



Mechanochemical synthesis of nano-structured TiC from TiO₂ powders

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ABSTRACT

Nano-structured TiC was successfully synthesized from mixtures of TiO₂ and graphite through high-energy mechanical milling and subsequent heat treatment at a temperature that was considerably lower than that used in conventional carbothermal reduction synthesis of TiC. TiO₂ powders mixed with graphite were milled in a planetary ball mill for 30–90 h. The milled mixtures were then heat treated at 1200 °C and 1300 °C for 60 min. The as-milled and heat treated powders were characterized using SEM-EDAX, DTA, and XRD techniques. As revealed in SEM, agglomeration was found to be more pronounced after 30 h milling. Even though the formation of TiC was not detected in as-milled powders milled for durations between 30 h and 90 h, TiC appeared in the powder mass after heat treatment as revealed by the XRD patterns. The crystallite size of TiC as a function of milling time was estimated from the XRD data using Scherrer equation and it was found to be increased with increasing milling time after heat treatment.

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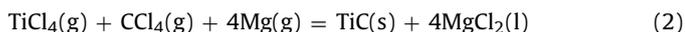
1. Introduction

Titanium carbide is widely used in the fields of wear resistant tools, grinding wheels and aerospace materials due to its extremely high melting temperature, high hardness, high chemical resistance to oxidizing atmosphere, and good electrical conductivity. The bulk production of materials containing TiC as a component has been made possible by the extensive application of TiC powder consolidation using powder metallurgy techniques [1,2]. TiC can be synthesized by direct chemical reaction between Ti and carbon under vacuum at high temperature. This method, however, is rather expensive because of the high cost of elemental Ti and because it is an energy intensive process [3].

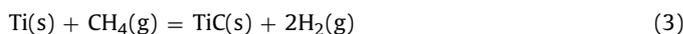
TiC is commercially produced by the carbothermal reduction of TiO₂ using carbon black as shown below [4]:



The synthesis of TiC by means of carbothermal reduction of TiO₂, however, requires high temperature (1700–2100 °C) and a long reaction time (10–24 h). Since the reactants (TiO₂ and carbon) both react in solid states, the reaction rate is rather slow [5]. Nano-structured TiC was synthesized by methods such as liquid-magnesium reduction of vaporized mixture of TiCl₄ and CCl₄ solution. The corresponding reaction takes place as follows [1]:



Thermal plasma has also been used for the synthesis of TiC using Ti and methane as starting materials [4]:



Many reports are available on the formation of TiC by mechanical milling from Ti and C as the starting materials [6–10]. Even though titanium is the ninth most abundant element in the earth's crust, the high cost of production of this element is the major constraint for its wider applications. Titanium is produced by the Kroll process which needs high temperature and method, involving complicated multistep operations and high-energy consumption [11].

Very few researchers pointed to synthesis of nano-structured titanium carbide from TiO₂ powders. Setoudeh et al. [12] studied the reduction of anatase and rutile. Mixtures of TiO₂ and graphite were prepared in accordance with the stoichiometry given by reaction (1) (68% TiO₂ and 32% C). Seven grams of each mixture were milled under vacuum for 50 h in a tumbling ball mill. The mill was loaded with five 25.4 mm diameter stainless steel balls giving a very high ball to powder mass ratio of 43:1. After milling, samples were heated to 1400 °C in an alumina crucible at 20 °C/min under flowing argon (100 ml/min) atmosphere when the reduction and synthesis of TiC occurred. Ren et al. [13] also studied similar systems towards the synthesis of TiC. They used mixtures of pure TiO₂ and graphite with carbon-to-titanium dioxide molar ratios of 3: 1 and 4:1 and the high-energy milling was conducted using a modified Szegvari attritor. A milling speed of 600 rpm and BPR of 60:1 were employed. Application of ultra high BPR still poses as the major limitation towards the synthesis of TiC using mechanochemical route because the productivity of TiC decreases with higher BPR.

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It was concluded by the researchers that the reaction tendency between TiO_2 and carbon can be greatly enhanced by mechanical activation through high-energy ball milling. However, the conditions employed by the above researchers are still too energy intensive. In an attempt to make this synthesis possible at lower BPR (10:1) and lower milling speed (400 rpm), the present work was undertaken. TiO_2 is a cheap and abundant material [14]. Through high-energy mechanical milling under moderate conditions and subsequent heat treatment at a temperature which was still considerably lower compared to that used in conventional carbothermal reduction synthesis of TiC, and elimination of a number of intermediate steps and thereby the cost of production of pure Ti as the starting materials, this method was attempted towards an alternate cheaper route for TiC synthesis.

2. Experimental

In the present study, the starting materials chosen were TiO_2 powder (purity 99.5%, 80–250 μm) and graphite powder (purity 99.4%, 10–100 μm) for the synthesis of TiC. TiO_2 and C were mixed at the stoichiometric ratio for a total of 25 g in which 1 g of zinc stearate ($\text{C}_{36}\text{H}_{70}\text{O}_4\text{Zn}$) was added to promote de-agglomeration. The TiO_2 and C powder mixture was mixed thoroughly in a horizontal mixing machine at 20 rpm for 2 h. Then this mixture was milled in a high-energy planetary mill with stainless steel balls of 20 mm size (average). A constant ball to powder ratio (BPR) of 10:1 and a rotational speed of 400 rpm were maintained all throughout. The powder mixture was milled for various milling durations (30–90 h) with intermittent sampling. A portion of the milled samples was heat treated at 1200 °C and 1300 °C under an argon protective atmosphere for 60 min in a tube furnace with a constant heating rate of 10 °C/min. Characterization of the samples was done using SEM-EDAX, and the phases evolved in the reaction products were investigated using XRD patterns.

