperature, with carbon as the reducing agent. The titanium tetrachloride is purified and then converted directly to the TiO_2 pigment with the liberation of elemental chlorine gas by heating the vapor in the admixture with oxygen or air at high temperatures either indirectly or in a flame. The titanium tetrachloride can also be reduced to get titanium metal sponge.

The chloride process, compared to the sulfate process, generates a small amount of waste and has better titanium pigment quality. However, it has the following problems:

1. High energy consumption by operating the reactor at high temperatures and by heating the reactants and cooling the products.
2. Rapid corrosion of the process equipment, the pipelines, and the control system by the chlorine or chlorides at high temperatures.
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

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accumulate in the fluidized-bed reactor and cause a bed agglomeration and cessation of the process.

4. The high cost of the raw material, because the natural rutile deposit is limited and high-purity synthetic rutile is costly.

Investigations of the chlorination of rutile have been made by many researchers (Dunn, 1960, 1979; Bergholm, 1961; Morris et al., 1976; Vijay et al, 1976; Robinson, 1979; Bonsack et al., 1982; Crosby and Robinson, 1983). However, the common conclusion obtained was that the rate of reaction was too low if the chlorination temperature was below 800°C. Therefore, the temperatures recommended in the research articles and patents were in the range of 800–1,500°C. Yang and Hlavacek (1998, 1999a,b) and Yang (1999) studied the kinetics and mechanism of carbochlorination of different metal oxides and obtained interesting results. They also pioneered the research in the low-temperature chloride process for extraction of Ti from rutile.

Millions of tons of titanium waste are generated from the old sulfate process each year. This waste contains about 50% TiO_2, and the recovery of the titanium value from the waste is of great importance.

The objective of this work is to develop a low-temperature process to recycle the titanium from the titanium waste.

Thermodynamic Simulation

Reaction system

The reactants in the reaction system are Ti-waste, Cl_2, and carbon black (MN 1100, 14 nm, Cabot Corporation). The ratio of Ti-waste/C is 3/1 by weight.

Ti-waste is a slurry of solid particles below 200 mesh. The composition of the waste by "inductively coupled plasma-atomic emission spectrometry" (ICP-AES) is listed as follows:

SiO_2	33.76%
Fe_2O_3	2.32%
K_2O	0.52%
MgO	0.47%
TiO_2	49.00%
MnO	0.65%
CaO	0.87%
Na_2O	0.23%
Al_2O_3	3.39%
Cr_2O_3	0.07%
P_2O_5	0.01%
LOI (loss on ignition)	2.15%

Thermodynamic calculations

Chemical equilibrium calculations of the Ti-waste/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: $P_{total} = 102.1$ kPa and $T = 200$–$1{,}000$°C. The components with content higher than 1% in the Ti-waste were considered for the calculation. The initial reactants have the following composition:

$$Cl_2 = 250 \text{ g}, C = 25 \text{ g}, SiO_2 = 33.76 \text{ g},$$
$$Al_2O_3 = 3.39 \text{ g}, Fe_2O_3 = 2.32 \text{ g}, TiO_2 = 50 \text{ g}.$$

This initial reactant input simulates our chlorination experiments in which the ratio of Ti-waste/C = 3:1 by weight and a sufficient amount of Cl_2 passes through the solid bed.

Results presented in Figure 1 are the equilibrium mole fractions at different temperatures from the thermodynamic simulation of the reaction system.

From the data in Figure 1 we conclude that a complete conversion of the two major components TiO_2 and SiO_2 can be achieved at all temperatures considered. The major equilibrium products are $TiCl_4$, $SiCl_4$, CCl_4, CO, and CO_2. The formation of CCl_4 starts when the temperature is lower than 600°C and it has a very high concentration below 400°C. The carbon monoxide, CO, is the only oxide of carbon above 750°C. However, CO_2 becomes dominant below 400°C.

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

$$TiO_2\,(s) + 2C\,(s) + 2Cl_2\,(g) = TiCl_4\,(g) + 2CO\,(g) \quad (1)$$
$$TiO_2\,(s) + C\,(s) + 2Cl_2\,(g) = TiCl_4\,(g) + CO_2\,(g) \quad (2)$$
$$SiO_2\,(s) + 2C + 2Cl_2\,(g) = SiCl_4\,(g) + 2CO\,(g) \quad (3)$$
$$SiO_2\,(s) + C\,(s) + 2Cl_2\,(g) = SiCl_4\,(g) + CO_2\,(g). \quad (4)$$

Obviously, Eqs. 2 and 4 are dominant at temperatures below 400°C.

