



# Synthesis and characterization of TiC nanopowders via sol-gel and subsequent carbothermal reduction process



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## ABSTRACT

TiC nanocrystalline powders were synthesized by in-situ carbothermic reduction of Ti-O-C precursor under vacuum atmosphere. And the Ti-O-C precursor was formed by sol-gel method from titanium butyrate (TBOT) and sucrose. To obtain stable sol, TBOT was directly added into mixed solution which contains water, sucrose, acetic acid (AcOH) and acetylacetone (ACAC). This procedure is more convenient and economical because it avoids the use of alcohol which is used as solvent in most reports of alkoxide hydrolysis sol-gel method. TG-DSC, XRD, FTIR and SEM/TEM were employed to analyze and characterize the product during the entire process. The phase composition and crystalline structure parameters of powders with different C/Ti molar ratio were investigated by Rietveld refinement method, and elemental quantitative analysis of the samples were performed. Furthermore, the optimal parameters of carbothermal reduction were obtained and the grain growth mechanism was demonstrated. The results show that TiC nanocrystalline powders (C/Ti molar ratio is 3.5 in the precursor) were synthesized at 1300 °C for 2 h, which have near standard lattice parameter, well crystallinity and fine average grain size (~37.4 nm).

## 1. Introduction

As an ultra-high-temperature ceramics, titanium carbide (TiC) is a remarkable material with a sequence of excellent properties, such as high melting point, very high hardness, outstanding wear and corrosion resistance and excellent electrical and thermal conductivity [1,2]. These extraordinary properties make TiC attractive for extensive applications in cutting tools, wear-resistant coatings, electronic components and aerospace field. In addition, TiC can also be used as reinforcement phase in composite materials, which can significantly improve the properties of the matrixes [3–6].

Until now, TiC powders have been synthesized by diverse methods. Traditionally, TiC powders are obtained from TiO<sub>2</sub> and carbon by carbothermal reduction, whose equation is shown as below [7]:



Carbothermal reduction is widely used to synthesize TiC due to a convenient process route, low cost of raw material and capacity of production. However, such process usually requires high temperature (1700–2100 °C) and a long production period. Additionally, the extent of the reaction is influenced by the contact area of reactant and the particle size of products depends on the size of raw material [8]. Therefore, it is difficult to prepare powders with a nano-level size and

the synthesized products usually have a relatively low purity [9]. Besides this, TiC powders also have been synthesized by following routes: (i) direct reaction method from Ti and C, which including traditional mechanical alloying (MA), mechanically induced self-propagation reaction (MSR) and self-propagating high temperature synthesis (SHS) [10–12], (ii) metallic thermal reduction of titanium oxides or titanium chloride [13,14], (iii) Chemical vapor deposition (CVD) from titanium chloride and hydrocarbon gases [15], etc. However, these methods couldn't prepare pure TiC nanopowders with low cost or convenient process, either.

In comparison with methods mentioned above, the sol-gel technique combined with carbothermal reduction is a promising method to produce carbide ceramics with fine grain size and high purity at a relatively low temperature. In addition, the composition of final products was mostly predetermined by sol-gel technology and the process flow are feasibly controlled. The sol-gel approach ensures a high homogeneity in chemical composition of final product as the original components can be mixed at molecular or atom level. The final products are synthesized via heating the precursor derived from sol-gel process. The enormous contact area of reactant in the precursor make the reaction conduct at a relatively low temperature, and the as-synthesized product usually has fine sizes and high purity [16]. Jie Zhong et al. applied titanium tetraisopropoxide (TTIP) and furfuryl

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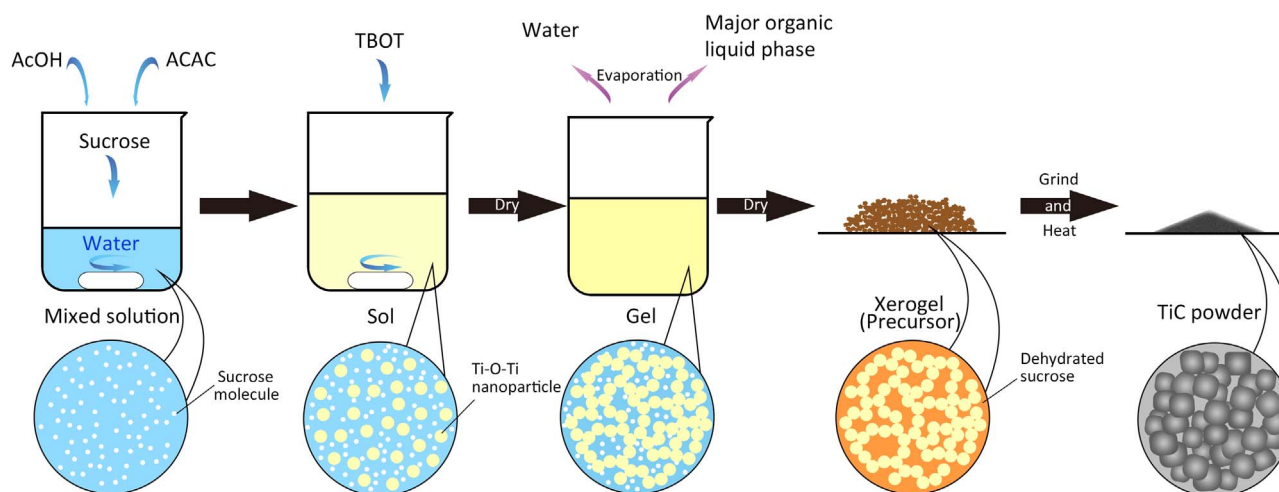


