Titanium Carbide: Synthesis, Properties and Applications

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Keywords

Titanium carbide,
Properties,
Microstructure,
Applications,
Nanostructure

Abstract

Composite materials are known in various forms. The two distinctive constituents of these composite materials are the matrix material and the reinforcement material. A variety of materials are used as reinforcing material in composites titanium carbide (TiC). TiC acquired considerable attention because of its unique properties, which make it very attractive for advanced applications. The current review summarizes various synthesis techniques to produce TiC nanocomposite and highlights the major industrial applications of TiC. It was found that for certain techniques, the TiC powder has been synthesized directly, with different shapes and sizes, within a relatively very short time by eliminating a number of intermediate processes. However, this review deals with the detailed literature survey carried out on the preparation of titanium carbide powder, and also covers analyzes the results from the experiments conducted on the preparation of powder by the works of several researchers. Therefore, in-depth conclusions have been done on the research processes that are being carried out on improving the properties of TiC reinforced composites.

1. Introduction

For a decade, titanium carbide (TiC) attracted considerable attentions due to its special characteristics like surface, shape, size, and interface. Among the ceramic materials, TiC is a well-known material reinforcing agent in metal composites due to its high melting point, elastic modulus, high Vickers hardness, low density, high flexure strength, good thermal conductivity, high resistance to corrosion and oxidation, and high thermal shock resistance. In recent years, significant research activities were focused on the synthesis of TiC nanoceramic. Thus, throughout all of those developments, TiC always reveals special morphology to follow the further applications.

However, TiC can be synthesized using several methods, which will be discussed in depth in this review. Indeed, methods like traditional method, chemical vapor deposition (CVD), laser igniting self-propagating high-temperature synthesis (LISHS), sol-gel, self-propagating high-temperature synthesis (SHS), mechanical alloying (MA), etc will be presented in details.

Titanium carbide has been widely used for high-temperature applications, such as aerospace, cutting tools, electronics, and chemicals. It is also used as reinforced particles in composites and hardening phase of super-alloys.

In this review paper, we will focus on the influence of titanium carbide synthesis methods on their properties and applications.

2. Structure of titanium carbide

Titanium carbide, with chemical formula TiC, crystallizes in the cubic system: NaCl type with space group $Fm\bar{3}m$ ($Z = 4$). The lattice constant is $a = 0.4327$ nm. Ti atoms occupy the origin positions (0,0,0), however, C atoms are located in $(1/2, 1/2, 1/2)$ positions. Ti and C atoms are

octahedrally coordinated with each other; consequently, TiC octahedra share edges [1]. Fig. 1 shows the schematic structure of titanium carbide. As can be seen, Fig.1a illustrates the typical crystal structure of TiC [2]. C atoms occupy the octahedral positions. Thus, if viewed along the direction perpendicular to the planes, Ti and C atoms form a hexagonal shape, as presented in Fig.1b [3].

Figure 1. (a) Crystal structure of TiC, and (b) projection of Ti-C atoms along direction [2]. The smaller and black atoms are C atoms.

3. Summary of properties of titanium carbide

Titanium carbide particles are effectively used as a reinforcement phase in composites due to its superior mechanical properties, unique electrical properties, and high temperature strength. Fine grained TiC can improve yield strength of the composites through dispersion and grain size mechanisms and improve toughness by hindering crack propagation [4, 5]. Table 1 summarizes the electrical, mechanical, chemical, and thermal properties of titanium carbide at room temperature [6-10].

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Table 1. Properties of TiC at room temperature

Electrical properties	
Molecular Weight	59.91
Density (g.cm ⁻³)	4.91
Electrical conductivity (10 ⁶ S.cm ⁻¹)	30
Electrical resistivity (μΩ.cm)	68
Hall constant (10 ⁻⁴ cm ³ /A.s)	-15
Magnetic susceptibility (10 ⁻⁶ emu/mol)	-7.5
Superconductive transition temperature (K)	1.15
Mechanical properties	
Vickers hardness (GPa)	28-35
Young's modulus (GPa)	410-510
Shear modulus (GPa)	186
Flexure strength (MPa)	240-390
Poisson's ratio	0.191
Chemical properties	
Chemical symbol	TiC
Color	Silver gray
Electronic configuration	Ti: [Ar]3d ² 4s ² C: [He]2s ² 2p ²
Chemical composition (%)	Ti content (79.95) C content (20.05)
Structure	Cubic B1 (NaCl)
Lattice parameter (nm)	0.4328
Space group	<i>Fm3m</i>
Pearson symbol	cF8
Thermal properties	
Melting temperature (°C)	3067
Boiling temperature (°C)	4820
Thermal conductivity (°C)	21
Enthalpy of formation (kJ.mol ⁻¹)	-184
Specific heat (J/mol.K)	33.8
Thermal expansion (×10 ⁻⁶ /°C)	7.6

4. Phase diagram of titanium carbide

Fig. 2 illustrates the binary phase diagram of Ti-C system [11]. The system consists of solids α -Ti, β -Ti, and a refractory monocarbide (TiC). As we can see, two other phases are present: liquid (L) and graphite (C). Thus, the system represents two eutectic and one peritectoid at 1646, 2776, and 920 °C, respectively.

5. Fabrication processes of titanium carbide

Titanium carbide occurs in nature as a form of the very rare mineral khamrabaevite [(Ti,V,Fe)C]. Traditionally, TiC powders are commercially produced by the reaction of titanium dioxide and carbon in the temperature range of 1700-2300 °C for 10-24 h [12]. The synthesis of TiC powders by the carbothermal reduction demands a significant amount of energy. Thus, there have been several methods regarding synthesis of titanium carbide [13, 14]. Every approach has varying features of morphology, particle size and distribution, condition of agglomeration, chemical purity, and stoichiometry [4].