Kinetics

Role of gas – solid – solid contact

Results in the preceding subsection proved that a low-temperature Ti extraction process is thermodynamically feasible.

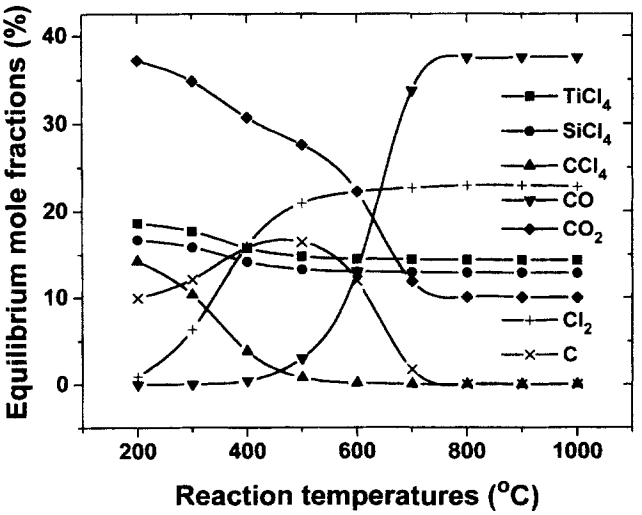

Figure 1. Chemical equilibrium in "Ti-waste + C + Cl_2" reaction system.

The problem is how to overcome the diffusion barrier to increase the rate of reaction of $TiO_2/C/Cl_2$ at a low temperature.

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 area of the three reactants, especially the solid–solid (TiO_2–C) contact, is critical for the reaction to proceed. The effect of TiO_2–C contact on the reactivity was investigated by Barin and Schuler (1980). They concluded that the rate of reaction is the highest for TiO_2–C contact and decreases with increasing TiO_2–C initial separation.

Intensification of TiO_2–C solid–solid contact

A simple technology was used to intensify the solid–solid contact.

Mixing and Milling. The Ti-waste slurry was first washed by water to remove the residual acid, and then carbon powder was added in the Ti-waste (dry basis):C = 3:1 ratio. The Ti-waste and C particles were mixed by a wet attrition ball mill. Water was the wetting agent and the weight of water in the slurry was equal to that of the Ti-waste and C mixture. Silicon nitride beads of $d = 4$ mm were used as the grinding medium. The attritor has a diameter of 150 mm and a height of 250 mm. A central shaft with arms rotating at 200 rpm produced sufficient mixing by the mechanisms of convection, shear, and diffusion.

Pelletizing. The well-mixed mixture was dried at 100°C to remove the water and then pelletized to disks with 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 1 metric ton was applied. The pellets were crushed and sieved to get granules of 0.25–0.42 mm. These granules were used in all the fluidization and chlorination experiments.

Fluidization of the Granules

The granules of the pelletized Ti-waste/C mixture fall into Group B of Geldart's classification of powder fluidization (Geldart, 1973). The fluidization of the granules of d_p = 0.25–0.42 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. The minimum fluidization velocity, $U_{mf} = 2.44$ cm/s, was determined by the data of ⟨gas velocity⟩ vs. ⟨bed pressure drop and bed height⟩ (Yates, 1983). This U_{mf} was then verified with the real reactant gas, Cl_2, at 300, 400, 600, 800 and 1,000°C. Under these conditions little particle entrainment was observed during the fluidization, and the fluidized bed behaved regularly.

