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Formation of TiC particle during carbothermal reduction of TiO_2

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Abstract

Formation of TiC particle during carbothermal reduction of titanium dioxide (TiO_2) was investigated. The mixture with TiO_2 and carbon resin was reacted at 1500 °C for 0–45 min under flowing Argon atmosphere. The powders were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The partially reduced TiO_2 particles were conglomerated in the initial stage of the reduction and the size of this conglomerate ranged from 500 to 1000 nm. After the complete reaction between Ti as a reduction product and C, the large conglomerates separated to homogeneous and fine TiC particles with a size of 80 nm.

Keywords: Carbothermal reduction; TiO_2; Powders-solid state reaction; Grain size

1. Introduction

Titanium carbide attracted great interest for many structural applications due to it's extremely high melting temperature, high hardness, high chemical resistance and good electrical conductivity. Therefore Titanium carbide can be used[1] in cutting tools, grinding wheels, wear-resistant coatings, high-temperature heat exchangers, magnetic recording heads, turbine engine seals, and bullet-proof vests, etc. In addition, a promising field of application comprises plasma and flame spraying processes in air, where titanium carbide-based powders[2] show higher-phase stability than tungsten carbide-based powders.

A fine-grained microstructure with a homogeneous grain size distribution is usually desired in TiC ceramics. Particularly, the mechanical properties of TiC ceramics with nano particle size are expected to be much higher than those of conventional bulk ceramics. So, it is very important to synthesize a TiC powders with homogeneous and fine particle size through economical route. Methods that have been used to synthesize TiC powders can be classified into three categories: (i) the direct carbonization[3] of titanium metal or titanium hydride, or combustion synthesis of TiC, (ii) the gaseous pyrolysis[4] of titanium halide, such as $TiCl_4$, in a carbon-containing atmosphere, and (iii) the carbothermal reduction[5–7] of TiO_2 with carbon in controlled atmospheres at high temperatures.

The most widely used process for TiC production is carbothermal reduction of titanium dioxide (TiO_2) in the presence of carbon (C). Carbothermal reduction produces large amounts of powder, and makes use of inexpensive precursor materials, however there is currently no commercial powder production process to produce TiC powder of sub micron size. Therefore, the aim of the work is to produce homogeneous and ultra fine TiC powders through the carbothermal reduction. In this work, formation of TiC particle during carbothermal reduction of TiO_2 is presented.

2. Experimental

The starting material was TiO_2 powder from Deggusa (P-25, Deggusa, NJ). Fig. 1 shows SEM (SEM, XL-30, Philips) micrograph for raw TiO_2 powder. Fig. 1 shows the average particle size of 20–30 nm.

TiO_2 and carbon resin (CB-8400, Kangnamchemical, Korea) as carbon source were mixed in methyl alcohol using an engineering plastic jar with Si_3N_4 balls for 2 h. The molar composition was TiO_2:C = 1:3. After milling, the slurry was dried in a rotary evaporator at 70 °C and granulated using an alumina mortar. The mixture were then reacted in a graphite furnace at 1500 °C for 0–45 min under argon atmospheric conditions.

The phase was identified by X-ray diffraction (XRD, Rigaku, Japan) using monochromatic Cu Kα radiation. The lattice parameter of the TiC reaction product was computed from XRD analysis. The scanning angle is calibrated by using standard Si wafer.