Figure 2. Ti-C phase diagram [11]

5.1. Carbothermal reduction

Carbothermal reduction is a simple and inexpensive process that produces large amounts of powder and makes use of inexpensive precursor materials. These reduction processes are basically carried out at high temperatures; hence they are known as carbothermal reduction process [4, 15]. Almost all commercial productions primarily use a carbothermal reduction due to its low cost [4, 16]. There is currently no commercial powder production process to synthesize submicron TiC powder [17]. TiO₂ was used as a raw material on an industrial scale due to its low cost and easy availability which reduces the cost of production and makes the process economical. Furthermore, TiC powder was commercially produced primarily by the reduction of TiO₂ by carbon, especially carbon black, in a temperature range 1700-2100 °C and long reaction times (10-24 h) [4, 18].

The chemical reaction in the carbothermal reduction is given by:

It has been proposed that this general equation consists of three reaction steps (Fig. 3) [19].

* Step I: In this first step, CO is formed by a solid-state reaction between the titanium dioxide (TiO₂) and carbon particles or by the destruction of oxygen-containing functional groups at the carbon surface, acts as a reducing agent, resulting in the formation of lower oxides (TiO_{2n-1}). At the end of this step, Ti₃O₅ or Ti₂O₃ oxide phase is formed, there is no incorporation of carbon into the oxide particles, and CO is regenerated by the immediate conversion of CO₂ to CO on the solid carbon.

* Step II: In this intermediate step, cubic TiC_xO_y is formed from Ti₃O₅ or Ti₂O₃ phase. Thus, CO acts as a reducing agent and simultaneously disproportionate at the surface, which is rich in lattice defects and which accommodates the incorporation of carbon into the crystal lattice. CO₂ is generated and immediately converted to CO on the solid carbon. Therefore, the oxide particles are the precursors for the oxy-carbide formed. The reaction rates of oxygen loss and carbon incorporation are not equal; consequently, the intermediate oxy-carbide is sub-stoichiometric.

* Step III: In this final step, there will be a substitution of oxygen by carbon in TiC_xO_y. The mass transfer is realized by the same reaction mechanism as in reaction step II.

Figure 3. Schematic of the reaction mechanism of the carbothermal reduction of TiO₂ [19]

There have been many studies on the fabrication of TiC powders by carbothermal reduction. TiC nanoparticles were fabricated by carbothermal reduction of precursor gels. Thus, TiC nanopowders with the specific surface area of 30 - 200 m²/g, and the crystallite size of 40-45 nm were obtained [20]. Moreover, titanium carbide allows new applications including various types of composite materials [2]. The experimental results show that the samples have average sizes ranging within 30-40 nm. There was other work regarding synthesis of TiC powders, with lattice parameter of 0.43631 nm, using carbothermal reduction from TiO₂, C, and Ti metallic form [21].

Wei et al. (2011) [22] prepared homogeneous and fine TiC powders via carbothermal reduction at 1550 °C for 4 h in a vacuum. In their study, the reduction of TiO₂ by graphite was also investigated. Sarkar et al. (2009) [23] studied the carbothermal reduction of nano-rutile by amorphous carbon. They reported that TiC nanoparticles with crystallite size smaller than 100 nm are obtained. Similarly, Berger (1992) [24] investigated the mechanism and kinetics of TiC formation from eight starting mixtures, four titanium dioxide grades (three rutile grades with various grain sizes and one anatase grade), and two carbon blacks (one furnace black and one acetylene). It was found that the use of anatase has no accelerating effect on the reaction kinetics, while the grain size of the rutile grades has an effect only at high temperatures. It was also shown that the carbon black grades give no clear picture of the influence of their particle size and degree of graphitization.

Maitre et al. (2000) [25] investigated the role of some technological parameters during carburizing titanium dioxide from mixtures TiO₂/C. They concluded that the carburizing rate of TiO₂ can be accelerated by using the fine C powders, and with an important gas flow for reducing the partial pressure of carbon monoxide in the reactor. In fact, high purity TiC material, with reasonable reaction times, was obtained. Chandra et al. (2009) [26] synthesized nano-TiC powder using carbothermal reduction of titanium gel precursor and carbon particles. Koc (1997) [27] found that fine particle size of TiC (0.1 - 0.3 µm), oxygen content of 0.57 wt% and lattice parameter of 0.4331 nm, was obtained by carbothermal reduction of carbon-coated titania.

Preiss et al. (1999) [28] produced TiC powder, with finer particle size (1 µm) and with lower oxygen content (1.2 - 3.4 wt%), by using the carbothermal process from rutile and carbon black. Gotoh et al. (2001) [29] successfully synthesized TiC nanoparticle using carbothermal reduction from a composite of TiO₂ nanoparticles and methylcellulose (organic polymer). Koc and Folmer (1997) [30] used carbothermal for the reduction of ultrafine titania powders. They concluded that high purity and nonagglomerated TiC powders, with finer particle size (0.1 µm) and with lower oxygen content (0.6 wt%), are obtained. Sen et al. (2010) [31] prepared fine TiC powders by carbothermal reduction of titania and charcoal at vacuum condition. They revealed that fine TiC powders (D50, 2.05 µm), with low impurities, were obtained at 1450 °C for 8 h when the system pressure was about 1- 60 Pa.

