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Reduction of Titanium Dioxide to Metallic Titanium Conducted under the Autogenic Pressure of the Reactants

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We report on a reaction to convert titanium dioxide to titanium. The reduction reaction was done under the autogenic pressure of the reactants at 750 °C for 5 h. The MgO, a by- product, was removed by acids to obtain pure metallic titanium.

1. Introduction

Metallic Titanium shows excellent physical and chemical properties, such as low density, high corrosion resistance at high temperatures, good mechanical strength, ductility, and fatigue resistance. It also exhibits a good biocompatibility and bio integration with the human body.[1]

Several techniques are currently used to synthesize Titanium. The first, is an electrochemical method for the direct reduction of solid TiO_2 in which the oxygen is ionized, dissolved in a molten salt, and discharged at the anode, leaving pure titanium at the cathode.[2,3]

The most popular method is the Kroll process. At the first step TiO_2 is converted to $TiCl_4$, after which titanium is produced by the reduction of titanium tetrachloride with an active metal such as magnesium at 800−900 °C according to the following reaction:[4−8]

$$2Mg_{(l)} + TiCl_{4(g)} \rightarrow 2MgCl_{2(l)} + Ti_{(s)}$$

The byproduct, $MgCl_2$, is removed by vacuum distillation, which complicates this process. The titanium is only partially reduced in the process and lower chlorides such as $TiCl_2$ and $TiCl_3$ are also obtained. Their removal makes the process very costly. Moreover, attempts in the electrochemical synthesis to separate the electrodeposited titanium from the ionic solutions have been hampered by difficulties. The current paper presents a simple process to convert TiO_2 to Ti, termed "RAPET" (**R**eaction under **A**utogenic **P**ressure at **E**levated **T**emperature). The RAPET reaction takes place in a closed cell (made of parts of the Swagelok company), and has been described elsewhere.[9,10] The union (made by Swagelok) is filled with the reactants, and the reaction is conducted without a catalyst or a solvent at high temperature and pressure. The pressure in the cell is generated from the evaporation of the reactants or the products, and the Swagelok union serves as a relief valve at 160 atm.

2. Experimental Details

All chemicals were obtained from Aldrich. A 3 mL closed vessel cell was assembled from stainless steel parts (Swagelok). A 3/8″ union part was plugged from both sides by standard caps. For this synthesis, 0.5 g of titanium dioxide (anatase) and 0.3 g of magnesium powder were introduced into the cell, and the cell was closed tightly at room temperature under nitrogen atmosphere (in a nitrogen- filled glovebox). The cell (Swagelok) was placed inside an iron pipe at the center of the tube furnace. The temperature was raised at a rate of 10 °C per minute. The closed cell was heated at 750 °C for 5 h. The reaction proceeded under the autogenic pressure of the precursor. The closed vessel cell (Swagelok) was gradually cooled (5 h) to room temperature. Magnesium oxide was removed by treatment with an aqueous solution of acetic acid for 1 day. The sample was collected by centrifugation (9000 rpm for 20 min, Hettich Universal 32) and was washed twice with water, once with ethanol, and then dried. Since we observed that not all the MgO was dissolved we continued the treatment by placing the products for an additional 2 days in formic acid, after which the washing and drying was repeated.