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 (1200°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 a 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. Two rubber stoppers sealed both ends of the reactor tube. Chlorine and argon were introduced from the cylinders into the reactor through plastic tubing, which is connected to the rubber stopper by a short piece of glass tube. 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 $U_{mf} = 2.44$ cm/min, which is low enough to minimize the attrition among granules and particle entrainment, was selected as the superficial gas velocity for chlorination reactions. For each run, the granules (d_p = 0.25–0.42 mm) of 6 g were 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 min at a flow rate of 250 mL/min, afterwards the heating process started. As the desired temperature was reached and was maintained for 10 min for stabilization, the argon stream was shut off and chlorine was fed into the reactor at $U_f = 1.03$ cm/s. After a specified reaction time elapsed, chlorine was replaced by argon again to purge the system. Heating was maintained for 5 min to ensure the complete removal of the volatile chlorides produced. Afterwards, 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 the TGA (Model ST-736, 20–1,600°C, Harrop Industries, Columbus, OH). The conversion of Ti-waste can be easily calculated based on the preceding data. The conversions of each component in the chlorinated sample were determined by ICP-AES.

Experimental results

Effect of Milling Time. The effect of milling time was tested experimentally. Chlorination of the samples milled for 1, 2, 6, 10, 15 and 20 h showed that after milling for 2 h, the conversion of Ti-waste did not increase with milling time. Therefore, 2 h of milling is enough for sufficient mixing of the T-waste and C mixture and was used as the milling time.

Effect of Reaction Temperature. The chlorination reactions were performed at temperatures of 300–1,000°C. Conversions of Ti-waste + C were obtained, and the corresponding conversions of Ti-waste were derived as described in the subsection on reaction procedures. The results are shown in Figure 2. It can be seen that the reactivity is rather high at temperatures as low as 300°C. The conversions of Ti-waste + C and Ti-waste increased with the reaction temperature. However, these conversions did not reflect the extent of extraction of each component in the Ti-waste, in other words, the conversion of Ti.

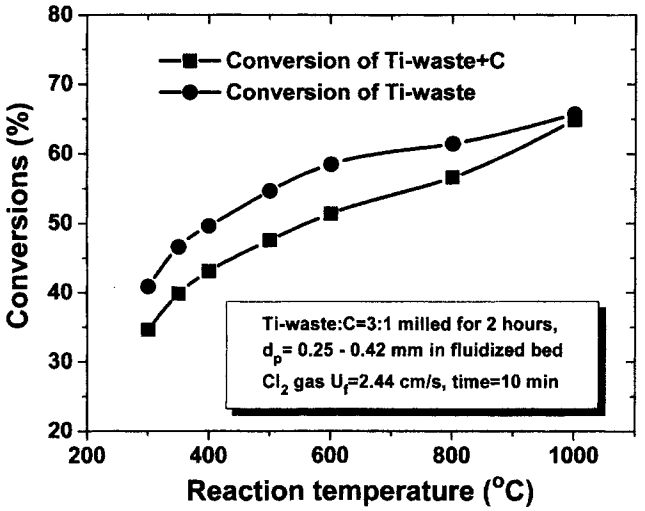

Figure 2. Global conversions of Ti-waste or "Ti-waste + C" vs. reaction temperature.

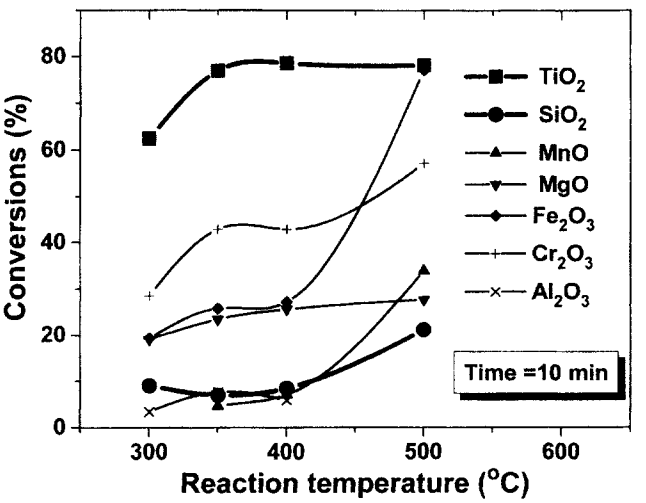

Figure 4. Conversions of each component in Ti-waste.

Effect of Reaction Time. The conversions of Ti-waste + C and the corresponding conversions of Ti-waste at different reaction times are plotted in Figure 3. The results show that the maximum extent of Ti-waste conversion is reached after chlorination for 5 min.