In this context, Shin and Eun. (2015) [32] used two precursors to synthesis TiC powders. For the first, TiC powder is synthesized from a micron-sized mesoporous metatitanic acid-sucrose precursor (precursor M) by a carbothermal reduction process. For the second, TiC powder is prepared using a nanosized TiO₂-sucrose precursor (precursor T). The TiC prepared using precursor M at 1500 °C for 2 h in argon exhibited similar properties to those of the powder obtained from precursor T in terms of the crystallite size (58.5 versus 57.4 nm), oxygen content (0.22 versus 0.25 wt%), and representative sizes of mesopores (2.5 versus 19.7-25 nm). Ren et al. (2015) [33] used carbothermal reduction method to synthesize TiC fine powders from titania and carbon black under vacuum. They obtained a fine TiC powders with grain sizes of about 200 nm.

Yu et al. (2007) [34] reported the synthesis of high surface area TiC-carbon composites with a SSA of 823 m².g⁻¹ formed from the carbothermal reduction of titanium citrate with a triblock copolymer template at 1000 °C which resulted in 4 to 5 nm TiC nanocrystals suspended in a mesoporous carbon matrix with an over all stoichiometry of ~TiC_{0.8}. Additionally, Galevsky et al. (2015) [35] studied the effects of the major specifications of the fabrication technique on the content of titanium carbide and free carbon in the end product. They showed that carbidization of titanium is a preferable method of titanium carbide plasma fabrication. The experiments were carried

out in the reactor heat-insulated by zirconium dioxide lining with wall thickness of 0.005 m and outside diameter of 0.066 m which reduces its diameter to 0.056 m. Thus, titanium powder (alternative 1) and titanium dioxide (alternative 2) powder were chosen as raw materials, natural gas with methane content of 96 % was used as carbide-forming agent.

Table 2 summarizes the methods and processing conditions on synthesis of titanium carbide by carbothermal reduction. Table 2. Comparison of the methods and processing conditions on the synthesis of titanium carbide by carbothermal reduction

Reactants	Process parameters	Product quality	Ref.
*Series A: Ti(IV) chloride+ ethyleneglycol+ acitic acid (0.05M; 0.12M; 0.8M)	*Series A: Heating rate 10-200 °C/h; 0.5 h; Ar	TiC nanopowder with specific surface area of 30 - 200 m ² /g.	[20]
*Series B: Ti(IV) n-propoxide + saccharose + acetic acid (T/C = 1:3.7)	*Series B: Heating rate 300-350 °C/h; 1-2 h; Ar	Crystallites size of 40-45 nm	
TiO ₂ , C ₉ , and Ti metallic form	T= 293- 2300 K; t= 1h and t= 3h; Under vacuum (10 ⁻² ≤ P (Pa) ≤10 ⁻¹)	TiC powders with lattice parameter between 0.43800 and 0.43631 nm	[21]
8 starting mixture: 4 titanium dioxide grades (3 rutiles grades + anatase grade) + 2 carbon blacks (1 acetylene + 1 furnace black)	T = 1000- 1500 °C; t =30 min; Ar	The particle size of Ti (C,O)from TiO ₂ ./acetylene black: 0.4-1.0µm The particle size of Ti (C,O)from TiO ₂ ./furnace black:0.2-0.6µm The particle size of Ti (C,O)from TiO ₂ ./furnace black 0.4-1.2µm The particle size of Ti (C,O)from TiO ₂ ./acetylene black:0.2-0.8µm	[24]
Powder of TiO ₂ (68.9 wt%) + powder of C (31.1 wt%)	T = 1200 °C; 4h; under argon (30 lh-1)	TiC of good purity	[25]
Titanium gel precursor + carbon particles	T = 1300-1580°C; t = 2h; Ar	Nano-TiC powder	[26]
Carbon+ coated titania powder (TiO ₂)	T = 1200-1550°C; t = 4h; Inertatmosphere	Fine particle size of TiC (0.1-0.3 µm), oxygen content of 0.57 wt%; lattice parameter of 0.4331 nm; uniform particle shape	[27]
Rutile (TiO ₂) + Carbon black	T=1600°C; t=2 h; Ar	TiC with finer particle size (1µm) and with lower oxygen content (1.2-3.4 wt%)	[28]
TiO ₂ particles (5 nm in diameter) + methyl cellulose (MC)	T=1200-1500°C; heating rate of 10°C/min; 2h; Ar	TiC nanoparticle with low oxygen content (0.60-2.32 wt%)	[29]
TiO ₂ powder consisting of anatase and rutile phases +carbon black	T=1100-1550°C; t=2-4 h; Ar	Submicron, high purity, TiC powders with finer particle size (0.1µm) and with lower oxygen content (0.6 wt%)	[30]
* Micron-sized mesoporous metatitanic acid-sucrose precursor (precursor M); * Nanosized TiO ₂ -sucrose precursor (precursor T)	T=1500°C; t=2 h; Ar	* Precursor M: Crystallite size of 58.5 nm and oxygen content of 0.22 wt%; * Precursor T: Crystallite size of 57.4 nm and oxygen content of 0.25 wt%	[31]
Titania + charcoal	T=1450°C; t = 8h; P=1-60Pa	Fine TiC powders (D50, 2.05 µm) with low impurities	[32]
Titania (TiO ₂ ≥ 99.5 wt%) + carbon black (C ≥ 99.5 wt%). The average particle size of TiO ₂ and C was 20 and 30 nm, respectively. The molar ratio of C to TiO ₂ was 3:1	T=1300°C; t = 1h; P=20Pa; in vacuum	Fine TiC grains with size of 200 nm	[33]
Titanium citrate + triblock copolymer	T = 600-1000°C; t=2-6h; Ar	TiC with particle size of 4-5 nm and with high surface areas (up to 800 m ² .g ⁻¹) TiC nanopowder oxidation	[34]
Alternative I (TiO ₂ + natural gas) Particle size, nm 38-42	Tempering temperature, K 2600-2800	107, kg O ₂ /m ² 12.5	[35]
Alternative II (Ti + natural gas) Particle size, nm 34-36	Tempering temperature, K 2600-2800	TiC nanopowder oxidation 107, kg O ₂ /m ² 8.6	[36]

Carbothermal reduction of TiO_2 is an economical way for the production of TiC, and probably the most important and economical method in industry for the commercial production of TiC. In the carbothermal reduction of TiO_2 , the raw materials TiO_2 and carbon generally exist in the solid state as separate particles. So the contact area between the reactants was not wide enough which makes reaction very slow. This limits the extent of the synthesizing reaction. The effect of these limitations was a product that includes unacceptable quantities of un-reacted titanium dioxide and carbon [4].