3. Results and discussion

3.1. Observation of microstructures under SEM

At the early stage of milling, the powders were fine and continuous milling created new surface on particles and enabled the powders to weld together and form large particles (agglomeration). This stage indicated that cold welding was dominant than fracturing of the particles as shown in Fig. 1. These SEM micrographs clearly show the different morphologies of powders milled for short and long milling time.

The heat treatment of the milled mixtures of TiO_2 and graphite at 1300 °C proceeded by three steps as follows. First, partially reduced TiO_2 particles were conglomerated in the initial stage of the heat treatment. During the intermediate stage, porosities among the particles due to the release of CO were observed and particles were separated to finer sizes. Finally, the homogeneous and fine powders containing TiC particles formed at 1300 °C as shown in Fig. 2.

3.2. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) studies were performed on the fresh as-milled samples where the samples were heated from room temperature to 1300 °C at a constant heating rate of 10 °C/min under ambient air atmosphere. Exothermic and endothermic peaks in the mixture of TiO_2 and graphite without milling or with milling were observed. Samples without milling indicated weak exothermic and endothermic peaks which might be due to the oxidation of graphite and transformation to lower oxides of Ti respectively. With milled samples, exothermic peaks might have occurred due to the oxidation of graphite and due to the formation of TiC [15,16]. Endothermic peaks might be due to the transformation to lower oxides of Ti [17]. Lower oxides of Ti are indicated in Fig. 3. The phase transition from anatase to rutile was not investigable by DTA because the exothermic effect was immeasurably low [18]. Samples milled for 90 h seemed to be more reactive compared to the other samples as shown in Fig. 3.

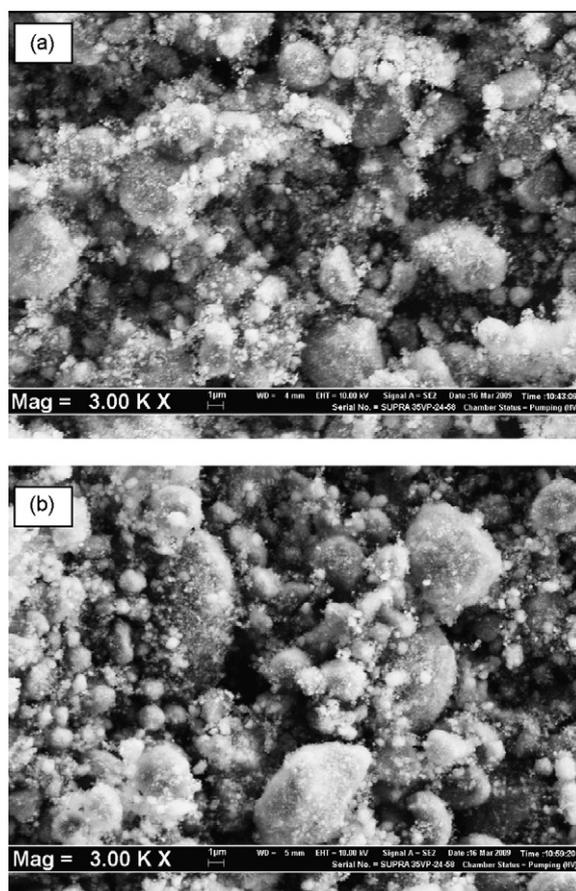


Fig. 1. SEM images of TiO_2 –graphite mixtures milled for (a) 30 h and (b) 90 h (both 3000 \times).

The DTA trace (a) in Fig. 3 did not reveal any strong peak. It indicated a possible reaction at about 950 °C referring to the oxidation of graphite. Trace (b) also showed a similar pattern as that of trace (a) as it did not contain any strong peaks except that it indicated a possible reaction at a temperature of about 850 °C. As the sample was further activated, a drop in this temperature was expected. Trace (c) displayed a relatively stronger exothermic peak at 750 °C which also referred to the oxidation of graphite and stronger endothermic peaks at 900 °C referring to the formation of lower oxides of Ti. The lowering in temperatures compared to that obtained in trace (b) was due to the higher activation due to extended milling. The other peaks at 1120 °C and 1270 °C might refer to the formation of TiC. Graphite powders thus tended to oxidize at lower temperatures with increasing milling time. Such a phenomenon corroborates with the observation made by Welham and Williams [19].

3.3. X-ray diffraction analysis

Fig. 4 shows the XRD patterns of as-milled mixtures of TiO_2 and graphite milled for different durations indicating the phase transformation from anatase to rutile taken place due to the application of mechanical energy through milling (mechanochemical process). Even though no TiC peaks were noticed in the XRD patterns, the powders got activated leading to the possibility of chemical reaction between them towards the synthesis of TiC in further processing steps e.g. heat treatment.

Broadening of the peaks as shown in Fig. 4 indicates the decrease in crystallite size and increase in lattice strain which occur by increasing milling time [20]. Decreases in crystallite size and

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