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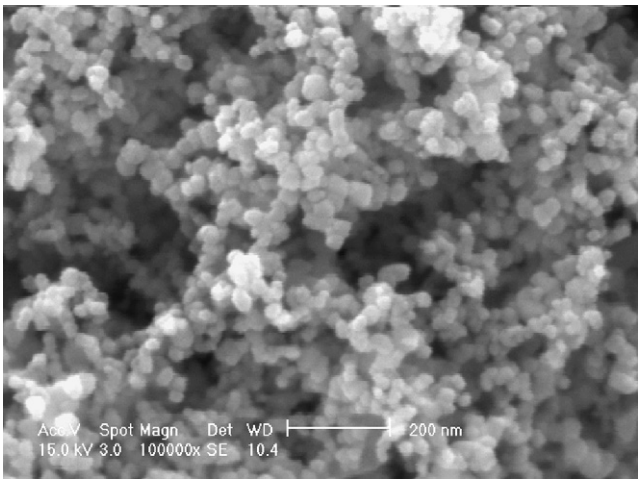

Fig. 1. SEM micrograph of raw TiO_2 powders.

Scanning electron microscopy and Laser particle size analyzer (Malvern Instrument Ltd.) was used for estimating particle size. Differential scanning calorimetric (DSC, SETARAM, France) was used for the identification of reaction temperature.

3. Results and discussion

TG/DSC curve of the mixed powder is shown in Fig. 2. The curve exhibits three clear endothermic reaction at 1052, 1204 and 1401 °C. The overall carbothermal reduction reaction[8] to be studied is:

$$TiO_2(s) + 3C(s) \rightarrow TiC(s) + 2CO(g) \quad (1)$$

This reaction proceeds thermodynamically at 1289 °C. However, the DSC data indicate that the mixed powder experiences three complete reactions up to 1500 °C. The following possible reaction series,[9] based upon Gibbs free energies, are proposed:

$$4TiO_2(s) + C(s) \rightarrow Ti_4O_7(s) + CO(g) \quad (2)$$

$$3Ti_4O_7(s) + C(s) \rightarrow 4Ti_3O_5(s) + CO(g) \quad (3)$$

$$Ti_3O_5(s) + 8C(s) \rightarrow 3TiC(s) + 5CO(g) \quad (4)$$

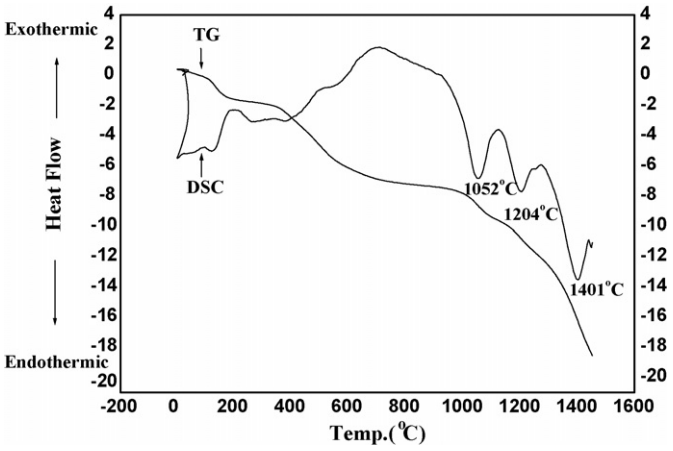

Fig. 2. TG/DSC curve of mixed powder until 1500 °C.

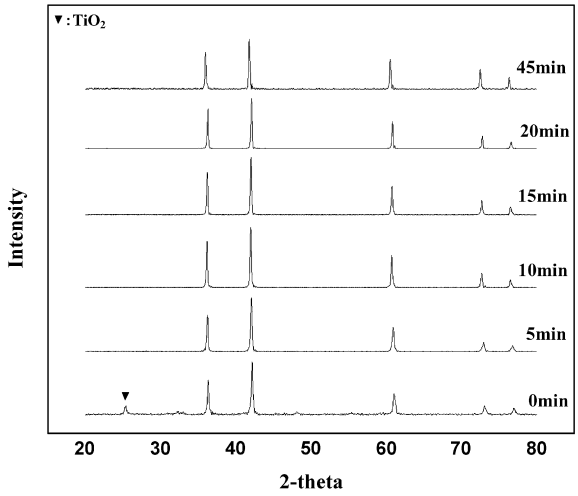

Fig. 3. XRD patterns of the powders reacted at 1500 °C under flowing Argon.