5.2. Chemical vapor deposition technique

Chemical vapor deposition technique (CVD) is the deposition of a solid on the heated substrate from reactants in the vapor phase. The term CVD was introduced since 1960 to distinguish chemical vapor deposition process [36]. In 1968, start of industrial use of CVD coated cemented carbide [37]. The chemical reactions involved in the precursor to material conversion can include thermolysis, hydrolysis, oxidation, reduction, nitration, and carboration depending on the precursor species used [38]. Once the gaseous species are in proximity to the substrate or the surface itself, they can either adsorb directly on the catalyst particle or on the surface. Diffusion processes, as well as the concentration of the adsorbates, are responsible for the growth of a solid phase at the catalyst-surface interface.

Generally, the deposition of carbides was obtained by reacting a halide with a hydrocarbon using hydrogen or nitrogen gas. Noel and Kovar (2002) [39] synthesized TiC nanoparticles using CVD technique from the deposition of titanium and carbon powders on tantalum using hydrogen gas, titanium tetrachloride (TiCl_4) and either methane (CH_4) or acetylene (C_2H_2) source gases. Amorphous fine titanium carbide powders have been prepared by CVD in the TiCl_4 - CH_4 system at temperature ranging from 850 to 1050 °C in hydrogen atmosphere with pressure varying from less than 100 Pa to 1 atm, as given in the following reaction [40]:

The final product of this reaction is a hard and wear-resistant coating that exhibits a chemical bond to the substrate.

Stjernberg et al. (1977) [41] investigated the influence of various parameters on the CVD rate of TiC prepared from TiCl_4 - CH_4 - H_2 mixtures. They proposed a model based on the Langmuir-Hinshelwood adsorption reaction mechanism. They concluded that the deposition rate increases slightly with increasing pressure, the deposition rate was proportional to the CH_4 content, the deposition rate was inversely proportional to the equilibrium HCl concentration in the reactor and the deposition rate was practically inversely proportional to the TiCl_4 content of the inlet gas when no HCl was added. Additionally, TiC films were synthesized by photo-CVD using D2 lamp and gas mixture of TiCl_4 - CH_4 (or CCl_4)- H_2 -Ar [42]. It was concluded that the deposition rate of the TiC films was increased by 1.5-2.3 times by irradiation from a D2 lamp compared with that without irradiation, while the lowering of the deposition temperature with irradiation could not be attained.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) have been used to investigate the fine-scale microstructure of TiC obtained by chemical vapor deposition [43]. It was revealed that the microstructures have a considerable influence over both in grain plasticity and microcrack paths during deformation. Thus, considerable densities of structural defects are grown into all coatings and are expected to influence mechanical properties such as hardness. Considerable interfacial diffusional exchange of species between the coating and the substrate may occur and may influence coating adhesion.

Additionally, Tong and Reddy. (2005) [44] synthesized titanium carbide nanopowders by thermal plasma using Ti and CH_4 as the starting materials. They reported that the average size of the obtained powders is less than 100 nm with non-stoichiometric composition. Kasimthumaniyan et al. (2016) [45] prepared a fine titanium carbide powder by using titania-rich slag as a cheap raw material. The result revealed that the average particle size of TiC powder was 2.54 μm .

5.3. Polymeric precursors based on either titanium alkoxides or other organic compounds

Polymerizations of metal-organic compounds and sol-gel provide a new routes to produce carbides [46]. The development of new routes to non-oxide ceramics based on pyrolysis of oxygen-containing metal-organic polymeric precursors was the subject of several researches [47-50]. In this context, Jiang and Rhine (1991) [51] prepared titanium carbide, at 1150 °C, by pyrolysis of a polymeric precursor formed by hydrolysis of a $\text{Ti}(\text{O}-n-\text{C}_4\text{H}_9)_4/\text{furfuryl}$ alcohol mixture under argon. They reported that the temperature observed for the formation of TiC was lower than those reported for the formation of TiC by carbothermal reduction.

Stanley et al. (1992) [52] synthesized binary and ternary carbides by using the reaction of titanium tetra-isopropoxide with glycerol and furfuryl alcohol. The latter being used to control the oxide/carbon stoichiometry in the subsequent coke. They concluded that, by incorporating more than one metal in the precursor, it is possible to produce ceramic alloys at lower temperatures than conventional means allow. Lang and Seyferth (1990) [53] used precursors such as $\text{TiCp}_2(\text{CCC}_6\text{H}_5)_2$ and $\text{TiCp}_{2-\mu}\text{-CH}_2$ to produce TiC. Gallo et al. (1990) [54] synthesized titanium carbide by pyrolysis of titanocene dichloride or titanocene dimethyl under argon atmosphere. Additionally, Ting et al. (1990) [55] reacted alkoxides with diacetates to form polymeric alkoxides and esters. They revealed, from XRD data, that the formed titanium carbide was sub-stoichiometric in carbon.