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Instruments. X- ray diffraction (XRD) patterns were collected using a Bruker AXS Advance powder X-ray diffractometer (Cu Kα radiation). Transmission electron microscope measurements were carried out using a transmission electron microscopy (TEM) instrument FEI Tecnal spirit 120 KV spirit biotwin. Samples for TEM were prepared by ultrasonically dispersing the products into absolute ethanol, placing a drop of this suspension onto a copper grid coated with an amorphous carbon film or onto a copper plate, and then drying in vacuum. High resolution TEM (HRTEM) was measured using a JEOL JEM-2100 electron microscope. The morphologies and nanostructure were characterized with a high-resolution scanning electron microscope (HRSEM) JEOL-JSM 840. Specific surface areas were measured by the Brunauer−Emmett−Teller (BET) method at 77 K using N_2 gas as an absorbent after heating the sample at 120 °C for 1 h. An Olympus BX41 (Jobin Yvon Horiba) Raman spectrometer was employed. Oxygen elemental analysis was measured by CHNS-O analyzer Thermo FlashEA 1112 series. For some measurements we had special cells that were filled with the product in the glovebox and carry the sample to the instrument without its exposition to air. Such were the XRD and RAMAN measurements. On the other hand the TEM, HRTEM, and SEM measurements were conducted after a minimal exposure to air. Since in each measurement the exposure time to air was different, the amount of oxygen, and a fire was or was not observed. In any case the oxygen level, as measured by elemental analysis, was low even in cases in which we had to expose the sample to air.

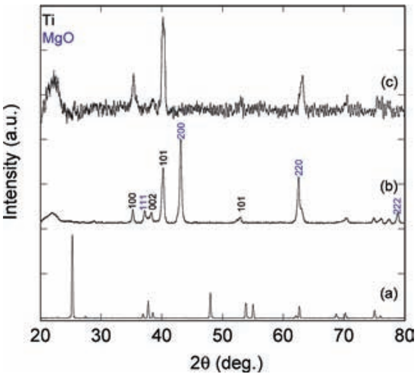

Figure 1. XRD patterns of (a) titania (anatase), (b) the titanium sample before treatment with acids, and (c) after reacting with acetic acid and formic acid.

3. Results and Discussion

Figures 1a shows an XRD pattern of the commercial titania (anatase). Figures 1b and 1c show the XRD patterns for the as-prepared product before etching the MgO and after the acid treatment, respectively. The diffraction peaks of Figure 1b, match well with the PDF tables of Ti and MgO, for Ti: 00−044−1294 and for MgO: 03−065−0476. The comparison between Figure 1b and the acid treated product, Figure 1c, clearly shows that the MgO diffractions have disappeared. Moreover, the reflection peak at $2\theta = 22°$

