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Cite this article as: Rare Metal Materials and Engineering, 2018, 47(4): 1082-1088.

ARTICLE

Synthesis of Stoichiometric Titanium Carbide by a Combination of Carbothermal Reduction and Molten Salt Method and Its Characterization

Song Yunfei, Zhu Hongxi, Deng Chengji, Yuan Wenjie, Ding Jun

The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

Abstract: A novel method of preparing stoichiometric titanium carbide (TiC) powders was present by combining carbothermal reduction and molten salt synthesis (MSS) from raw materials of titanium oxide (anatase), C (carbon black), and sodium chloride. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), laser particle size analysis, energy spectrum analysis (EDS), and thermodynamic analysis were used to characterize the powders. The effects of heating temperatures and molar ratios of titania to carbon black on the preparation of TiC were discussed. Results show that the use of MSS reduces the synthesis temperatures of both stoichiometric and pure TiC from 1700 °C to 1550 °C and the time required for synthesis decreases from 10 h for conventional carbothermal reduction of TiO₂ to 3 h. A dissolution-precipitation mechanism of synthesis of TiC by MSS was established based on these observed results.

Key words: TiC; carbothermal reduction; molten salt synthesis; dissolution-precipitation mechanism

TiC, a transition metal carbide with a face-centered cubic structure, has many useful properties such as low density (4.93 g/cm³), high melting point (3067 °C), pronounced hardness (28~35 GPa), high Young's modulus (300~480 GPa), superior chemical and thermal stability, and excellent wear resistance. It has been widely used for various superhard material tools, such as tool bits, blades, screws, industrial knives, compaction dies, wear parts for aerospace, and abrasive materials in the manufacture of sintered carbide plates for cutting tools^[1-3]. It is also used as an additive in plastic and rubber parts. There are many methods of producing TiC powder^[4-10]. For example, it can be synthesized by carbon/magnesium reduction of titanium metal (combustion synthesis) through the following reaction^[11,12]:

$$Ti(s)+C(s)=TiC(s)$$
(1)

However, using metallic titanium as a starting material is relatively expensive and the product is generally characterized by a high oxygen content. Other methods include chemical reaction between TiCl₄, H_2 , and C; self-propagating high-temperature synthesis; reaction of titanium sulfide with carbon; reaction of titanium hydride with carbon; chemical vapor deposition; and the sol-gel method. These routes are also considered unsuitable for industrial application, because of their extreme operating conditions and the need for more expensive raw materials. In general, carbothermal reduction of titanium dioxide (TiO₂) is an economical way of TiC production; nevertheless, the conventional carbothermal reduction method requires a high temperature (>1700 °C) and a long reaction time (>10 h) due to the use of solid TiO₂ and carbon powder as raw materials, so it requires considerable energy and time, which renders the production of titanium carbide expensive and restricts its use. The reaction equation is:

$$TiO_2(s)+3C(s)=TiC(s)+2CO(g)$$
(2)

Molten salt synthesis (MSS) is a large scale, one-step, rapid, and environmentally friendly method of preparing functional materials. It has gained extensive attention. Salt melts have a long history of use as solvents in research and in industry.

Received date: April 25, 2017

Foundation item: National Natural Science Foundation of China (51574187, 51502215)

Corresponding author: Deng Chengji, Ph. D., Professor, The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, P. R. China, Tel: 0086-27-68862089, E-mail: cjdeng@wust.edu.cn

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This paper presents a novel approach to the preparation of TiC powder through combination of carbothermal reduction of TiO_2 and MSS. This novel combination is a simple and effective method of preparing highly pure and stoichiometric TiC powder at low temperatures. Molten salt was used to produce a liquid state to promote atom diffusion and crystal growth. A detailed description of this route, including formulas, sintering temperatures, gas atmospheres, and thermodynamic processes was presented here. The physical, chemical, and crystalline nature of this prepared powder was characterized. The mechanism by which TiC powder was synthesized using molten salt is described.