5.4. Gas phase reactions of titanium tetrachloride (TiCl_4) and hydrocarbons

The production of high pure product not achievable using conventional techniques because of problems such as crystallization, volatilization, or high melting temperatures. Gas phase reactions of TiCl_4 and hydrocarbons are a new approach to synthesizing TiC [56]. The basic raw material for this method was TiCl_4 and the process generally based on the gas-phase reaction between TiCl_4 and an appropriate compound or hydrocarbon such as C_2H_2 , CCl_4 , CH_4 , and CaC_2 .

Grove et al. (2010) [57] fabricated titanium carbide nanoparticles by flowing methane through a plasma generated from an arc discharge between two titanium electrodes. Thus, different methane concentrations were employed to investigate the effects of carbon concentration on particle morphology. TiC cubes are synthesized at a low methane concentration and cuboctahedrons at a high methane concentration. However, Harbuck et al. (1986) [58] synthesized titanium carbide using sodium reduction of TiCl_4 at 800 °C in a methane atmosphere. They concluded that only 20 % of the TiCl_4 was converted to powder, and XRD analysis showed that it composed of TiO with a small amount of un-dissolved NaCl and no appreciable amount of titanium carbide. Hence, uniformly fine size powders, suitable for industrial applications, are produced.

5.5. Self-propagating high-temperature synthesis

Self-propagating high-temperature synthesis (SHS) technology, which was originally discovered by Goldschmidt (1895) [59] and later was systematically developed by Merzhanov (1990) [60], has been proved to be an efficient and energy-saving method for obtaining many high melting point materials. SHS processes present great possibilities to control the sizes and morphology of synthesized ceramic particles [61]. Thus, SHS was a promising method to produce structural materials because it features simplicity of the process and equipment, efficiency in energy and time, and high purity of products [62]. However, SHS of powder compacts was also known as combustion synthesis and proceeds via exothermic reactions. Since the process occurs at high temperatures, this method can be used as an alternative to conventional furnace technology [63].

Nersisyan (2002) [64] used SHS method to synthesize nanosized TiC powder. They added sodium chloride (NaCl) as inert and inorganic compounds to prevent particle agglomeration in the combustion synthesis. They found that the mechanism of TiC formation contains four steps (as shown in Fig. 4). In the first stage, NaCl was added to the initial mixture reactants (Ti and C). The second stage: melting of NaCl occurs. During the third stage: melting of Ti. Finally, during the last

stage: crystallization of TiC and subsequent protection by NaCl (formation of submicron and nanosized TiC particles).

Nanostructured TiC powders have been prepared by self-propagating high-temperature synthesis [65]. It was shown that the TiC grain size depends on temperature, in the range of $T_{\max}$ -1000 K, and on time elapsed in this temperature range.

Zhang et al. (2012) [66] prepared TiC terraces by self-propagating high-temperature synthesis reaction with 10 wt. % Fe-Ti-C elemental powder mixtures. They found that the dissolution reaction precipitation mechanism was responsible for the formation of TiC.

Figure 4. Mechanism of TiC structure formation according to SHS reaction stages: (a) initial step, (b) melting of NaCl, (c) melting of Ti, and (d) crystallization of TiC and subsequent protection by NaCl[64]

Similarly, Ali-Rachedi et al. (2010) [67] concluded that the heat loss during the SHS reaction significantly influences combustion temperature, propagation rate, stability, and the geometry of a reactant sample becomes an important factor because of the effect of dimension on heat loss. However, it was concluded that the combustion rate increased as the diameter of a cylindrical sample increased and remained constant after the diameter reached a certain value, which was dependent on the reaction system [68, 69].

5.6. Mg-thermal reduction

The techniques already mentioned have weak points such as easy oxidation, formation of the non-stoichiometric composition; require initial powder of high purity, and coarse particle formation. However, nanostructured titanium carbides were synthesized by liquid-magnesium reduction of vaporized $\text{TiCl}_4 + \text{CCl}_4$ solution [70, 71]. Fine TiC particles were obtained from Ti and C, and vacuum was used to remove the residual phases of MgCl_2 and excess Mg. The crystallite size was about 50 nm and the lattice parameter of the TiC was 0.43267 nm. Lee et al. (2009) [72] fabricated ultrafine titanium carbonitride particles ($\text{TiC}_{0.7}\text{N}_{0.3}$) by the nitridation treatment at 1473 K of $\text{TiC}_{0.7}$ nanoparticles, which were produced by the magnesium reduction of the gaseous $\text{TiCl}_4 + x\text{C}_2\text{Cl}_4$ at temperature of 1163 K. Thus, the stoichiometry form of the product was $\text{TiC}_{-0.67}\text{N}_{-0.27}$ could be successfully produced by post nitrification heat treatment at 1373 K and their purity higher than 99.5 % showing a mean particle size of about 100 nm.

Additionally, Lee et al. (2013) [73] synthesized nanosized TiC and TiCN powders by magnesiothermic reduction from $\text{TiCl}_4 + \text{C}_2\text{Cl}_4$ solution. They revealed that the mean particle size was about 100 nm, and the surface morphology of the final product was closer to round shape. Lee et al. (2005) [74] produced nanophase titanium carbonitrides by Mg-thermal reduction of the $\text{TiCl}_4 + \text{C}_2\text{Cl}_4$ solution in the isolated chamber with nitrogen atmosphere. High quality of crystal form of $\text{TiC}_{0.46-0.53}\text{N}_{0.46-0.51}$ and about 0.1 wt% free carbon were produced. The reaction temperatures and the solution feeding rates significantly influenced the stoichiometry not of C but of the N side. The products showed porous sponge shape agglomeration with fine particles with size of about 50 nm.