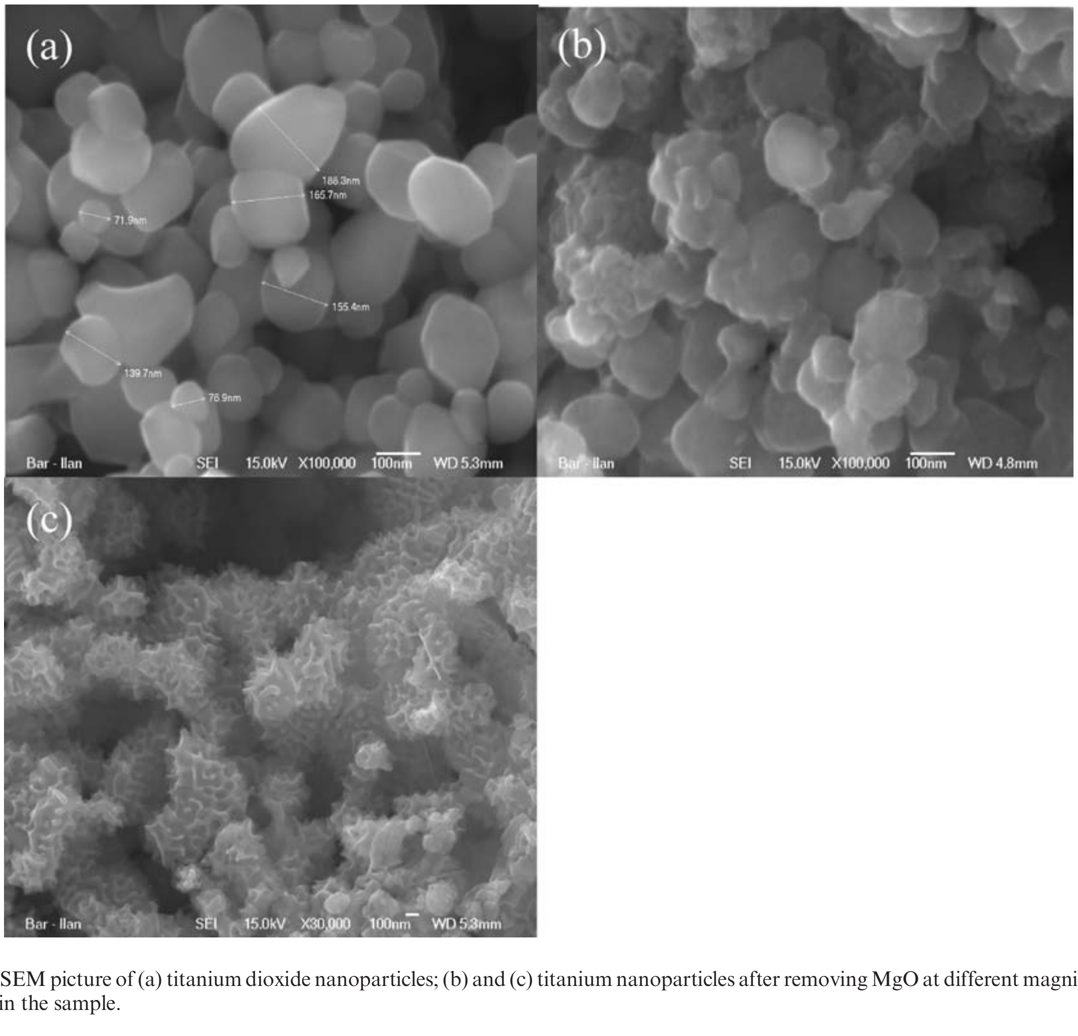

Figure 2. HRSEM picture of (a) titanium dioxide nanoparticles; (b) and (c) titanium nanoparticles after removing MgO at different magnifications and in different areas in the sample.

