Kinetics and phase evolution during carbothermal synthesis of titanium carbide from ultrafine titania/carbon mixture

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The kinetics and phase evolution of the TiC formation process by carbothermal reduction of ultrafine titania/carbon mixture were investigated using thermogravimetric analysis (TGA), X-ray diffraction (XRD) and oxygen analysis. Titania (TiO₂) first lowered its oxidation state to Ti₃O₅ via an unidentified phase (possibly one of the Magneli phases). Then Ti₃O₅ was further reduced to Ti₂O₃, followed by the formation of titanium oxycarbide (Ti₅C₃O₃) phase and its purification toward high purity TiC thereafter. Ti₂O₃ was the oxide phase with the lowest oxidation state before forming TiCₓOᵧ phase. In the isothermal TGA trace, the formation of Ti₃O₅ showed a diffusion-controlled process; possibly carbon diffusion limited the solid state reaction. The formation of Ti₂O₃ and Ti₅C₃O₃ was interpreted to be associated with CO gas-assisted reduction reaction, based on constant reaction rate for each process. The activation energy for the formation of Ti₃O₅ (from Ti₂O₃) and Ti₅C₃O₃ (from Ti₂O₃) phase were calculated to be 415.6 and 264.3 kJ mol⁻¹, respectively. The TiC powder synthesized at 1550 °C for 4 h in flowing argon atmosphere showed fine particle size (0.3–0.6 µm) with oxygen content of 0.7 wt% and lattice parameter of 0.4328 nm while interparticle agglomeration was moderate. © 1998 Chapman & Hall.

1. Introduction
Titanium carbide is a ceramic material with many applications in key high technologies from mechanical to chemical and microelectronics because of its high melting point (3260 °C), high hardness (Knoop’s = 32.4 GPa), high electrical conductivity (30 × 10⁻⁶ Ω⁻¹ cm), high thermal conductivity (16.7 W mK⁻¹), high thermal shock resistance, high chemical stability, high wear resistance, and high solvency for other carbides [1]. Titanium carbide powder is used for the manufacture of cutting tools, grinding wheels and the like or can be combined with other ceramic systems such as aluminium oxide (Al₂O₃), silicon nitride (Si₃N₄) and silicon carbide (SiC) for the fabrication of structural components used in high temperature, erosive and/or corrosive applications [2–6]. Titanium carbide can also substitute for tungsten carbide (WC), a common machining material, because of its similar properties. Important benefit of the substitution results from the fact that WC requires cobalt as a binder material [7]. This binder is imported to the US from foreign and occasionally politically unstable sources. Titanium carbide compounds use nickel as a binder which has a more stable source and costs only half as much. For all these applications, the synthesis of titanium carbide powders with a homogeneous chemical composition, fine particle size, a narrow particle size distribution, and a loose agglomeration is of great importance.

Methods that have been developed to synthesize TiC powders include the direct carbonization of titanium metal (combustion synthesis) [8] or titanium hydride [9], gaseous pyrolysis of titanium halide such as TiCl₄ in a carbon containing atmosphere [7], and carbothermal reduction of TiO₂ with carbon in controlled atmospheres at high temperatures [3, 10]. Metallic titanium as a starting material is relatively expensive, and furthermore, the oxygen contained in the metal can hardly be reduced, so that the product is generally characterized by a high oxygen content [3]. Titanium chloride as a precursor is of importance in the field of chemical vapour deposition, but it is very expensive. An inexpensive method applied commercially involves the carbothermal reduction reaction of titania (TiO₂) and carbon particles [10].

In the carbothermal synthesis of titanium carbide from a mixture of carbon and titania, the overall reaction governing the formation of TiC is

TiO₂ + 3C = TiC + 2CO (g)  (1)

The reaction (Equation 1) is highly endothermic and proceeds above 1289 °C for a partial pressure of CO below 1.013 × 10⁵ Pa. However, the actual titanium carbide production is achieved at much higher temperatures than the thermodynamic onset temperature because of kinetic barriers such as limited contact area between reactants and uneven distribution of carbon in the reactants. These limitations and higher
temperature processing result in grain growth, particle coalescence, non-uniform particle shape, and considerable quantities of unreacted TiO₂ and carbon in the final product. For example, in the commercial production of titanium carbide [10], reactants are fired at 1900 °C to 2300 °C in an inert atmosphere while sintered lumps of titanium carbide are produced. This then requires crushing using jaw crushers and fine-milling thereafter.

Of the number of efforts to develop the carbothermal processing of titanium carbide in the author’s research group [11,12], results based upon the use of the currently available ultrafine titania powder as the titanium source is reported herein. Such a fine powder would increase the homogeneity of the reactants and the high specific surface energy of the powder would result in decreasing the processing temperature. This would then ensure less chance of grain growth and particle agglomeration. While the development of carbothermal processing for titanium carbide requires fundamental research concerning the reactions, a number of inconsistencies in the phase evolution of titanium carbide formation are noticed in the literature. In the present study, the phase evolution and kinetics of carbothermal reduction of ultrafine titania/carbon powder mixture are established.

