

# A thermochemical and experimental study for the conversion of ilmenite sand into fine powders of titanium compounds

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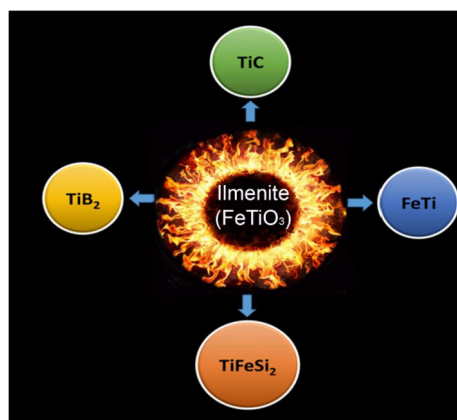
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## HIGHLIGHTS

- Natural ilmenite was used as a precursor for synthesizing Ti compounds.
- Combustion temperatures and phases were determined in FeTiO<sub>3</sub>-αMg-C(B, Si)-kNaCl system.
- The effect of Mg and NaCl concentration on the combustion temperature was revealed.
- The ilmenite was converted into FeTi, TiC, TiB<sub>2</sub>, and TiFeSi<sub>2</sub> fine powders.
- A reduction pathway in the synthesis of Ti- compounds was proposed.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

The adiabatic temperatures and equilibrium phases in the FeTiO<sub>3</sub>-αMg-C(B, Si)-kNaCl system (where α = 0.2–15, k = 0–3) were analyzed to predict the formation of fine powders of titanium compounds from natural ilmenite sand. From the parametric study, the critical variables were identified and optimized for the synthesis of FeTi, TiC, TiB<sub>2</sub>, and TiFeSi<sub>2</sub> under a combustion regime. The experimentally measured temperatures were in good agreement with those predicted from thermochemical calculations in the 900–1800 °C range. The purified products were characterized using X-ray diffraction, transmission electron microscopy, and Raman spectroscopy. The fine powders of titanium compounds were mainly single phase with a purity of at least 95 wt %. Considering the various stages of the synthetic process, a mechanism is proposed to explain how the process of ilmenite recovery occurred.

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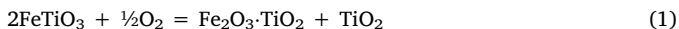
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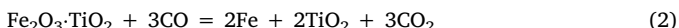
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## 1. Introduction

Ilmenite is a titanium-iron oxide mineral with an idealized formula of  $\text{FeTiO}_3$ . From a commercial perspective, ilmenite is the most important ore of titanium dioxide. An industrial process (the Becher process) to upgrade ilmenite ore to synthetic rutile ( $\text{TiO}_2$ ) has been developed [1,2]. In the Becher process, ilmenite is heated in air in a rotary kiln to oxidize the iron to  $\text{Fe}^{3+}$ . This allows the treatment of weathered ilmenites with a wide range of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios by converting them to a uniform material more suited to the subsequent reduction step, as represented by Eq. (1).



Oxidized hematite is heated to approximately 1200 °C in a separate coal-fired kiln to give metallic iron and rutile ( $\text{TiO}_2$ ) by the reduction of “pseudo-brookite” ( $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ ) with CO.



Then, agitation of the reaction product in 1%  $\text{NH}_4\text{Cl}$  solution with aeration results in the formation of a fine iron oxide powder, which is separated from the coarser “synthetic rutile.”

Besides the fabrication of rutile, ilmenite is also used to produce ferrotitanium alloys ( $\text{FeTi}$  and  $\text{Fe}_2\text{Ti}$ ). These processes are known as ilmenite reduction methods, and they can be classified into two main groups: (1) aluminothermic reduction and (2) electrochemical reduction in molten electrolyte. The aluminothermic reduction is a batch process in a refractory-lined crucible or an electric furnace, depending on the process variation [3,4]. Aluminum metal is generally used as a reducing agent, and the ilmenite is mixed with powdered aluminum metal, preheated to 400–600 °C, and ignited. The exothermic reaction between Al and  $\text{FeTiO}_3$  produces a molten ingot of  $\text{FeTi}$ , which is mechanically separated from the  $\text{Al}_2\text{O}_3$  slag.

The electrochemical reduction of ilmenite into  $\text{FeTi}$  is a laboratory-scale process and is performed in the molten electrolyte, such as  $\text{CaCl}_2$ – $\text{NaCl}$  [5–7],  $\text{CaCl}_2$  [8,9], and  $\text{LiCl}$ – $\text{KCl}$  and  $\text{LiCl}$ – $\text{KCl}$ – $\text{CaCl}_2$  [10]. During the reduction,  $\text{FeTi}$  and  $\text{Fe}_2\text{Ti}$  are deposited on the cathode at 700–800 °C when a 3.0–3.2 V cell voltage is applied. This process produces porous ferrotitanium, which, after crushing, is converted to micrometer-sized powder. However, the large amount of salt used in the experiment makes the electro reduction of ilmenite less effective and a high-cost process.