These reactions occur thermodynamically at a temperature of 1087, 1182 and 1334 °C, respectively.

Fig. 3 shows the XRD pattern of the powder reacted at 1500 °C under argon atmospheric condition. The formation of lower oxides of titanium such as Ti_4O_7 and Ti_3O_5 was not found. Only small amount of unreacted TiO_2 was observed in the specimen treated at 1500 °C for 0 min. The formation of TiC_xO_y was completed in the specimen reacted at 1500 °C for 5 min. Above 5 min, the TiC_xO_y lost more oxygen as the purification of TiC proceed.

The carbon content in the TiC_xO_y reaction product was estimated from lattice constant measurements, where the compositional parameter[10] x of the TiC_xO_y varies systematically with lattice parameter. As can be seen in Fig. 4, the lattice parameters increase with reaction time. The observed lower lattice parameter of the TiC, reacted at 1500 °C for 0 and 5 min, indicate the TiC_xO_y with high oxygen content. Above 10 min, almost pure TiC formed and the reduction was completed.

Micrographs of the particles, formed by carbothermal reduction at 1500 °C for various time, are shown in Fig. 5. It is interesting to note that the partially reduced TiO_2 particles were

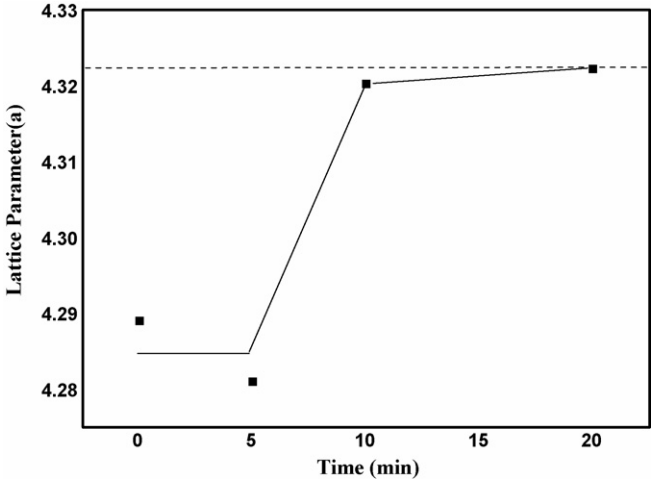

Fig. 4. Plot of lattice parameters as a function of reaction time.