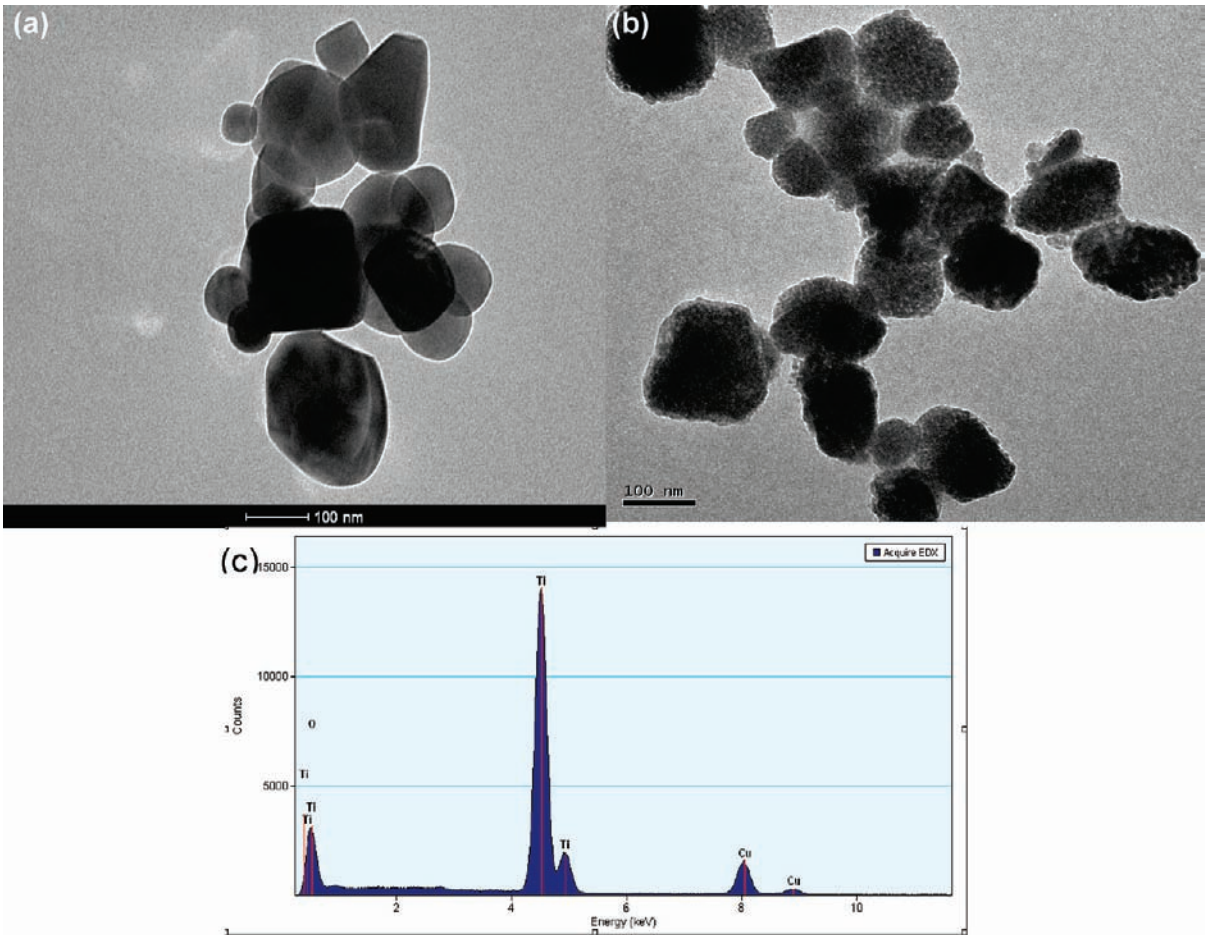

Figure 3. TEM images of (a) titanium dioxide nanoparticles, (b) titanium nanoparticles after the removal of MgO, and (c) overall EDS spectra of the sample presented in Figure 3b.

(Figures 1b and 1c) is due to the plastic layer that surrounds the special inert XRD cell to avoid the oxidation of the Ti sample. The peak at $2\theta = 22°$ does not appear in Figure 1a because there was no need to isolate TiO_2 from ambient air. In addition, the reduced intensity of the titanium in Figure 1c as compared to Figure 1b can be explained as follows: The acid according to our interpretation damages the crystalinity of the product, because part of the H^+ ions are incorporated in the Ti unit cell. Indeed minor shifts in the peak position are observed. According to elemental analysis, the oxygen was found to be in a very low concentration of 0.0157% (wt). This substantiates our XRD results, demonstrating that the fabricated material is indeed Ti, and not an oxide.

Figure 2a depicts a HRSEM photograph of the reactant titania before the RAPET reaction. The titania particles reveal a smooth surface, and their diameter ranges from 70 to 200 nm. Figures 2b, and 2c illustrate the product after the acid treatment. Figure 2b shows that some particles retain there smooth morphology, whereas Figure 2c show that some of the particles became rough and porous.

The porous nature of the product formed, i.e, metallic Ti, is further confirmed by the TEM images presented in Figure 3. The comparison of the TEM image of the titania, Figure 3a, to that of titanium, Figure 3b, indicated clearly the porous nature of the Ti product. The porous nature can be explained as follows: when the reaction occurs at 750 °C the liquid atoms of Mg diffuse into the TiO_2 structure and rupture the bond between the titanium and the oxygen. Therefore, when the MgO is removed, cavities are left inside the particles, causing the porosity of the titanium product. The average diameter of the titanium nanoparticles calculated from Figure 3b was found to be 157 nm. The increase in the size of the product, as compared with the size of the TiO_2 (70−200 nm) reactant is due to the sintering of the product at the high temperature of the reaction. The size distribution of the titanium particles is not homogeneous. Some particles break up to form smaller particles of larger size than that of the titania's original size.

