

Article

The Microwave-Assisted Green Synthesis of TiC Powders

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Abstract: Titanium carbide (TiC) is an important engineering material and has found widespread applications. Currently, TiC is typically synthesized through carbothermal reduction, requiring a high temperature (ca. 1700–2300 °C) and long reaction time (ca. 10–20 h), which is not eco-friendly. During a conventional reaction path, anatase TiO₂ (A-TiO₂) was first converted to rutile TiO₂ (R-TiO₂), which was subsequently reduced to TiC. Herein, we explored the synthesis of TiC powders with the assistance of microwave heating. In particular, we achieved the conversion of A-TiO₂, which was more reactive than R-TiO₂ for the carbothermal reduction, to TiC, which was directly due to quick microwave heating. As such, the carbothermal reduction started at a much lower temperature of ca. 1200 °C and finished within 30 min when reacting at 1400 °C, leading to significant energy saving. This study shows that microwave-assisted synthesis can be an effective and green process for preparing TiC powders, which is promising for future large-scale production. The influence of the reaction temperature, the reaction duration, and the carbon content on the synthesis of TiC powders was investigated.

Keywords: TiC powders; microwave-assisted synthesis

1. Introduction

Titanium carbide (TiC) is an important engineering material because of its superior hardness, high melting temperature, good electrical conductivity, and outstanding abrasion resistance [1–3]. Therefore, TiC powders have been used extensively in cutting tools, grinding wheels, polishing pastes, etc. [3–6].

Currently, TiC powders are mainly synthesized by the carbothermal reduction of TiO₂, and the heat during the process of reaction is usually provided by an external heating system. The synthesis is typically in the temperature range of 1700–2300 °C for 10–20 h [7]. The size of the synthesized TiC powders not only depends on the size of raw materials, but also on the synthesis conditions. Therefore, it is difficult to prepare uniform TiC powders by conventional heating processes [8,9].

As an alternative heating technology, microwave heating has advantages such as high thermal efficiency, selective heating, quick heating, and short processing time. It has been implemented in many industrial applications in recent years [10–12]. The major difference between microwave heating and conventional heating is the inverse temperature profile inside microwave-heated samples [13,14]. The center of the sample becomes hotter than the surface, which is exposed to the colder furnace atmosphere [15]. Many materials including ceramics, polymers, and metallic powders can be directly exposed to microwaves [16]. In microwave carbothermal reduction process, two factors might be

favorable for lowering the onset reaction temperature. One is the existence of thermal and non-thermal effects from microwave heating [17]. The other is the uniform heating achieved by the energy directly delivered to the starting materials via molecular-level interactions under an electromagnetic field [18,19]. Microwave-assisted synthesis is attractive for the preparation of TiC because it is faster and more effective than conventional heating. Carbon, one of the reactants for the synthesis of TiC, is a very effective absorber of microwave radiation, offering extra facilitation of the reaction. Cross and coworkers [20,21] made some early explorations of the synthesis of TiC via microwave heating and proved that it was viable and indeed more effective to synthesize TiC via microwave heating.

In this report, microwave heating was adopted to synthesize TiC powders by carbothermal reduction of TiO₂. The influence of reaction temperature and carbon content on the phase composition of the produced TiC powders was systematically investigated. In particular, we aimed to achieve the direct conversion of anatase TiO₂ (A-TiO₂), which was more reactive than rutile TiO₂ (R-TiO₂), for the carbothermal reduction to TiC by taking advantage of quick microwave heating.

2. Experimental

2.1. Materials

Both A-TiO₂ powders (99%, ~40 nm in diameter) and carbon black (99%, ~10 nm in diameter) were purchased from Tuoyi Co. (Guangzhou, China). Ethanol was acquired from Fuyu Fine Chemical Co. (Fuzhou, China). Polyacrylic acid (PAA) was obtained from KeMiOU Chemical Co. (Tianjin, China). All the chemicals were used as received without further purification.

2.2. Synthesis

First, a 20.0 wt % A-TiO₂ ethanol dispersion was ultrasonicated for 30 min to form a uniform system, which was mixed with polyacrylic acid (PAA/TiO₂ = 0.5 wt %) to stabilize the dispersion of A-TiO₂ in ethanol. Subsequently, a pre-determined amount of carbon black was mixed with the above dispersion. The reaction precursor was obtained after evaporating ethanol.

The synthesis was carried out in a KL-2D-16 microwave furnace (Kailin Microwave Equipment Co., Guangzhou, China). During reaction, the microwave frequency was 2450 ± 50 MHz, and microwave power was 6000 W. Thermocouples were used to measure the temperatures during reaction. The entire reaction was carried out under argon protection.

