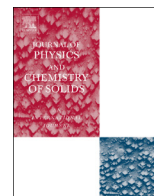




ELSEVIER

Contents lists available at ScienceDirect

## Journal of Physics and Chemistry of Solids

journal homepage: [www.elsevier.com/locate/jpcs](http://www.elsevier.com/locate/jpcs)

# Rapid reduction of titanium dioxide nano-particles by reduction with a calcium reductant



Tatsuya Kikuchi<sup>a,\*</sup>, Masumi Yoshida<sup>a</sup>, Shiki Matsuura<sup>b</sup>, Shungo Natsui<sup>a</sup>, Etsuji Tsuji<sup>a</sup>, Hiroki Habazaki<sup>a</sup>, Ryosuke O. Suzuki<sup>a</sup>

<sup>a</sup> Faculty of Engineering, Hokkaido University, N13-W8, Kita-ku, Sapporo 060-8628, Hokkaido, Japan

<sup>b</sup> Graduate School of Chemical Science and Engineering, Hokkaido University, N13-W8, Kita-ku, Sapporo 060-8628, Hokkaido, Japan

## ARTICLE INFO

## Article history:

Received 1 March 2014

Received in revised form

10 April 2014

Accepted 28 April 2014

Available online 4 May 2014

## Keywords:

Electronic materials

Metals

Microporous materials

Chemical synthesis

Microstructure

## ABSTRACT

Micro-, submicron-, and nano-scale titanium dioxide particles were reduced by reduction with a metallic calcium reductant in calcium chloride molten salt at 1173 K, and the reduction mechanism of the oxides by the calcium reductant was explored. These oxide particles, metallic calcium as a reducing agent, and calcium chloride as a molten salt were placed in a titanium crucible and heated under an argon atmosphere. Titanium dioxide was reduced to metallic titanium through a calcium titanate and lower titanium oxide, and the materials were sintered together to form a micro-porous titanium structure in molten salt at high temperature. The reduction rate of titanium dioxide was observed to increase with decreasing particle size; accordingly, the residual oxygen content in the reduced titanium decreases. The obtained micro-porous titanium appeared dark gray in color because of its low surface reflection. Micro-porous metallic titanium with a low oxygen content (0.42 wt%) and a large surface area ( $1.794 \text{ m}^2 \text{ g}^{-1}$ ) can be successfully obtained by reduction under optimal conditions.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Metallic calcium can easily reduce a large number of metal oxides directly to metals because calcium has a strong reducing ability. The reduction of metal oxides with a calcium reductant in calcium chloride molten salt at high temperature, well known as the calciothermic reaction, has long been widely investigated by many researchers. During oxide reduction, calcium chloride molten salt acts as a suitable solvent and has a high solubility for calcium and calcium oxide as a byproduct formed by reduction. Metallic titanium [1], zirconium [2], hafnium [3], niobium [4], tantalum [4], vanadium–titanium [5], titanium–aluminum–vanadium [6], titanium–chromium [7–9], samarium–iron [10], and niobium aluminide [11] are formed via reduction of these oxides with a calcium reductant in calcium chloride molten salt. The residual oxygen in the reduced metal decreases continuously by deoxidation with a calcium reductant [4]. Pure metals, alloys, and intermetallic compounds with a lower residual oxygen content can be successfully fabricated by a one-step reduction technique. Reduction with a calcium reductant is a simpler technique for the production of these metals without complicated processes such as the Kroll process, although reduction is a batch-type production method.

In recent years, a method for the successive reduction of metal oxides was developed by electrolysis in calcium chloride and calcium oxide mixture molten salts. Ono and Suzuki reported that calcium oxide in molten calcium chloride becomes the reductant source for the reduction of metal oxides during constant-voltage electrolysis [12]. For example, metallic calcium formed electrochemically at a cathode reacts with metal oxides, and reduced metals with a low residual oxygen content can be formed (OS (Ono and Suzuki) Kyoto process). Metallic titanium [13–15], niobium [16], nickel [17], and other alloys and intermetallic compounds [18,19] can be formed via the OS process. In addition, the electrochemical decomposition of carbon dioxide gas by an advanced OS process using a solid electrolyte anode has been reported [20,21]. Fray, Farthing, and Chen investigated the cathodic deoxidation of metal oxides in calcium chloride and calcium oxide mixture molten salts and reported the production of metallic titanium [22–26], iron [27], chromium [28], zirconium [29], hafnium [30], tantalum [31], and other alloys [32–34] through the FFC (Fray, Farthing, and Chen) Cambridge process. Several other research groups have also investigated the successive reduction of metal oxides based on electrolysis in molten calcium chloride [35–43].

