



Direct magnesiothermic reduction of titanium dioxide to titanium powder through combustion synthesis

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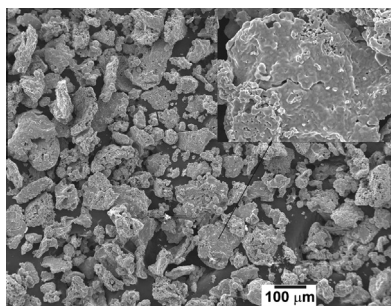
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HIGHLIGHTS

- Combustion process in TiO₂–Mg–Ca(OH)₂ system is investigated under argon pressure.
- The maximum temperature was between 1650 and 1690 °C during the combustion. was measured.
- Ti powder with 1.5 wt% of oxygen was obtained after acid-leaching of as-combusted sample.
- A deoxidation by Ca at 850–900 °C resulted 50–300 μm size Ti aggregated containing 0.2–0.3 wt% O₂.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnesium was used as a reductant to synthesize directly titanium powder from titanium oxide (TiO₂) through combustion. The feed material (TiO₂), reductant (Mg), and calcium hydroxide (Ca(OH)₂) were mixed and combusted under pressure in an argon atmosphere. The temperature–time profiles were intermittently measured during combustion in order to analyze the combustion temperatures and wave velocities. The combustion product was subsequently leached to produce Ti powder with ~1.5 wt% oxygen. The Ti powder was further deoxidized with calcium to decrease the oxygen content in the powder to 0.2–0.3 wt%. The morphology and size of the Ti particles was examined, and the mechanism by which Ca(OH)₂ reduced the content of oxygen in the Ti powder was discussed.

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1. Introduction

Titanium is a lightweight, very strong, and highly corrosion-resistant material. Thus, it has recently been applied to a broader range of applications, so the demand for Ti is increasing. The high strength-to-weight ratio of titanium is advantageous in the aerospace and transport industries; the excellent corrosion resistance makes it an obvious choice in the chemical, petrochemical, and maritime industries; and the biocompatibility of Ti enables numer-

ous medical applications to be developed [1–3]. At present, titanium is industrially manufactured using the Kroll process [4], which is based on the magnesiothermic reduction of titanium chloride. Despite numerous large-scale modern facilities that are dedicated to metal production through the Kroll process, titanium is not currently being used in its full range of potential applications mostly because the cost of producing titanium is significantly higher than that of producing either aluminum or steel. Much of the high cost of producing titanium is attributed to the expensive and inefficient processes used to produce it. Therefore, many researchers are trying to develop more efficient methods of reduction as alternatives to the Kroll process. Chen et al. [5] directly electrochemically reduced TiO₂ to titanium metal in molten CaCl₂.

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Despite the inherent low current efficiency of their process, which is named the Fray–Farthing–Chen (FFC) Cambridge process, has been reported as successful at the laboratory scale. The FFC is currently scaling for industrial production of titanium powder [6]. Ono and Suzuki [7] developed a similar method by calciothermally reducing TiO_2 powder in molten CaCl_2 . Okabe et al. [8,9] used calcium as a reductant to develop a method of reducing titanium in which titanium powder was prepared from TiO_2 through an electronically mediated reaction (EMR).

These methods of directly reducing titanium oxide to Ti metal have the potential to be the next-generation methods of producing titanium. However, they have some drawbacks that must be overcome before they can be commercialized. Specially, a large amount of molten salt is required, and the reduction process is slow. Therefore, magnesiothermally reducing TiO_2 without using a molten salt is a very attractive and promising alternative for a next-generation method of synthesizing titanium powder. Many technological steps (especially the chlorination of TiO_2) do not have to be used when TiO_2 is used as a raw material and Mg is used as a reductant. Bolivar and Friedich [10] used a mixture of TiO_2 and Mg in a molar ratio of 1:3 under an argon atmosphere. The mixture was heated at 12 °C/min to 800 °C during the synthesis. They found that MgO, $\text{Mg}_{1.5}\text{Ti}_{1.5}\text{O}_4$, Ti, and Ti_2O were in the final product. They achieved TiO_2 reductions in the range 78–83% (or 7–9 wt% oxygen). Kubaschewski and Rostron magnesiothermally reduced TiO_2 powder [11,12]. Although Kubaschewski obtained titanium with 2.8 wt% oxygen, the best oxygen content in the Rostron experiments was only 4.0 wt%.

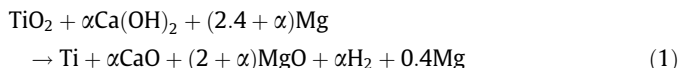
In early 1980, Frolov and Fetsov [13] first attempted to produce Ti powder from a precursor mixture of TiO_2 and Mg in a molar ratio of 1:2 through combustion. Unfortunately, no details about the powder characteristics are available in the literature. We have recently synthesized Ti powder through an exothermic reaction between TiO_2 and Mg mixed in a 1: to 1:4 molar ratios [14]. We manipulated with Mg concentration to produce Ti powder with low oxygen. The best oxygen content in our experiments was only 2.5 wt% that was reached with 2.7 mol of Mg.