Technologically, the reduction of ilmenite by magnesium is considered a promising process for obtaining not only ferrotitanium but also some refractory compounds of Ti. It has already been shown that magnesiothermic reduction is promising for the reduction of metal oxides, halides, and other salts [11–14], as well as the synthesis of nanostructures of refractory metals (for example, Ti, Zr, W, and Mo), carbides (for example,  $\text{TiC}$ ,  $\text{WC}$ ,  $\text{SiC}$ , and  $\text{MoC}$ ) [15–18], and nanoporous inorganic materials, such as silicon, graphene, and silicon–carbon composites for use in lithium-ion batteries [19–21]. Despite the importance of ilmenite as a commercially available starting material for titanium, its reduction by magnesium has been studied very little. In an early report by Welham et al. [22], a mixture of  $\text{FeTiO}_3$ – $\alpha\text{Mg}$  (where  $\alpha = 1, 2$ , or 3) was prepared and ball milled for 100 h in a laboratory ball mill, yielding useful products. However, only binary and complex oxides ( $\text{TiO}_2$ ,  $\text{Ti}_3\text{O}_5$ , and  $\text{MgTiO}_3$ ) were obtained in this process, and no alloy phases were detected. In Ref. [23], the combustion synthesis of  $\text{TiFe}$  alloy powder by the magnesiothermic reduction of ilmenite is reported. According to the XRD analysis, multiphase products consisting of  $\text{MgO}$ ,  $\text{Mg}_2\text{TiO}_4$ ,  $\text{TiO}$ ,  $\text{TiFe}$ ,  $\text{TiFe}_2$ , and  $\text{Fe}$  were obtained. In addition, an acid leaching process was conducted to dissolve the oxide phases. The authors claim that after more than 10 h of acid leaching, they were able to obtain  $\text{FeTi}$  and  $\text{Fe}_2\text{Ti}$  alloy powders. However, the acid leaching procedure was not reported.

In this paper, we report a general combustion strategy for a number

of titanium compounds ( $\text{FeTi}$ ,  $\text{TiC}$ ,  $\text{TiB}_2$ , and  $\text{TiFeSi}_2$ ) using a  $\text{FeTiO}_3$ – $\alpha\text{Mg}$ – $k\text{NaCl}$ – $\text{C}$  (B, Si) precursor mixture (where  $\alpha$  and  $k$  are the number of moles of Mg and NaCl, respectively). The amount of Mg ( $\alpha$ ) was varied in the range of 0.2–15 mol to provide adjustable combustion parameters and control of the phase composition and combustion product morphology. Thermochemical analysis and experimental data allowed us to propose a chemical pathway for the conversion of ilmenite to Ti-containing compounds, such as  $\text{FeTi}$ ,  $\text{TiC}$ ,  $\text{TiB}_2$ , and  $\text{TiFeSi}_2$ .

## 2. Experimental

### 2.1. Materials

Ilmenite sand with a particle size in the range of 100–600  $\mu\text{m}$  was purchased from SKY Machinery Co. Ltd, Australia. Before mixing with other components, the ilmenite sand was ground into a fine powder with a particle size of less than 50  $\mu\text{m}$ . Magnesium powder (99% pure, particle size: 50–200  $\mu\text{m}$ ), NaCl powder (99.5% purity; particle size  $\leq 120 \mu\text{m}$ ), and black soot (purity 99%) were purchased from Samchun Chemicals and Metals Co., Ltd., Korea. Silicon powder (purity 99.5%, particle size  $\leq 45 \mu\text{m}$ ) was obtained from Junsei Chemicals, Japan. Amorphous boron powder (purity 95%, particle size  $\leq 5 \mu\text{m}$ ) was purchased from Haihang Industry Co. Ltd, China.

### 2.2. Synthesis and purification

The synthesis involves two main steps: magnesiothermic reduction of ilmenite under the combustion regime and acid leaching of the combustion products (Fig. 1). In a typical experiment, approximately 100 g of the initial mixture was prepared and compacted by hand in a paper cup (diameter: 4.0 cm, height: 7–8 cm). The cup containing the reaction mixture was subsequently placed under a nickel/chromium coil in a combustion chamber. The reactor was tightly sealed, and the air was pumped out with a vacuum pump. Subsequently, the reactor was filled with argon to a pressure of 2.0 MPa. Local ignition of the reaction sample was achieved within 1–2 s using a nickel-chromium filament electrically heated to 900–1000 °C (Fig. 1, step 1).

The surface layer of the combusted sample was mechanically removed, and the remaining sample was ground by hand and placed in a 500-mL beaker for acid leaching (Fig. 1, step 2). The reaction by-products were dissolved in diluted  $\text{HNO}_3$  solution at room temperature for 30 min. Then, the acid-leached powder was washed with distilled water, rinsed with ethanol, and dried at 80–100 °C.

### 2.3. Analytical methods

Thermochemical analysis of the adiabatic combustion temperature and the equilibrium composition of reaction species was carried out using the “THERMO” software package [24]. The amount of each phase was calculated as a function of temperature based on the minimization of the Gibbs free energy. “THERMO” does not account for the kinetics of the chemical reactions. Thus, it can only approximate the actual system. Nevertheless, the results enable the rapid screening of the appropriate scope of reaction conditions that should be studied through experiment, thereby minimizing expensive trial-and-error chemistry.

The crystal structures and morphologies of the final powders were characterized using an X-ray diffractometer with  $\text{Cu K}\alpha$  radiation (XRD, PANalytical X'Pert Pro, Netherlands). Field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F, Japan) and transmission electron microscopy (TEM, JEOL JEM-2100F, Japan) were used for microstructural characterization of the purified products. Raman scattering spectra were obtained at room temperature using a Horiba Jobin Yvon LABRAM-HR800 laser micro-Raman spectrometer with a 514-nm laser.

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