Conversion of Each Component in the Ti-waste. Samples after chlorination were pretreated and then analyzed by ICP-AES to get the compositions of the samples. The pretreatment of the chlorinated samples included burning the residue carbon, removal of the nonvolatile chlorides by dissolving/washing them using water, and drying the samples. The mass loss for each step was recorded and the conversion of each component was then calculated.

Selectivity of Extraction vs. Temperature. Figure 4 shows the conversions of the two major components and some of the minor components in the Ti-waste after chlorination for 10 min at temperatures of 300–500°C. The conversion of TiO_2 increases with temperature from 300° to 350°C. Further increase of the temperature does not contribute to any increase of the TiO_2 conversion. The conversion of SiO_2 at 300–400°C is below 10%. However, it increases rapidly with temperatures above 400°C. The minor components have also low conversion below 400°C. It is obvious that chlorination at 300–400°C selectively extracts Ti from the Ti-waste, which reduces the load of the downstream separation process. Reactions at higher temperatures increase the global conversion (or conversions of undesired components) but not the conversion of TiO_2.

Extent of Ti Extraction vs. Time. Figure 5 represents the time dependence of TiO_2 conversion at 350°C. The conversion of TiO_2 does not increase with reaction time after 5 min, which is the same as the results presented in the subsection on the effect of reaction time.

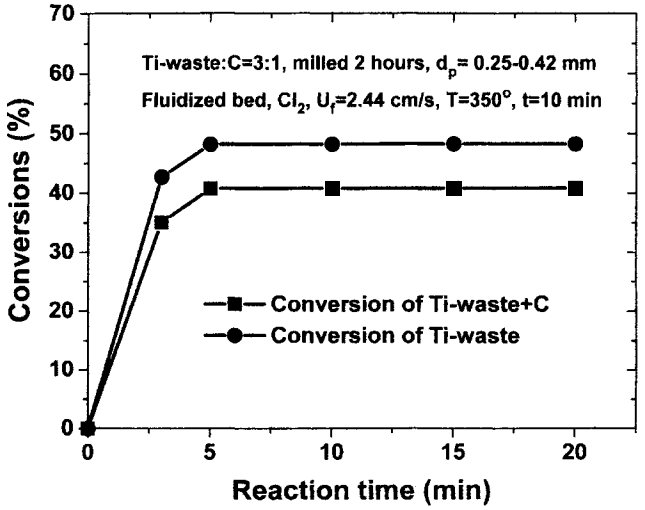

Figure 3. Global conversions of Ti-waste or "Ti-waste + C" vs. reaction time.

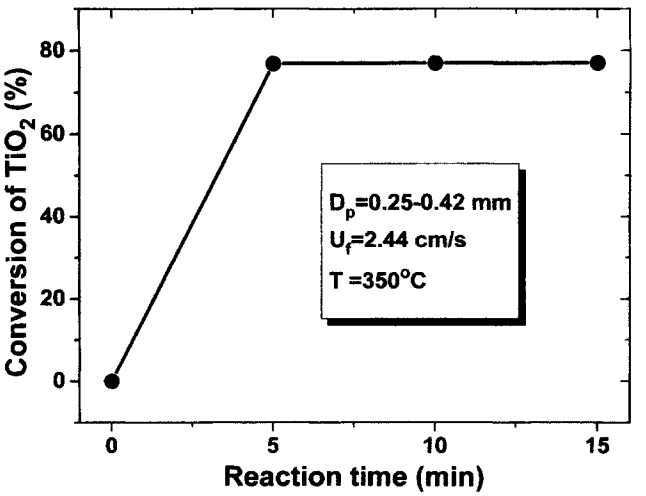

Figure 5. Conversion of TiO_2 vs. reaction time.

Conclusions

1. Thermodynamic calculations reveal that complete extraction of TiO_2 by C and Cl_2 is feasible at a temperature as low as 200°C.

2. By introducing milling and pelletization steps, the TiO_2–C solid–solid contact is improved and the diffusion barrier is substantially reduced. Therefore, the extraction of Ti is realized at low temperatures (350–400°C).

3. Chlorination at low temperatures (350–400°C) can selectively extract the titanium from the Ti-waste, because the other undesired components have relatively low reactivity at low temperatures.

4. Ti-waste can be used as a primary raw material as a substitute of the expensive rutile. Eighty percent of titanium in the waste can be recycled at 350°C in 5 min.

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

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