Table 1 presents results of EDS measurements taken on various particles exhibited in Figure 3b. No traces of Mg are detected. It means that MgO was removed upon the acid treatment. At one point when Mg was found its concentration was very low. However, oxygen is detected in the EDS measurements. This is because the transfer of the sample to the EDS machine exposed the sample to air, and the Ti burned for a few second upon this exposure. The fire that bursts upon exposure to air is by itself an indication for the formation of zero-valent Ti.

Figure 4 exhibits a high magnification TEM image of titanium. The well- defined electron diffraction (ED) spots are shown as an inset in Figure 4. The ED pattern confirms the crystalline nature of the metallic titanium. The dominant intensity spots relate to a d- space of 2.28 Å, assigned to diffractions from the (101) plane of Ti which fits the PDF

Table 1. Results of the EDS Measurements of the Sample after the Removal of the MgO[a]

area in the sample	element	weight %	atomic %	uncert. %	detector correction
1	O (k)	15.69	35.78	0.49	0.49
	Ti (K)	84.3	64.21	0.55	0.98
2	O (k)	32.64	58.05	1.33	0.49
	Ti (K)	64.0	38.01	0.62	0.98
	Mg (K)	3.35	3.92	0.14	0.88
3	O (k)	17.67	39.12	0.34	0.45
	Ti (K)	82.32	60.87	0.4	0.98

[a] The concentration of the elements was measured at three different places on the grid.

table (No. 00-044-1294). Clear fringes are observed in Figure 4 and can assist in assigning the product. The measured spacing was found to be 2.24 Å

BET analysis of the nitrogen adsorption- desorption isotherms of titanium (after the treatment with the two acids) shows a small hysteresis behavior. The surface area is 34.4 m^2/g and the pore volume is 0.1027 cc/g, whereas the surface area of pure titania was found to be only 8.5 m^2/g. This increase in the surface area is the result of the pores formed in the reaction.

We have conducted Raman measurements in an inert cell which has avoided the exposure of the sample to air. The purpose of the Raman scanning was to monitor the presence of residual Ti oxides. Titanium oxides are known to show scattering features at the following wavenumbers: Ti_2O_3 has 4 peaks at the range of 200−400 cm^{-1}, and TiO_2 has a peak at 600 cm^{-1}.[11] No Raman peaks have been detected in the range of 200−700 cm^{-1}. We could not detect the scattering peak at 137 cm^{-1} assigned to metallic titanium because of instrument limitations. On the other hand, we can state clearly that Ti oxides are absent in the product mixture.

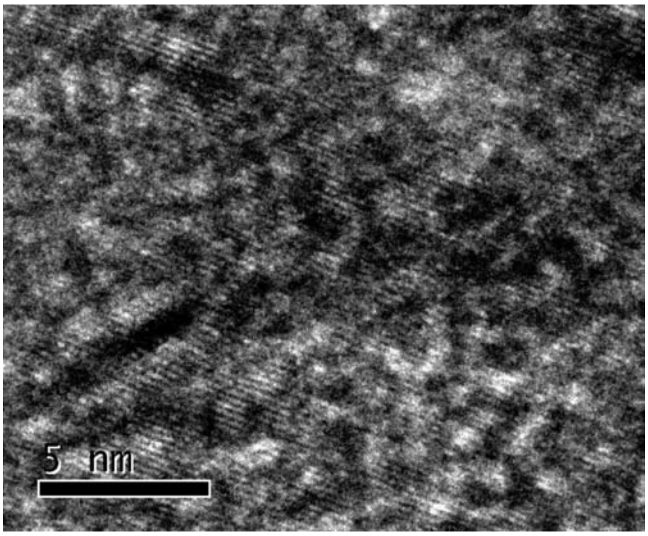

Figure 4. HRTEM image of titanium.

4. Conclusion

The paper reports on an easy and simple method for the preparation of titanium. During the reduction process the morphology has changed and led to an increase of the surface area. As we have seen, the by-product, MgO, was removed completely to obtain pure titanium.

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