1 Experiment

Titania powder (anatase, TiO₂>98.8%, size<0.0074 mm), a source of carbon (carbon black, C>99.0%, size<0.0084 mm), and sodium chloride (NaCl, 99.0 % pure) were used as starting materials. To prepare TiC powder, the molar ratios of titania to carbon black were 1:2, 1:3, 1:3.2, 1:3.4, 1:3.6, 1:3.8, and 1:4. Titania and carbon black were previously mixed using hand milling with a mortar for 30 min. Then the titania-carbon mixture was added to the planetary ball mill with additional NaCl for ball milling with alcohol as shown in Fig.1. The mass ratio of NaCl to the rest of the mixture was 1:1. Afterwards, the homogeneous mixture was dried at 70 °C for 12 h and fired in a tube furnace at 1300~1550 °C for 3 h in flowing argon atmosphere at a purity of 99.9999 wt% to produce the powder. To remove residual sodium chloride and unreacted carbon black, the resulting grey-black suspension was filtered off and the raw product was washed first with distilled water and then ethanol. Finally, the resulting black product was dried at 90 °C for 24 h. It was TiC powder.

Phases in the synthesized powder were studied using X-ray diffraction (XRD, Philips, X'Pert Pro), Spectra were recorded

at 40 mA and 40 kV, using the Cu K α radiation (λ =0.1542 nm) within the range of 10° and 90° (2 θ). Thep owder diffraction (PDF) card used for identification was TiC (03-065-8808). The microstructure and morphology were observed by scanning electron microscopy (SEM, FEI, Nova 400 Nano), high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2000F), and energy dispersion spectrum analysis (EDS). Particle size distributions of the synthesized powders were determined using a laser scattering method (Mastersizer 2000).

2 Results

2.1 Heating temperatures and $n(C)/n(TiO_2)$ and the synthesis of stoichiometric TiC

Powder X-ray diffraction was used to determine the phase composition of the products. The formation of TiC powders was studied in the temperature range of 1300~1550 °C in NaCl salt media. Fig.2 represents the XRD patterns of samples fired at different temperatures in argon atmosphere, when the molar ratio of TiO₂ to C was 1:3. It could be noted that carbon shows no reflection characteristics in either of the XRD, indicating that the carbon black is almost fully consumed in reaction or thoroughly washed away. As shown in the Fig.2, all peaks corresponding to the raw powders are sharp and smooth, which show the particle size of TiC powder to be large and the elements to be almost completely free from lattice strain. The phases in the sample sintered at 1300 °C contain Ti_xO_y and low nonstoichiometric titanium carbide-TiC_x $(0.47 \le x \le 0.99)$ peaks. The Ti_xO_y phase gradually disappears as the temperature increases to 1550 °C, but the opposite is true for the TiC_x phase. Results show that heat-treated temperature of 1550 °C gives Ti_rO_v an absolute conversion to TiC_r .

The formation of stoichiometric TiC was clearly observed by the XRD patterns of the product powders in Fig.3. When the molar ratio of TiO₂:C is 1:2, Ti_xO_y and TiC_x are identified. When the mole ratio of C to TiO₂ is increased to 3:1 at the



Fig.2 XRD patterns of samples synthesized via combining carbothermal reduction and molten salt method (n(C)/ n(TiO₂)=3:1)



Fig.1 Schematic diagrams of agate jar (a) and tube furnace (b) in experimental process



Fig.3 XRD patterns of samples with different molar ratios of TiO₂:C synthesized via combining carbothermal reduction and molten salt method (1550 °C/3 h)

same temperature, Ti_xO_y disappears and pure TiC_x powders are produced. Results show that the peaks of TiC_x are not consistent with the peaks of stoichiometric TiC as indicated by the dotted line in Fig.4. Based on these results, it can be deduced that the ratio of raw materials is dominant at 1550 °C. The TiC_x lattice parameter decreases with reduction of carbon in TiC lattice. In order to confirm that the TiC powders synthesized in molten salt media are stoichiometric, it is necessary to calculate the lattice parameter of TiC. The lattice parameter of TiC was obtained using X-ray diffraction pattern with the following equations:

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \tag{3}$$

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$$
(4)

Because the systematic error in $\sin 2\theta$ decreases as θ increases, the values of α for high diffraction angles are probably more accurate. For this reason, the current work focuses on the values of α for high diffraction angles. As shown in Table 1,



Fig.4 Amplificatory XRD patterns of Fig.3 at the 2θ range of $34^{\circ} \sim 38^{\circ}$

Table 1	Indexing the X-ray diffraction patterns of TiC				
2θ (JCPDS	Standard TiC	Experimental 2θ (the	Measured TiC		
card 03-065-	lattice para-	molar ratio of	lattice		
8808)/(°)	meter, a/nm	TiO ₂ :C=1:3.2)/(°)	parameter, a/nm		
60.637	0.43160	60.629	0.43165		
72.589	0.43160	72.632	0.43159		
76.378	0.43160	76.379	0.43159		

while the mole ratio of TiO₂ to C is 1:3.2, all values of α calculated from the diffraction pattern of the TiC powders starting from 2θ =60.6285° are nearly equal to their corresponding values of α calculated from the standard lattice parameter α (0.4316 nm), so it can be concluded that the composition of synthesized TiC powders is nearly stoichiometric.

It is concluded from these XRD patterns that the higher temperatures and higher molar ratio of C to TiO_2 are favorable to the synthesis of pure and stoichiometric TiC powders in molten salt media. The molar ratio of TiO_2 to C is the dominant factor to prepare TiC, while the temperature is 1550 °C. Only if the molar ratio of C to $TiO_2>3:1$, are the TiC powders prepared at 1500 °C for 3 h in the NaCl salt media considered stoichiometric.

2.2 Microstructure characterization

The morphology of the synthesized powders and point-and-shoot EDS analysis in special area are shown in Fig.5. Two sorts of typical particles are observed after 3 h of synthesis at 1550 °C in molten salt media, and the molar ratio of TiO₂ to C is 1:4. The pure stoichiometric TiC phase is confirmed using EDS analysis. It is consistent with the XRD patterns. As shown in Fig.5a, the atomic fraction of C is 48.31 and that of Ti is 51.69. The ratio is close to 1:1 in the absence of impurities. The close-up SEM image shows these particles consist of tiny octahedral and columnar shapes and the octahedral particles are expected to be the primary particles from TiO₂ sources. The crystal size is about 3 µm. Fig.5c exhibits distinctly different microstructure with uninhibited grain size. Long strips of crystals with characteristic rhombohedral shaped heads are present. They are derived from grain growth when there is enough space. The difference in crystal size distribution along the horizontal and vertical directions is vast.

Fig.6 displays the particle size and distribution of TiC powders tested using a Mastersizer 2000. As can be seen from the picture, particle size is mainly distributed in about 10 μ m. The mean volume diameter and the mean surface area diameter of synthesized TiC powder particles measured by laser scattering method are 18.737 and 9.237 μ m, respectively as shown in Table 2. The data of the mean volume diameter



Fig.5 SEM images and EDS spectrum of samples synthesized via combination of carbothermal reduction and molten salt methods $(n(C)/n(TiO_2)=4:1, 1550 \text{ °C/3 h}):$ (a) TiC, (b) octahedral TiC marked A in Fig.5a, and (c) columnar TiC marked B in Fig.5a; (d) EDS spectrum of TiC



Fig.6 Particle size and distribution of TiC powders synthesized at 1550 °C for 3 h in NaCl

Table 2Parameters of TiC synthesized via combining carbothermal
reduction and molten salt method $(n(C)/n(TiO_2)=4:1,$
1550 °C/3 h) measured by laser particle size test

Specific surface area/m ² ·g ⁻¹	Surface weighted mean diameter/µm	Volume weighted mean diameter/µm	d(0.1)/ μm	d(0.5)/ μm	d(0.9)/ μm
0.643	9.237	18.737	4.480	13.619	39.331

are much lower than those of the diameter of the surface area. This is caused by particle agglomeration, which takes place because of the contact between reactants or the sintering promoted by reaction medium of NaCl. In this way, the conglomeration of the particles could explain the decreased mean surface area diameter of sample particles and thus partially compensate for the SEM measurement error in particle size.