The carbothermal reduction of TiO₂ is a complex process. Under a conventional heating process, before the reduction reaction, A-TiO₂ is first converted to R-TiO₂. With the rising of temperature, the reduction consists of a series of intermediate reactions, producing various intermediate products and phases (Equations (1)–(4)). The general procedures of the carbothermal reduction reaction between carbon black and R-TiO₂ through conventional heating to generate TiC are as follows [22,23]:



Total reaction:



In this work, we aimed to achieve a direct reduction of A-TiO₂ to TiC under the assistance of microwave heating, as illustrated in Figure 1. Such a direct reduction route is expected to occur at a lower temperature, thus saving energy and time. In order to investigate the reduction process of TiO₂ by microwave heating, we monitored the phase transition of the reaction products at various temperatures and reaction durations by X-ray diffraction, and studied the influence of carbon content on the synthesis of the TiC powders.

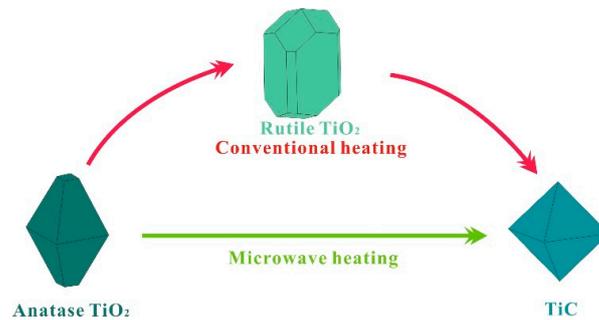


Figure 1. Schematic of different reaction routes between conventional and microwave heating.

2.3. Characterization

Phase composition of the reaction products was determined by X-ray diffraction on a PANalytical X-ray diffractometer (XRD, monochromated Cu K α radiation) at 25 °C. The morphology of the powders was imaged by scanning electron microscopy (SEM) on a Nova S-430 microscope operated at 20 kV, which was equipped with an energy-dispersive X-ray spectrometer (EDS).

3. Results and Discussion

3.1. Effect of Temperature and Reaction Time

The XRD patterns of the samples synthesized at various temperatures (1100, 1200, 1300, and 1400 °C) and durations of reaction (10 and 30 min) at a TiO₂ and C molar ratio of 1:3.6 are presented in Figure 2.

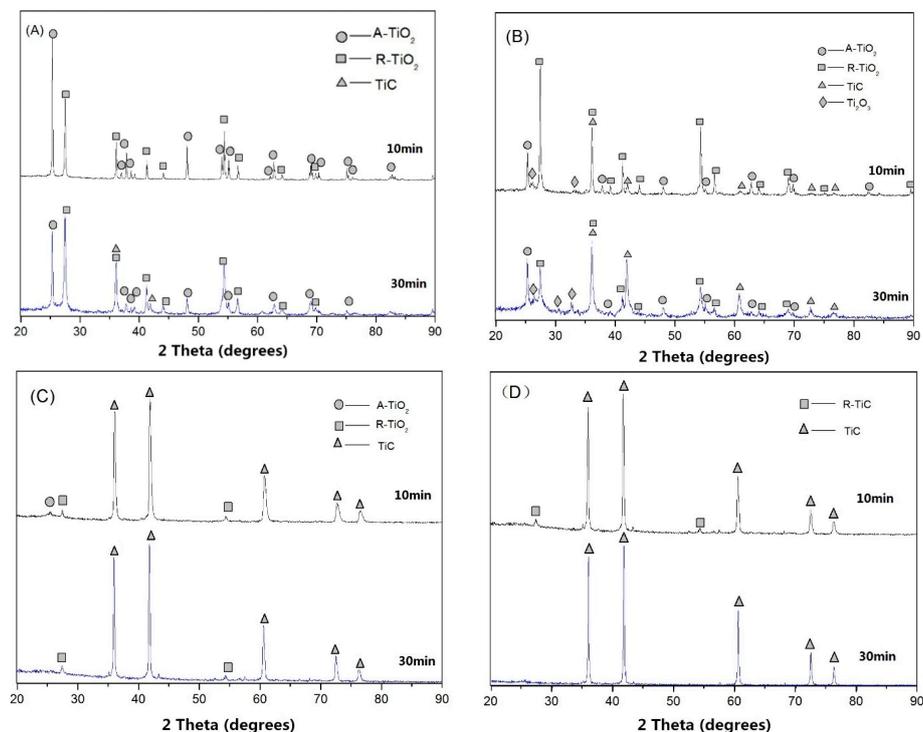


Figure 2. X-ray diffractometer (XRD) patterns of the synthesized samples at various temperatures: (A) 1100 °C; (B) 1200 °C; (C) 1300 °C; (D) 1400 °C.