In this study, a two-stage process consisting of the combustion synthesis of titanium powder from TiO_2 –Mg– $\text{Ca}(\text{OH})_2$ mixture, and the high-temperature deoxidation of as-prepared Ti powder with metallic calcium was fundamentally researched to produce Ti powder with a low oxygen (less than 0.3 wt%). Here, we present some basic laboratory-scale experimental evidence to illustrate this concept. The technical aspects reported in this paper may be very useful for developing a method of magnesiothermally reducing TiO_2 to Ti metal on an industrial scale.

2. Experimental

Titanium dioxide rutile powder (TiO_2 , 99% pure, particle size: 0.1–0.3 μm , Millennium, USA), magnesium powder (Mg, 99% pure, particle size: 50–300 μm , Samchun Pure Chemical Co., Ltd., South Korea), calcium hydroxide powder ($\text{Ca}(\text{OH})_2$, 98% pure, particle size: <5–50 μm , Samchun Pure Chemical Co., Ltd.), and granular calcium (Ca, 99.5% pure, granule size: 2–5 mm, Junsei Chemical Co., Ltd.) were used in the experiments.

The Ti metal was prepared in a two-stage process consisting of the combustion synthesis of titanium powder and the high-temperature deoxidation of the powder with metallic calcium. The general reaction for synthesizing Ti powder is as follows:



here α shows the mol number of $\text{Ca}(\text{OH})_2$ used in the experiments. The flow diagram of entire process is shown in Fig. 1. For the com-

busion experiment, approximately 280–300 g of the mixture was hand-compacted into a 6.0-cm-diameter, 10–12-cm-high stainless steel cup. Two 100- μm -diameter, -shaped tungsten–rhenium thermocouples (WR-26/WR-5) were placed inside the sample near the central part during compaction. The thermocouples were preliminarily placed into thin ceramic pipes to prevent the thermocouples from reacting with the powder bed at elevated temperatures. Approximately 3–5 g of an exothermic mixture composed of Ti + 0.9C (black soot) + 0.1[(C_2F_4)_n–Teflon®] was used as an agent to easily ignite the reaction sample and was placed on top of it. The cup containing the reaction mixture and thermocouples was subsequently placed under a nickel/chromium coil in a combustion chamber. The chamber was then evacuated and filled with argon to 2.0 MPa pressure. A nickel–chromium filament electrically heated to 900–1000 °C was used to ignite locally the reaction sample within 1–2 s. A computer-assisted data logger (GL100A, Graphtec Co., Japan) continuously recorded the temperature–time history of the process at 10 Hz. The combustion velocity was calculated as $U_c = x/t$, where x represents the physical distance between the thermocouples, and t represents the length of time that elapsed between the start of combustion and the arrival of the combustion front at each thermocouple.

The burnt sample was cooled to room temperature. The surface layer (1–2 mm) of the sample was mechanically cleaned, and the sample was transferred to a 2.0-L beaker for further purification. The sample was purified by mixing it with dilute HNO_3 and by magnetically stirring the mixture on a cold plate to remove the reaction byproducts (i.e., MgO, CaO, and Mg). The acid-leached powder was rinsed with distilled water and subsequently dried at 80–100 °C. As-synthesized Ti powder was then prepared for deoxidation by mixing it with the Ca granules (5–10 wt%) and by filling the mixture into an alumina boat. The reaction mixture was deoxidized in an argon atmosphere in a laboratory pipe furnace at 850–900 °C for 2 h. The deoxidized reaction product was

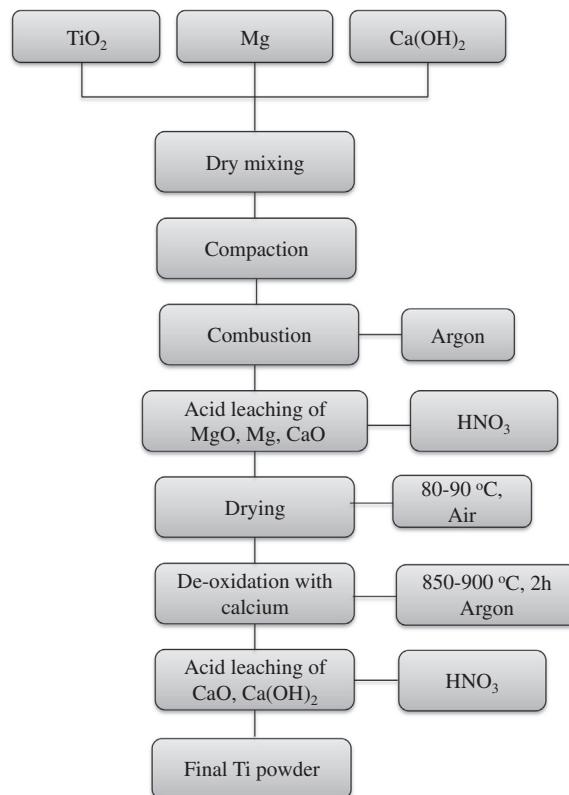


Fig. 1. Process flow diagram.

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