TEM images further indicate the presence of two typical types of particles in the synthesized powders: one is octahedral with size>1 μ m and the other is columnar-shaped with tetrahedral heads (Fig.7). The electron diffraction pt terns confirm that the particles are TiC phase with cubic crystal system, like those displaced in JCPDS card 03-065-8808.

3 Discussion

3.1 Thermodynamic analysis

The Gibbs free energy for the carbothermal reduction of TiO_2 was calculated using the data and formula given in a previous work^[18]. The initial reaction temperature at atmospheric pressure was found in this way. Some possible reactions between TiO_2 and C are listed below.

$$TiO_2(s) + 2C(s) = Ti(g) + 2CO(g)$$

 $\Delta G = 661\ 071 - 359.70T\ (J \cdot mol^{-1})$
(5)



Fig.7 TEM images and SAED patterns of samples synthesized via combination of carbothermal reduction and molten salt method (n(C)/n(TiO₂)=4:1, 1550 °C/3 h): (a) octahedral TiC and (b) columnar TiC

$$TiO_{2}(s) + 3C(s) = TiC(s) + 2CO(g)$$

$$\Delta G = 522\ 643 - 350.34T (J \cdot mol^{-1})$$
(6)

$$2TiO_{2}(s) + C(s) = Ti_{2}O_{3}(s) + CO(g)$$

$$\Delta G = 234\ 675 - 178\ 43T\ (J \cdot mol^{-1})$$
(7)

$$3TiO_{2}(s) + C(s) = Ti_{3}O_{5}(s) + CO(g)$$

$$\Delta G = 272\ 707 - 209.77T\ (J \cdot mol^{-1})$$
(8)

$$4\text{TiO}_{2}(s) + C(s) = \text{Ti}_{4}O_{7}(s) + CO(g)$$

$$\Delta G = 262\ 366 - 206.41T\ (\text{J} \cdot \text{mol}^{-1})$$
(9)

The relationship between Gibbs free energy and temperature is shown in Fig.8. All of these reactions are endothermic. ΔG is a measure of the thermodynamic driving force that makes the reaction proceed. It can be expressed as:

$$\Delta G = \Delta H - T \Delta S \tag{10}$$

here ΔG is Gibbs free energy, ΔH is the enthalpy change, ΔS is entropy change and *T* is temperature. If $\Delta G < 0$, the chemical reaction proceeds spontaneously. Moreover, the more negative the value of ΔG , the more likely that the reaction toward positive will proceed^[19]. As shown in Fig.8, except for reactions of Eq.(5), ΔG of other reactions is always below zero at 1550 °C. Comparing the value of temperatures at the point of $\Delta G=0$, we can see the formation sequence of the products in Ar atmosphere is to be Ti₄O₇, Ti₃O₅, Ti₂O₃, and TiC. Results are consistent with the data of XRD patterns. The reaction shown in Fig.8 might occur and Ti phase might exist, if the temperature of heat-treatment exceeds 1837 K. The total synthesis reaction of TiC using NaCl salt as a reaction medium can be expressed using the following equation:



Fig.8 Gibbs free energy of the potential reactions at different temperatures

$$TiO_2(s) + 3C(s) = TiC(s) + 2CO(g)$$
(11)

Based on the basic formula of chemical equilibrium, the Gibbs free energy as a function of temperatures is given as follows:

 $\Delta G = \Delta G^{\theta} + RT \ln K = \Delta G^{\theta} + RT \ln (P_{\rm CO}/P^{\theta})^2$ (12) here ΔG is the Gibbs free energy of the reaction, ΔG^{θ} is the standard Gibbs free energy, *K* is the equilibrium constant, $P_{\rm CO}$ is the pressure of CO gas, P^{θ} is the standard atmospheric pressure and *R* is the gas constant. It is here concluded that the system does reach thermodynamic equilibrium through the present process if ΔG =0. This Gibbs equation shows that the lower the pressure of CO, the smaller the value of ΔG .