Very recently, the authors have investigated the fabrication of a metallic titanium and zirconium micro-porous alloy by reduction with a calcium reductant in calcium chloride molten salt for novel electrolytic capacitor applications [44]. It is known that defect-free,

\* Corresponding author. Tel.: +81 11 706 6340; fax: +81 11 706 6342.

E-mail address: [kiku@eng.hokudai.ac.jp](mailto:kiku@eng.hokudai.ac.jp) (T. Kikuchi).

high-capacitance composite anodic oxide films can be formed on substrates by anodizing a Ti–62.5 at% Zr alloy [45–51]. Therefore, a simple fabrication process for creating a micro-porous Ti–Zr alloy with large surface area must be developed to create novel Ti–Zr capacitors. In our previous investigation, a metallic Ti–Zr alloy was formed by reduction in the presence of excess calcium reductant and possessed a micro-porous morphology because of the sintering of each reduced oxide particle during the reduction. The micro-porous alloy, which had a low oxygen content (0.20 wt%) and a large surface area ( $0.55 \text{ m}^2 \text{ g}^{-1}$ ), was successfully obtained under optimal reduction conditions. In this investigation, titanium and zirconium oxide micro-particles measuring a few  $\mu\text{m}$  in diameter were used as the starting materials for reduction. Reduction using smaller oxides, including submicron- and nano-particles, may yield the following advantages for electrolytic capacitor applications: (a) an increase in the reduction rate, (b) an increase in the surface area of the reduced metal micro-porous structure, (c) a decrease in the residual oxygen content in the reduced alloy, and (d) the formation of an alloy with uniform chemical composition. Conversely, the residual oxygen content may increase with decreasing the particle size because of re-oxidation of the titanium surface during the washing step. Therefore, the residual oxygen content will be a compromise between these advantages and disadvantages.

In the present investigation, we studied the effect of particle size on the reduction of titanium dioxide to metallic titanium through reduction with a calcium reductant in calcium chloride molten salt. In the process, titanium dioxide micro-, submicron-, and nano-particles as the starting oxide materials were reduced by calcium in molten salt at high temperature. The reduction of submicron- and nano-particles was expected to rapidly yield metallic titanium micro- or nano-porous structures with large surface area. The reduction rate, residual oxygen content, and obtained metallic titanium morphology were investigated from the viewpoint of novel electrolytic capacitor applications, and the reduction mechanism of the calcium reductant was also examined.

## 2. Experimental

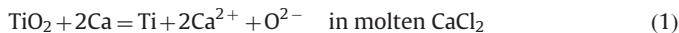
### 2.1. Starting materials

Three types of commercially available titanium oxide powders were used as the starting materials: micro-particles (99.9 wt%, average diameter of particles,  $D=2.0 \mu\text{m}$ , determined by scanning electron microscopy (SEM), Furuuchi Chemical, Japan), submicron-particles (99.99 wt%,  $D=90 \text{ nm}$ , identified by SEM, Ishihara Sangyo, Japan), and nano-particles (99.986 wt%,  $D=13 \text{ nm}$ , identified by BET method, Tecnan, Spain). The oxides and anhydrous calcium chloride (99.0 wt%, Kojundo Chemical Laboratory, Japan), which was used as a molten salt, were dried in a vacuum oven at 473 K for several hours. Metallic calcium lumps (99.0 wt%, Hitachi Alloy, Japan) were also used as a reductant for the reduction of titanium oxides in molten salt.