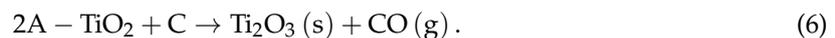
Figure 2A displays the XRD patterns of the samples reacted at 1100 °C for 10 and 30 min. It shows that TiC phase was not formed at 1100 °C for 10 min of reaction, but a small amount of TiC was

generated after 30 min of reaction. The conversion from A-TiO₂ to R-TiO₂ was observed at this temperature. A number of studies reported that A-TiO₂ began to transform to R-TiO₂ at a temperature up to 610 °C [24,25]. With an increase in reaction time, more R-TiO₂ was generated, as evidenced by stronger R-TiO₂ phase diffraction peaks in the XRD pattern. The XRD patterns of the samples synthesized at 1200 °C (Figure 2B) showed that most A-TiO₂ was converted to be R-TiO₂; meanwhile, Ti₂O₃ started to form after 10 min of reaction at 1200 °C. After 30 min of reaction at 1200 °C, the TiC phase started to appear as evidenced by the corresponding XRD peaks. The TiC phase could be clearly observed on the XRD pattern when the reaction temperature was raised to 1300 °C. With an increase in reaction time, a higher concentration of TiC was generated, as supported by the more intensive diffraction peaks of TiC (Figure 2C). According to the XRD pattern, the virtually pure TiC phase was synthesized after 30 min of reaction at 1400 °C (Figure 2D).

Based on the above observations, the reaction mechanism is proposed as follows. At 1100 °C, the main reaction was the transformation from A-TiO₂ to R-TiO₂, but this is a relatively slow process:



It was reported that the activity of A-TiO₂ with C was higher than that of R-TiO₂ [26–28], so the rate of Reaction (6) is faster than that of Reaction (1):



During conventional heating, A-TiO₂ tends to transform to R-TiO₂ before the reduction reaction. This is one of the key reasons that a much higher temperature; thus, much more energy is required to convert the less active R-TiO₂ to TiC. If one can quick heat to directly convert A-TiO₂ to TiC, it is much more favorable in terms of energy consumption. Microwave heating can help achieve this process. Because the rate of microwave heating is very fast, it takes a very short time to raise the temperature from 1100 to 1200 °C. Therefore, when the temperature was quickly increased to 1200 °C, some A-TiO₂ remained. Such unconverted A-TiO₂ can quickly react with C to form TiC at relatively lower temperatures compared with the reduction reaction temperature of R-TiO₂ to TiC. Figure 2C shows that, after 30 min of reaction at 1300 °C, there was still some R-TiO₂ left but no A-TiO₂. As such, a high heating rate is very desirable to directly reduce A-TiO₂ to TiC, which allows for the synthesis of TiC at lower temperatures while saving energy. After 30 min of reaction at 1300 °C, most TiO₂ was reacted to form TiC, which began to be the dominating phase.

With an increase in reaction temperature and time, it was observed that the (200) peak of the synthesized TiC shifted from 41.90° to 41.70° (Figure 3A,B). The lattice constant of the TiC (1300 °C, 10 min) and TiC (1400 °C, 30 min) were calculated to be 4.321 Å and 4.324 Å, lower than the standard value of 4.327 Å. The results show that a higher temperature and longer reaction time are beneficial for the growth of TiC, which was also reported by Preiss et al. [29,30].

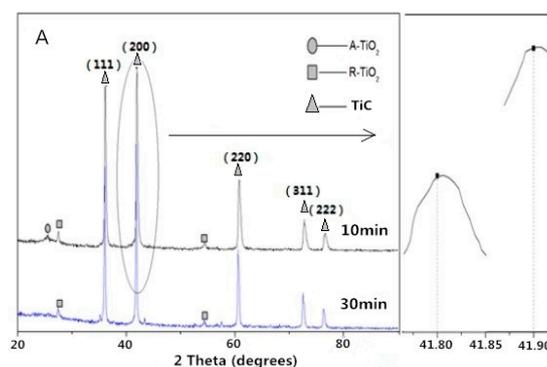


Figure 3. Cont.

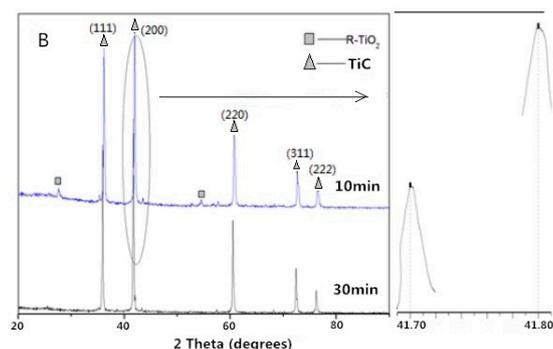


Figure 3. XRD patterns of the samples synthesized at (A) 1300 °C and (B) 1400 °C.