The relationship curve of the pressure of CO and TiC-generating temperature was drawn using a computer program, FactSage, based on its thermodynamic database, as shown in Fig.9. Thermodynamic analysis was performed at different pressures of CO from $0\sim0.2$ MPa. It is apparent that the initial reaction temperatures decreases obviously when the pressure of CO declines. In this way, the fast escape of CO gas contributes to the formation of TiC powder.



Fig.9 TiC-generating temperature as a function of CO pressure



Fig.10 Schematic illustration of the synthesis process of TiC powder by carbothermal reduction of TiO₂ with carbon black in NaCl salt media

3.2 Process of MSS

When the temperature of the perform is up to the melting point of NaCl (801 °C), TiO₂ and carbon black powders begin to be soluble in the molten salt media; as a result, the TiO₂ and carbon black are surrounded by melted NaCl. Increasing temperature from 998 °C starts the reactions between TiO₂ and carbon black with gas release of CO. At the end of reaction, only TiC particles are synthesized. In order to understand this process visually, the whole synthesis process of TiC is illustrated schematically in Fig.10. In previous study^[20-22], the solubility of bivalent metal oxides increases with the decreasing of the melting point and the cation radius. Unfortunately, seldom relevant research on the solubility of TiO₂ and carbon black in NaCl salt has yet been performed, but they may be soluble in the molten salt at the low temperatures needed for synthesis of TiC. In this case, it may be possible to synthesize TiC via precipitation from the salt containing the dissolved reactants ("dissolution- precipitation" mechanism)^[23]. Unlike the conventional reaction of carbothermal reduction of TiO₂, which requires high temperatures (1700~2100 °C) and a long reaction time (10~24 h), this route has low cost, lower reaction temperature (1550 °C), and shorter reaction time (3 h). This is attributable to the more homogeneous mixing and rapider diffusion of species such as Ti^{4+} and O^{2-} through the molten salt.

4 Conclusions

1) Stoichiometric and pure TiC with octahedral and columnar microstructures have been produced in Ar atomosphere at a relatively low temperature using MSS with titanium dioxide powder and carbon black as raw materials. The formation sequence of TiC powders is Ti_4O_7 , Ti_3O_5 , Ti_2O_3 , and TiC with increasing temperature.

2) Compared with traditional method to produce TiC powders, the application of MSS reduces the synthesis temperature from 1700 °C to 1550 °C. The time required for synthesis is reduced from 10 h to 3 h.

3) The synthesis of TiC by MSS involves a dissolutionprecipitation mechanism.

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碳热还原结合熔盐法制备碳化钛粉末与表征

宋云飞,祝洪喜,邓承继,员文杰,丁 军 (武汉科技大学 省部共建耐火材料与冶金国家重点实验室,湖北 武汉 430081)

摘 要:以NaCl为熔盐介质,采用锐钛矿型钛白粉和炭黑为原料,探索一种碳热还原结合熔盐法合成高纯碳化钛(TiC)的方法。借助XRD 研究了反应温度和原料配比对合成碳化钛的影响,采用SEM、TEM、EDS、粒度分析仪、热力学分析等检测分析手段对合成产物的特性 和过程进行分析。结果表明:相比传统的碳热还原合成碳化钛的方法,NaCl熔盐介质的引入可以有效地降低碳化钛的合成温度(从1700 ℃ 到1550 ℃)以及合成高纯碳化钛的时间(从10 h到3 h)。结合研究成果,提出了熔盐介质中溶解-沉淀的合成机理。 关键词:碳化钛;碳热还原;熔盐法;溶解-沉淀机理

作者简介: 宋云飞, 男, 1992 年生, 硕士, 武汉科技大学省部共建耐火材料与冶金国家重点实验室, 湖北 武汉 430081, 电话: 027-68862089, E-mail: 1054827854@qq.com

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