Fig. 1. Illustration of the experimental process.

alcohol (FA) as raw materials to gain mesoporous TiC microspheres with nanosized TiC crystals (30–50 nm) via sol-gel method combined carbothermal reduction process. [17]. Haijun Zhang et al. had prepared pure TiC powders with crystalline size about 100–150 nm (some of them were 20–30 nm) at 1200 °C by sol-gel and microwave carbothermal reduction using tetrabutyl titanate and sucrose as the starting materials [16]. Ilmārs ZĀLĪTE et al. had successfully synthesized 40–50 nm TiC nanopowders by carbothermal reduction, and two kinds of precursor gels whose Ti sources were Ti (IV) chloride and Ti (IV) n-propoxide were used [18]. To our knowledge, almost all metal alkoxides tend to react with water spontaneously and rapid hydrolysis, and then it leads to precipitation [19]. Therefore, absolute alcohol solvent was used to dissolved titanium alkoxides in above reports. However, it is uneconomical that a large amount of alcohol was used and the alcohol evaporated during the subsequent heat treatment.

This study aimed at synthesizing pure TiC nanopowders at lower cost and temperature via sol-gel method combined with carbothermal reduction process. Here, deionized water rather than alcohol was used as solvent, and titanium alkoxide was directly added into a mixed solution in the end. In the presence of acetic acid (AcOH) and trace amount of acetylacetone (ACAC) in the mixed solution, hydrolysis and condensation of the titanium alkoxide were controlled, thus stable alkoxide sol could be obtained [19,20]. Sucrose was selected as carbon source because it can decompose to carbon and H<sub>2</sub>O completely, so that the C/Ti molar ratio in the Ti-O-C precursor can be fixed precisely [19]. Some works have been done to analyze chemical reactions, thermal behavior, elemental composition, evolution of phase and crystalline structure during the process. Furthermore, the effect of C/Ti molar ratio and process parameters of carbothermal reduction on grain size, phase composition and microstructure of the final powders have been investigated.

## 2. Experimental

### 2.1. Starting materials

Titanium butyrate (TBOT, Ti(C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub>) and sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) were utilized as starting materials in the present work. Acetic acid (AcOH) and acetylacetone (ACAC) were used as chelating agent and chemical modifier. These chemicals are all analytical reagent grade and without further purification.

### 2.2. Preparation of Ti-O-C precursor

In a typical process, the volume ratios of TBOT: AcOH: H<sub>2</sub>O were 1: 1.33: 0.83, and ACAC was added as 0.15 vol% of the total system. The Ti-O-C precursor was prepared as following. Firstly, in order to control

the molar ratio of C and Ti, a certain amount of sucrose was dissolved in deionized water with magnetic stirring at 35 °C (by a Thermostat Magnetism Msier). Subsequently, AcOH and ACAC were added in the solution, and magnetic stirring was lasted for tens of minutes to make the mixed solution uniform. While continuously vigorous stir, TBOT was dropwise added into the solution and the temperature was kept at 30 °C. During the whole stirring process, the color of the solution changed from transparent to yellowish at the beginning of adding TBOT and then turned to transparent golden yellow after a few minutes of stirring. This phenomenon indicates the hydrolysis and condensation of TBOT. After several hours of continuous stirring, homogeneous sol was obtained. To prepare Ti-O-C precursor, the sol was dried in oven at 120 °C for 24 h firstly. With the evaporation of water and other organic liquid phase, sol turned into gel and became xerogel in the end. The xerogel was ground to powders (Ti-O-C precursor) in a mortar prior to next procedure.

### 2.3. Carbothermal reduction

The Ti-O-C precursor powders were placed into an Al<sub>2</sub>O<sub>3</sub> crucible. Afterwards the carbothermal reduction was carried out at 200 °C–1400 °C at a heating rate of 7 °C/min and maintained at the maximum temperature for 30 min ~ 2 h under dynamic vacuum. Samples were taken out after the furnace cooled down to room temperature normally. The illustration of the synthesized process is shown in Fig. 1.

### 2.4. Characterization

To analyze reactions occurred in the precursor during the heating process, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted in Ar from ambient temperature to 1200 °C at a heating rate of 10 °C/min, through a simultaneous thermal analyzer (NETZSCH STA 449 C). Fourier transform infrared spectrometer (FTIR) was employed with Nicolet 6700 (wavenumbers range from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>) to monitor the changes of chemical bonds and groups of TBOT, sol, precursor powders, precursor powders heated at 200 °C and 400 °C for 1 h under vacuum. Phase constitution and crystallinity were identified by powder X-ray diffraction (XRD, Bruker Advance D8) working at 40.0 kV 40.0 mA (Cu k<sub>α</sub> radiation, λ = 1.54060 Å), and the XRD data were collected in a 2θ range of 20°~80° with a step width of 0.02°. The crystallite size was calculated by Debye-Scherrer equation from the full width at half maximum (FWHM) and the lattice parameters were determined by Rietveld refinement method through XRD patterns (step-scanning, and the data were collected in 2θ of 30°~50° for an acquisition time of 1.2 s in

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