SEM images of the samples synthesized at various temperatures (1100, 1200, 1300, and 1400 °C) for 30 min are shown in Figure 4. With an increase in reaction temperature, the size of the powders became larger, changing from ca. 0.2 μm at 1100 °C to ca. 0.4 μm at 1200 °C. When the reaction temperature was increased to 1300 °C, the TiC powders exhibited a pseudocubic morphology (Figure 4C) with a particle size of ca. 0.7 μm . It should be noted that, although no other diffraction peaks were observed in Figure 2D, amorphous carbon should still exist because excessive carbon was added to ensure a complete carbothermal reduction, because carbon black acts as both the carbon source and the media to transform microwave dielectric to heat.

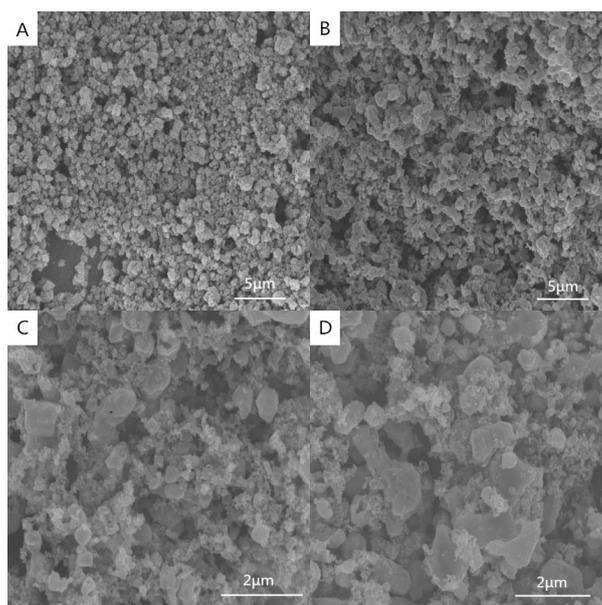


Figure 4. SEM images of the products synthesized at various temperatures for 30 min: (A) 1100 °C; (B) 1200 °C; (C) 1300 °C; (D) 1400 °C.

3.2. Effect of Carbon Content

TiO₂ is a poor microwave absorber, while carbon black absorbs microwave very effectively. During the reaction, carbon black not only participates in the reaction but also serves as a medium to absorb microwave radiation to help heat the mixture of the reactants. Its content was reduced along the reaction; therefore, excessive carbon black was added during the reactions. In order to study the role of carbon content in the process of the reduction of TiO₂, mixtures of TiO₂ and C at various molar ratios (1:3.0; 1:3.2; 1:3.4, and 1:3.6) were reacted at 1400 °C for 30 min via microwave heating.

Table 1 presents the results calculated from the data of the XRD and EDS measurements of the products from the samples starting at various TiO₂ and C mole ratios. The results showed that, with

an increasing amount of carbon in the mixture, both the concentration and lattice constant of TiC increased, which suggests that a higher concentration of C is favorable for the growth of TiC.

Table 1. Product composition after reaction at 1400 °C for 30 min under various TiO₂ and C ratios.

TiO ₂ :C (mol:mol/wt:wt)	Composition of Product (wt %)			TiC (200) Peak Position (Degree)	Lattice Constant of TiC (Å)
	TiO ₂	C	TiC		
1:3.0/1:0.45	15.5	4.2	80.3	41.92	4.319
1:3.2/1:0.48	6.7	5.7	87.6	41.86	4.320
1:3.4/1:0.51	2.4	8.3	89.3	41.78	4.322
1:3.6/1:0.54	0	9.4	90.6	41.70	4.324

4. Conclusions

In conclusion, our experimental results showed that pure and pseudocubic TiC phase could be synthesized by directly reducing A-TiO₂ instead of R-TiO₂ with the assistance of quick microwave heating. The lattice constant of TiC increases with an increasing reaction temperature and time. Carbon black acts as both the carbon source and the media to transform microwave dielectric to heat. A high ratio of C to TiO₂ in the starting materials is favorable for improving the conversion rate and quality of TiC powders. Compared with the carbothermal reduction using conventional heating to synthesize TiC powders, which typically requires a temperature of 1700–2400 °C for 10 to 24 h, TiC powders could be synthesized at a temperature of as low as 1200 °C during microwave heating, and the carbothermal reduction can be finished within 30 min at 1400 °C. Therefore, the preparation of TiC powders via microwave heating is much more energy-effective and thus promising for large-scale production.

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Author Contributions: Hui Wang and Lingke Zeng conceived and designed the experiments; Wencheng Zhou performed the experiments; Lingke Zeng and Luyi Sun analyzed the data; Yanchun Liu contributed in experiments and characterizations; Wang Hui and Luyi Sun wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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