Lee et al. (2007) [75] fabricated TiC and TiCN nanoparticles by magnesium thermal reduction process. This process was performed in four steps: the transfer of $\text{TiCl}_4 + \text{C}_2\text{Cl}_4$ solutions into a liquefied magnesium protected with Ar, the magnesium reduction of metal chlorides, the formation of a titanium carbide by the reaction of Ti and C atoms released by the magnesium reduction, and finally the

vacuum separation of the residual liquid Mg and MgCl_2 . The average particle size of both TiC and TiCN was about 80 nm each. Lee et al. (2005) [76] produced nanosized titanium carbide particles by the reaction of liquid magnesium and vaporized $\text{TiCl}_4 + x\text{C}_2\text{Cl}_4$ solution. They concluded that the use of the $\text{TiCl}_4 + \text{C}_2\text{Cl}_4$ solution was more advantageous for increasing the stoichiometry of titanium carbide than $\text{TiCl}_4 + \text{C}_2\text{Cl}_4$. The crystallite size of the final product was about 50 nm and the lattice parameter was 0.43267 nm. The following Table 3 summarizes the obtained results of the as synthesized materials:

Table 3. Properties of TiC prepared by Mg-thermal reduction

Starting materials	Final product	Groove dimensions (size, lattice parameter)	Reference
$\text{TiCl}_4 + \text{CCl}_4$	TiC particles	d ~ 50 nm a = 0.43267 nm	[70, 71]
$\text{TiCl}_4 + \text{C}_2\text{Cl}_4$	$\text{TiC}_{0.7}\text{N}_{0.3}$ particles	High purity (99.5 %) d ~ 100 nm	[72]
$\text{TiCl}_4 + \text{C}_2\text{Cl}_4$	TiC and TiCN nanosized powders	Round shape d ~ 100 nm	[73]
$\text{TiCl}_4 + \text{C}_2\text{Cl}_4$	$\text{TiC}_{0.46-0.53}\text{N}_{0.46-0.51}$	Porous sponge shape d ~ 50 nm	[74]
$\text{TiCl}_4 + \text{C}_2\text{Cl}_4$	TiC and TiCN nanoparticles	d ~ 80 nm	[75]
$\text{TiCl}_4 + \text{C}_2\text{Cl}_4$	TiC nanosized particles	d ~ 50 nm a=0.43267 nm	[76]

5.7. Sol-gel process

Sol-gel technology has already long history, starting with processing of oxide materials including glass and ceramics about 30 years ago. Since then, the technology was employed in preparation not only of oxides, but also of non-oxide materials including nitrides, carbides, fluorides, and sulfides as well as oxynitride and oxycarbide glasses. Processing of organic-inorganic materials is now a very active field of research, which has been expanded even in the field of biotechnology as is represented by research on encapsulation of enzymes, antibodies and bacteria. Sol-gel process is a known chemical route to prepare powders, microtubes, fibres, and films [77, 78]. Moreover, the use of molecular precursors and the control of the synthesis conditions make it possible to prepare homogeneous and pure multicomponent systems [79].

Press et al. (1995) [80] used sol-gel method to obtain precursors which included metal alkoxide and polymeric carbon for the formation of TiC nanoparticles with high homogeneity at a molecular scale. Generally, the materials produce by sol-gel technique are highly porous in nature due to the evolution of gases during carbonization and carbothermal reduction of gel precursors and thus exhibit lower densities compare with the theoretical value of 3.21 g/cm³ [81].

5.8. Mechanical alloying

Since 1970, the term mechanical alloying (MA) has been used to refer to the production of homogeneous composite particles with intimately dispersed uniform internal structure [82]. This technique also was easily-design component, reliable, more safety, and without considering the melting point of starting elements.

The main experimental parameters that must be taken into account to control the final products of a milling process are:

- Type of mill,
- Milling container,
- Milling speed,
- Milling time,
- Type, size, and size distribution of the milling medium,
- Ball-to-powder weight ratio,
- Extent of filling the vial.
- Milling atmosphere,

- Process control agent,
- Number and diameter of balls,
- Temperature of milling.

Since 1996, the first work reported by El-Eskandarany (1996) [83] reported the possibility of preparing titanium carbide nanopowders by MA from elemental Ti and C powders at room temperature under argon atmosphere. Based on the XRD analysis it was concluded that the fcc-Ti₄₄C₅₆ powders was obtained after a very short milling time (20 ks).

Razavi et al. (2008) [84] concluded that the temperature for the synthesis of TiC can be reduced by increasing the milling time of precursors. Furthermore, milling led to increase of strain and decrease of TiC lattice parameter. Razavi et al. (2007) [85] fabricated nanosized TiC powders from impure Ti chips by MA in planetary ball-mill. They found that the crystallite size of the produced TiC is less than 10 nm, after 15 h of milling, and raising the milling time caused the increase of the strain and the fineness of the particles. Nanocrystalline TiC, with average crystallite size of 4 nm, was synthesized by MA for 15 h from Ti powders and different carbon resources like carbon fibers, carbon nanotubes, and activated carbon [86].

Fig. 5 illustrates the mechanism of formation of nanocrystalline TiC by MA of Ti and activated carbon powders. During the initial stage of milling, the carbon powders are crushed into smaller particles and the titanium particles are deformed and fragmented caused by plastic deformation induced during MA. In this stage, no TiC can be formed. During the second stage of milling, with increasing milling time, the titanium and carbon powders are refined: the fine particles of carbon are entrapped between the big particles of titanium. In addition, no TiC can be formed. During the third stage of milling, a little amount of TiC was formed on the surface of the Ti particles caused by defects. Finally, the as-milled products are completely composed of nanocrystalline TiC powder.