### 2.2. Reduction of titanium oxide

Oxide powder (2.0 g), calcium chloride (100 g), and metallic calcium (3.0 g) were placed in a titanium crucible (SH-632B-Ti, Sugiyama-Gen, Japan). The crucible was set in a SUS316L stainless steel vessel, and the vessel was covered by two large SUS316L plates and screws. The vessel was placed in a reaction chamber (SUS316L), and the chamber was then slowly heated to 873 K within 30 min under vacuum conditions. The temperature was held at 873 K for 10 min to remove residual moisture from the materials. After the removal of moisture, argon gas (101.3 kPa) was introduced into the chamber. The temperature was then gradually

increased to 1173 K within 10 min and held for an additional 15–360 min for the reduction of titanium oxides by the calcium reductant (melting point,  $T_m=1112 \text{ K}$ ) in the calcium chloride molten salt ( $T_m=1045 \text{ K}$ ). The reduction of titanium oxides can be expressed by the following reaction:



The theoretical amount of metallic calcium required for the complete reduction of titanium oxides was defined as  $e=100\%$ , and the quantities of metallic calcium used as the reductant were adjusted to  $e=150\%$  (50% excess calcium, 3.0 g) because of the small amount of liquid calcium that evaporated from the surface of the molten salt. In a previous investigation, we observed that excess calcium reductant caused the complete reduction of titanium and zirconium oxides. The details of the reduction setup used in the present investigation have been described elsewhere [44].

After reduction, the reaction chamber was cooled to room temperature for 12 h. The titanium crucible was removed from the vessel and then washed with water to remove the solidified calcium chloride salt. The reduced materials obtained from the crucible bottom were washed again with acetic acid, ethanol, and acetone to remove residual impurities. Finally, the materials were dried and stored in a vacuum desiccator.

The phase composition of the obtained materials was identified by X-ray diffraction analysis (XRD, XpertPro, Phillips). The residual oxygen content in the materials was quantitatively analyzed by an inert gas fusion-infrared absorption method using an oxygen/nitrogen analyzer (TC600, LECO). Structural changes in the materials caused by reduction were examined by SEM (Miniscope TM-1000, Hitachi). The specific surface area of the specimens was determined by the Brunauer, Emmett, and Teller method (BET, BELSORP-mini, BEL Japan).

## 3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the  $\text{TiO}_2$  (a) micro-, (b) submicron-, and (c) nano-particles, which were prepared as the starting materials for reduction. In the case of the micro-particles (Fig. 1a), strong diffraction peaks from the rutile phase and weak peaks from the anatase phase were detected. Specifically, the  $\text{TiO}_2$  micro-particles were identified as rutile micro-particles accompanied by a small amount of anatase micro-particles. In

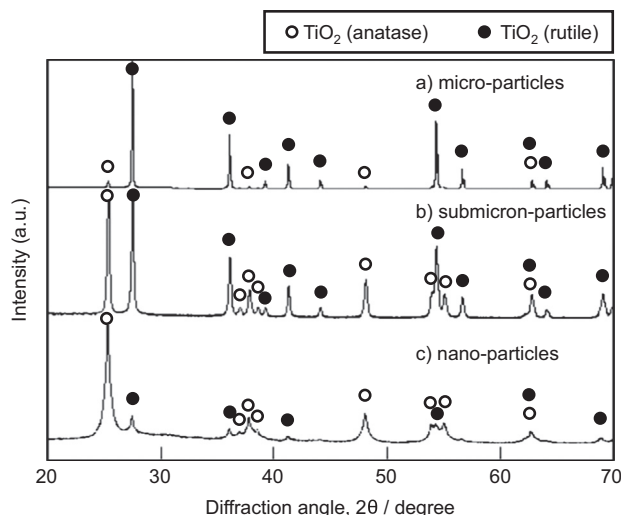


Fig. 1. X-ray diffraction patterns of the  $\text{TiO}_2$  (a) micro-, (b) submicron-, and (c) nano-particles as the starting materials for reduction with a calcium reductant.

Download English Version:

<https://daneshyari.com/en/article/1515693>

Download Persian Version:

<https://daneshyari.com/article/1515693>

[Daneshyari.com](https://daneshyari.com)