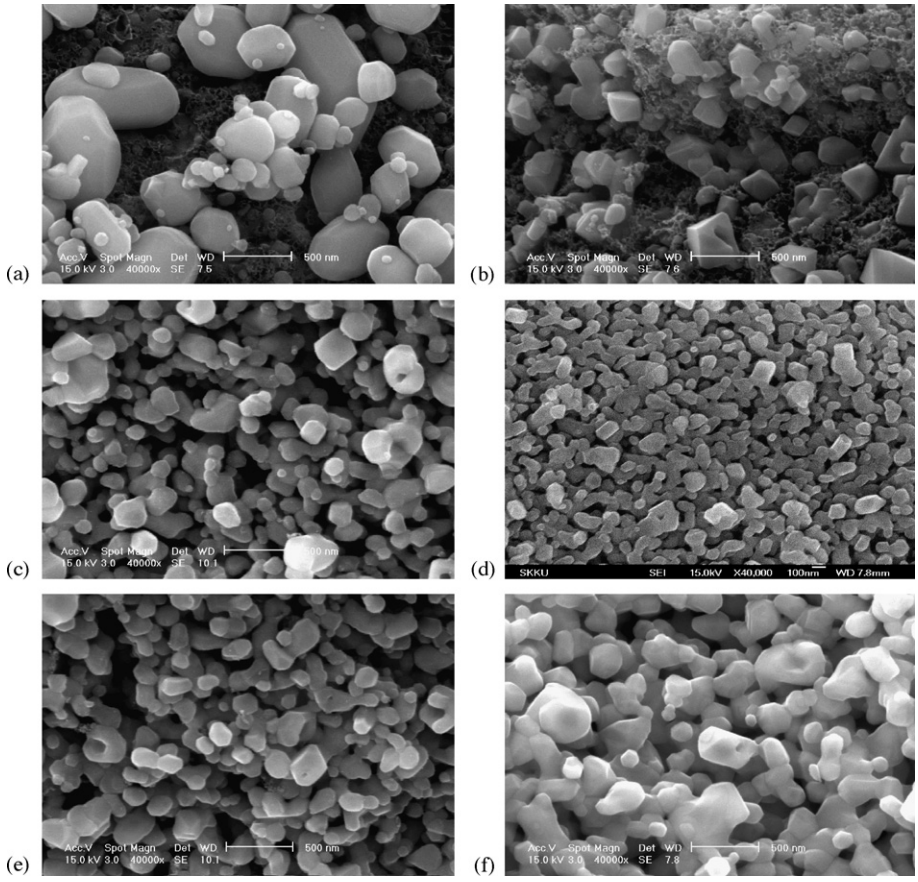

Fig. 5. SEM morphologies of the particles by carbothermal reduction at 1500 °C for (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min and (f) 45 min.

conglomerated and formed large round particles in the initial stage of the carbothermal reduction (Fig. 5(a)). The particles size of the large conglomerates were determined to be 500–1000 nm. This provides evidence that the vapor reaction existed in the formation of TiC_xO_y at 1500 °C. In the intermediate stage of the carbothermal reduction, Fig. 5(b) and (c), the large conglomerates separated to the fine particles. In this stage, many holes in the middle of the particles as an open hollow structure were observed. It is believed that these holes were resulted from the release of gaseous reduction product such as CO during the further reduction. Finally, homogeneous and fine TiC particles with the particle size less than 100 nm formed at 1500 °C for 15 min. Above 15 min, TiC particles grew and the size of TiC particles reacted at 1500 °C for 45 min reached up to 500 nm. The particle size distribution of the TiC reacted 1500 °C for 15 min, determined by laser particle size analyzer, is shown in Fig. 6. The average size of the TiC particles was found to be 80 nm.

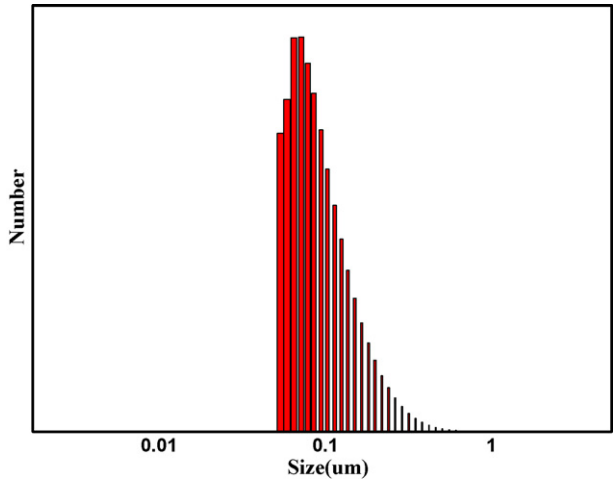

Fig. 6. Estimated particle size distribution for the TiC powder formed at 1500 °C for 15 min.

4. Conclusions

The carbothermal reduction of the mixture with TiO_2 and carbon resin at 1500 °C proceeded by three steps as follows. First, partially reduced TiO_2 particles were conglomerated in the initial stage of the carbothermal reduction and the size of this conglomerate ranged from 500 to 1000 nm. In intermediate stage, the particles were separated to the fine particles and the many holes in the middle of the particles due to the release of gaseous reduction product such as CO were observed. Finally, the homogeneous and fine TiC particles with a size of 80 nm formed at 1500 °C for 15 min.

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