Figure 5. A schematic showing the reaction progress of Ti and activated carbon powders during MA. (a) Initial stage, no TiC; (b) second stage, the refinement of the Ti and carbon powders, no TiC; (c) third stage, a little amount of TiC formed on the surface of the Ti particles; (d) final stage, the milled products completely composed of nanocrystalline TiC [86]

Moreover, Cui et al. (2002) [87] used reactive milling to synthesize titanium carbide powder from the milled blends of titania/titanium/petroleum coke. They also studied the effect of percentage composition of element Ti on the synthesis of TiC. They concluded that the amount of element Ti added played an important role in the transformation from TiO₂ to TiC. Zhu et al. (2001) [88] reported that MA was a power process to obtain nanocrystalline TiC powder with particle size of 5.64 μm and crystalline size of 10 nm. Lohse et al. (2007) [89] found that when milling Ti₅₀C₅₀ and Ti₆₀C₄₀

powder mixtures in impact mode using a magneto ball mill, TiC was formed via a mechanically induced selfpropagating reaction, indicated by an abrupt increase in the temperature of the milling vial that corresponded to the formation of TiC. Thus, when milling Ti₇₀C₃₀ in impact mode using the same ball mill, the reaction to form TiC proceeded gradually as milling progressed.

In this context, TiC nanocomposite powder was synthesized from rutile and carbon black by mechanically activated sintering [90]. The mixture was MA in a planetary ball mill for 50 h under argon atmosphere to avoid oxidation. For complete reaction of the activated milled powder, heat treatment was carried out in an atmosphere controlled tube furnace. Tang et al. (2006) [91] prepared nanocrystalline Ti₅₀C₅₀ powder via MA from elemental titanium and graphite powder for 80 h of milling. Similarly, Ali and Basu (2010) [92] synthesized nanostructured TiC powder from industrial ferrotitanium MA for 40 h and subsequently heat treated at 1000 °C for 15 min.

Ghosh and Pradhan (2010) [93] obtained nanocrystalline TiC powder after 35 min of milling in a high energy planetary ball mill. El-Eskandarany et al. (1996) [94] prepared nanocrystalline Ti₄₄C₅₆ powder by MA of elemental titanium and graphite powders in a planetary mill after 200 h of milling. Viljus et al. (2001) [95] produced TiC by milling of Ti and C powders for 8 h with attritor ball mill at room temperature. Fine grained TiC powder was obtained. Similarly, Zhu et al. (2001) [96] synthesized nanocrystalline TiC powder from elemental Ti and C powders by using GN-2 ball mill during 10 h of milling. Thus, nanocrystalline TiC, with crystallite size of ~ 20 nm, was obtained for 120 min of milling. However, after the subsequent milling, the crystalline size decreased gradually to reach ~ 7 nm for 10 h of milling.

5.9. Liquid phase sintering technique

Liquid phase sintering (LPS) is today a well known and established manufacturing route in powder metallurgy [97]. This approach permits the formation of dense, pore-free carbides with properties superior to any previously known cutting materials. In LPS a powder mixture consisting of the alloy powder and sometimes a binder/lubricant is pressed into a green body. This green body was then heated to a temperature where a liquid phase was formed. The consolidation of the green body into a dense body consists of three stages: (i) particle rearrangement due to surface forces within the compact, (ii) solution reprecipitation type of rearrangement of the particles, and (iii) final pore closure and grain growth. It can be shown that the driving force for the densification, as well as being a function of the surface energy of the liquid phase, was directly affected by the contact angle liquid-solid [98-100]. However, one of the most important key parameters for LPS process is to control excessive grain growth due to grain boundary motion and Ostwald ripening of carbide phase during LPS [101].

Very often hot pressing has also been used at 2073-2473 K temperatures. In this context, Meredith and Milner (1976) [102] studied the densification of TiC-Co system by varying Co contents (0, 5, 10, 20, 30, 40, 50, and 60 vol.%) sintered in 0.2 torr of argon at 1400 °C, i.e. 40 °C above the eutectic temperature. After 2 min, at temperature of 1400 °C, the density of the nominally 0 %Co alloy increased by about 15 % and thereafter, with extended sintering times, there was a small but steady increase. They concluded that TiC-Co system show some anisotropy of particle shape, characterized by steady densification accompanied by the growth of neck contacts between particles, rounding of particles, and particle growth. Molybdenum was added to TiC-base alloys to prevent grain growth and improve the toughness. Thus, the effect of Mo was studied by adding it to the 1/2-2 μm TiC-Co system. It was shown that molybdenum reduces the rates of enhanced surface and interfacial diffusion and therefore reduces the rate of material transport, so that there is less densification and particle growth. It also studied the densification of TiC-Ni by LPS process. It was found that TiC-Ni exhibits mixed isotropic and anisotropic characteristics: densification takes place by the growth of neck contacts between particles but the particles take up individual prismatic forms which act against collective close-packing and densification. Viljus et al. (2012) [103] synthesized Ti-C-Ni-Mo composite from elemental powders of Ti, Ni, Mo, and C by using a high energy ball-milling followed by reactive sintering. The carbide was produced during low temperature heating (1000 °C), which eliminates expensive long-time, high-temperature

(1800 - 2000 °C) synthesis of TiC powder. The surface of as formed nanosize carbide particles was free from oxide film, absorbed gas or other detrimental surface contamination. It was shown that thermodynamically stable carbide grains, within the metal matrix, are formed.

For the case of two mixed powders, the mechanism of the microstructure changes during LPS process is shown in Fig. 6 [104]. During heating, the solid grains undergo solid-state sintering. In fact, different microstructure evolutions are possible, depending on the solid liquid solubility relations. The common situation was for the liquid to wet the solid. In this case, the formed liquid penetrates between the grains, dissolves the sinter bonds, and causes grain rearrangement. Further, the liquid improves transport rates responsible for densification and coarsening, because of solid solubility in the liquid. The surface energy associated with pores leads to their annihilation, while there is progressive microstructure coarsening and bonding to increase rigidity.