2. Literature review

While earlier works [13] proposed that the formation of titanium carbide by carbothermal reduction of titania/carbon proceeded via Ti₂O₃ and TiO, Samsonov [14] suggested that the reduction of titania proceeded through Ti₃O₇, Ti₂O₅, and TiO. However, Kucev and Ormont [15] concluded that the titanium carbide formation proceeded via Ti₃O₅, which in turn, resulted in titanium oxy-carbide TiC₃O₅ in excess of carbon or Ti₂O₃ in deficiency of carbon. On the other hand, Quensanga [16] came to the result that the lowest oxide of titanium existing in the system was TiO as and the composition of initial TiC₂O₃ was x = 0.67 and y = 0.33. According to Lyubirnov et al. [17], TiO₂ lowered its oxidation states to Ti₁O₅, Ti₂O₇, Ti₃O₅, TiO₂, TiO and Ti. While metallic titanium and TiO could not be detected on X-ray diffraction (XRD), their presence was drawn from chemical analysis results. Recently Berger [3] observed Magneli phases (Ti₃O₂₋₃n with n ranging between 4 and 10 [18]), various TiO₂ modifications, and Ti₃O₅ on XRD while one of his carbon/titania mixtures showed a peculiar behaviour as the intermediate products Ti₂O₃ and Ti₂O₅ were missing. Concerning the lattice parameter of pure titanium carbide, different values have been reported, probably due to the difference in processing: 0.4328 [19] and 0.4331 nm [10].

3. Experimental procedure

Titania powder (titanium dioxide, P25, Degussa Corp., Ridgefield, NJ) used in this work had 70% anatase (30% rutile) phase, based on manufacturer’s report. Its average particle size and specific surface area were reported to be 21 nm and 50-60 m² g⁻¹, respectively. The carbon source was carbon black powder (Monarch 880, Cabot, Waltham, MA) with an average particle size of 16 nm and specific surface area of 220 m² g⁻¹. A total of 10 g of titania 67.4 wt % and carbon black (32.6 wt %) powders were placed into a plastic container (inner diameter of 5 cm and height of 7 cm) and hand mixed using a spatula. Then two polymer balls (diameter of 0.35 cm) were added to the mixture in the plastic container and milled for five hours in a Spex mixer (model 8000 Mixer/Mill, Metuchen, NJ).

For thermogravimetric analysis (TGA) (model TG-171, Cahn Instruments, Inc., Cerritos, CA), 0.2 g of the mixture was taken in a cylindrical graphite holder (internal diameter 1.25 cm and height 1.9 cm). The graphite holder was then placed in a cylindrical alumina holder (internal diameter 1.9 cm and height of 2.5 cm) with platinum hanger. The texture (sample, graphite holder, and alumina holder) was hung from a high precision balance. The B-type thermocouple, protected by an alumina tube, was placed at about 1 cm below the alumina sample holder. The system was surrounded by a perpendicularly positioned alumina tube furnace (internal diameter 3.2 cm). Argon gas was flowed from the bottom to the top for 6 h before increasing the temperature, and continued throughout the run. In order to minimize the degree of reaction before reaching the destination temperature, the maximum allowable heating rate of the instrument was applied for operation: 70 °C min⁻¹ up to 1000 °C and then 20 °C min⁻¹ for temperatures above 1000 °C. After reaching the destination temperature (1145–1350 °C), the sample was fired for 2 h followed by furnace cooling down to 1000 °C (at 10 °C min⁻¹) at which point the furnace power was turned off. Data acquisition was performed every 5 s to a computer disk.

The samples fired in the TGA instrument were subject to XRD (model DMAX-B, Tokyo, Japan) analysis for the study of phase evolution using CuKα radiation and a zero-background sample cell. Speed of scanning 20 angle was from 27 to 80° at 2° min⁻¹.

For the production of titanium carbide powders, 20 g of the carbon/titania mixture (33.7 wt % carbon) were placed in a graphite boat and then the boat with sample was positioned in the centre of a horizontally positioned alumina tube furnace (Model CTF 17/75/300, Carbolite, Hope, Sheffield, UK) with an internal diameter of 70 mm. Argon gas was flowed for 2 h before increasing temperature and continued throughout the run (11 min⁻¹: LPM). Temperature was increased to 1300–1550 °C at 4 °C min⁻¹ heating rate followed by 2 h of soaking time. The sample was cooled at 4 °C min⁻¹ down to 800 °C where the furnace power was switched off. The temperature reading was based on the B-type thermocouple located between the alumina tube and molybdenum disilicide heating element.

The lattice parameter, oxygen content, and morphology of the titanium carbide product were investigated using XRD, chemical analysis (LECO, St. Joseph, MI), and transmission electron microscopy.