Figure 6. Mechanism of the microstructure changes during LPS process [104]

5.10. Spark plasma sintering technique

A novel sintering process recently developed in Japan, known as spark plasma sintering (SPS) [105] consisting of generating internally heat by means of DC current pulses directly through a graphite die containing the powder compact. In fact, the SPS technique has several advantages that distinguish it from the traditional sintering methods such as hot pressing and sintering of pre-compacted billets without pressure [106]. SPS enables liable control of the material microstructure and sintering process parameters.

In the last few years, increasing attention has been paid to fabricate carbides by SPS technique. El-Eskandarany and Al-Haza (2014) [107] used this technique to synthesize fully dense nanocrystalline $\text{Ti}_{55}\text{C}_{45}$ bulk material. Thus, the powders MA for 200 h were binderless consolidated in vacuum at 1500 °C under a pressure of 34.5 MPa, with heating rates of 20 °C/min and 500 °C/min, respectively. They found that the sintered powders maintained their nano-scale. Hence, the vickers hardness, young's modulus, shear modulus and fracture toughness of the bulks were 32 GPa, 358 GPa, 151 GPa, and 6.4 $\text{MPa}\cdot\text{m}^{1/2}$, respectively.

Cabrero et al. (2011) [108] used SPS, at 1800°C and under 75 MPa, to consolidate nanosized TiC powder (with particle size of 80 nm) and achieved a density of ~ 95.4%. It's interesting to remark that even with decreasing the particles size from micro to nano range, higher density can't be reached.

Cheng et al. (2012) [109] consolidated micro-sized TiC powder (2 μm in size), at 1500 °C and at pressure of 50 MPa, using SPS. The achieved density of the compact reaches about 95.7 %. Additionally, Li et al. (2015) [110] fabricated TiC-ZrC composite by SPS of TiC with 20 mol.% of ZrC particles at 1900 °C and at a pressure of 100 MPa and achieved 99 % density. Similarly, Wang et al. (2004) [111] reinforced 30 wt.% of SiC nanoparticles in TiC and produced TiC-SiC composite by SPS at 1600 °C under a pressure of 70 MPa and achieved about 99 % density.

6. Applications of titanium carbide

Titanium carbide attracted great interest for several structural applications. Therefore, TiC can be used in cutting tools because of its

combination of wear resistance and high hardness. It can also be used as a coating for abrasive steel bearings and wear resistant tools. In addition, it can be used to enhance the conductivity of materials and as a nucleating agent.

In the middle of the 1960s, the wear resistance of such tools was increased appreciably by the deposition of thin coatings of TiN, TiC, and other refractory compounds [112]. The increase in the lifetime of the tools due to such coatings depends on the improved wear resistance and the lower cutting temperature due to a reduced friction between the tool and the work material. During the last years, the domains of application for these coatings have been extended to ordinary steel tools and high-speed steels. Commercially, high-speed steel drills coated with TiN have been introduced [113]. The wear life of such coated drills is 4 to 6 times longer than that of uncoated drills. In addition, coated drills show better resistance to corrosion and erosion [114]. TiC are also used in electronic devices, as diffusion barriers in integrated circuits [115], molded bipolar plates for high-voltage battery, and fuel power sources [116].

Moreover, TiC is employed as coatings for pump shafts, packing sleeves, feed screws for the chemical industry, as coatings for molding tools, and kneading elements for plastic processing. They are also utilized as coatings for fusion-reactor applications. TiC is very suitable for use high-speed **cutting tool** applications for reducing thermal stresses and cracking [117].

Furthermore, TiC is effectively utilised in cermets due to its low friction coefficient and higher oxidation resistance compared to cemented tungsten carbide [118]. TiC is also widely used in different branches of machine construction due to its high strength and hardness [119].

7. Conclusions

We review the synthesis and application of titanium carbide material; in particular, the properties and mechanisms are summarized. Particular attention has been paid to the study of all parameters involved in TiC production. At the present time, we note that solid chemical precursors can be used to synthesize material with desired properties. The applications of this material in ceramic science, engineering, and electronic are also reviewed. We also believe that this work will benefit physicists, engineering, and chemists with interest in titanium carbide and their applications.

Based on the above literature, it is good to think about those different ways of manufacturing TiC powder, because there is a high demand for composite materials with superior intrinsic properties for various industrial applications.

At present, most of the works on titanium carbide material are still at the laboratory level, with few reaching the practical application level. Therefore, it is necessary to predict the following suggestions:

- It is necessary to ensure the homogeneity and integrity of TiC material.
- The significant challenge is that the fabrication of high performance structural material with superfine microstructures.
- TiC is widely used in structural applications. It is necessary to develop functional applications.

Nomenclature

TiC	: Titanium carbide
CVD	: Chemical vapor deposition
LISHS	: Self-propagating high-temperature synthesis
TiCl_4	: Titanium tetrachloride
MA	: Mechanical alloying
LPS	: Liquid phase sintering
SPS	: Spark plasma sintering technique

Declaration of Conflict of Interests

The authors declare that there is no conflict of interest.

Acknowledgments

The authors are grateful to Dr. Faïçal Khliissa for helpful comments on a draft of this manuscript.

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How to Cite This Article

Mhadhbi, M. and Driss, M., Titanium carbide: Synthesis, properties and applications, *Brilliant Engineering*, 2 (2021), 1-11. <https://doi.org/10.36937/ben.2021.002.001>