Microstructure and Mechanical Properties of Carbide Reinforced TiC-Based Ultra-High Temperature Ceramics: A Review

Haobo Mao 1,2, Fuqiang Shen 1, Yingyi Zhang 1,*©, Jie Wang 1, Kunkun Cui 1, Hong Wang 1,3, Tao Lv 2, Tao Fu 1 and Tianbiao Tan 2

1 School of Metallurgical Engineering, Anhui University of Technology, Maanshan 243002, China; L14999234208163.com (H.M.); sfq1955630201@126.com (F.S.); wangjiemaster0101@outlook.com (J.W.); 15613581810@163.com (K.C.); wanghong0531@126.com (H.W.); ahgydxtaofu@163.com (T.F.)
2 School of Civil Engineering and Architecture, Anhui University of Technology, Maanshan 243002, China; lvtao456@163.com (T.L.); tantianbiao96@163.com (T.T.)
3 Beijing Metallurgical Equipment Research Design Institute Co., Beijing 100000, China
* Correspondence: zhangyingyi@cqu.edu.cn; Tel.: +86-173-7507-6451

Abstract: TiC ceramics have become one of the most potential ultra-high temperature structural materials, because of its high melting point, low density, and low price. However, the poor mechanical properties seriously limit its development and application. In this work, this review follows PRISMA standards, the mechanism of the second phase (particles, whiskers, and carbon nanotubes) reinforced TiC ceramics was reviewed. In addition, the effects of the second phase on the microstructure, phase composition and mechanical properties of TiC ceramics were systematically studied. The addition of carbon black effectively eliminates the residual TiO₂ in the matrix, and the bending strength of the matrix is effectively improved by the strengthening bond formed between TiC; SiC particles effectively inhibit the grain growth through pinning, the obvious crack deflection phenomenon is found in the micrograph; The smaller grain size of WC plays a dispersion strengthening role in the matrix and makes the matrix uniformly refined, and the addition of WC forms (Ti, W) C solid solution, WC has a solid solution strengthening effect on the matrix; SiC whiskers effectively improve the fracture toughness of the matrix through bridging and pulling out, the microscopic diagram and mechanism diagram of SiC whisker action process are shown in this paper. The effect of new material carbon nanotubes on the matrix is also discussed; the bridging effect of CNTs can effectively improve the strength of the matrix, during sintering, some CNTs were partially expanded into GNR, in the process of crack bridging and propagation, more fracture energy is consumed by flake GNR. Finally, the existing problems of TiC-based composites are pointed out, and the future development direction is prospected.

Keywords: TiC; composites; mechanism; microstructure; mechanical property

1. Introduction

High temperature structural materials have attracted extensive attention with the development of national defense industry [1–3]. In recent decades, the high-temperature structural ceramics have been widely used in high-speed machining, aerospace, and other fields. High temperature structural ceramics are mainly composed of borides (ZrB₂ (Zirconium diboride), HfB₂ (Hafnium diboride), TaB₂ (Tantalum diboride)), carbides (HfC (Hafnium carbide), TaC (Tantalum carbide), ZrC (Zirconium carbide), NbC (Niobium carbide)) and nitride (HfN (Hafnium nitride), NbN (Niobium nitride), and ZrN (Zirconium nitride)) [4], as shown in Figure 1. According to the research and development of ultra-high temperature ceramics in recent years, scholars have done a lot of research on single boride ceramic and its composite materials, including preparation methods, oxidation resistance, and mechanical and thermophysical properties, and made breakthroughs...
progress [5]. However, the research on carbide ceramic composites is relatively little. In carbide ceramics, HfC and TaC are limited in large-scale application because of their high price and high requirements of preparation technology and equipment. Because titanium resources in the crust are abundant, the production cost of TiC is relatively low. At the same time, TiC also has excellent properties of carbide ceramics. Therefore, the research on TiC is of more practical value. TiC has a high melting point (3140 °C) and low density (4.94 g/cm³) [6]. It has more application value in some high temperature environments with strict requirements on material weight. TiC ceramic has excellent properties such as high hardness (25.1 GPa), excellent low electrical resistance (68 μΩ·cm) and excellent thermal conductivity (21 W/m·K) [7]. TiC ceramic has become a potential candidate material for cutting tools because of its good chemical attack resistance, wear resistance, and thermal deformation resistance [8]. In addition, TiC ceramic is also widely used in the inert matrix materials of the fourth-generation reactor because of its small neutron absorption cross section [9]. Moreover, TiC has also attracted wide attention in the field of thermal protection materials for aircraft because of its good high temperature performance [10].

![Graph comparing melting points and density of metals and ultra-high temperature ceramics](image)

**Figure 1.** Comparison of melting points and density of metals ultra-high temperature ceramics.

Although TiC has great application potential, the intrinsic brittleness of carbide greatly limits its application range. Therefore, the second phase is used to improve the toughness of ceramic materials. At present, the main additives for toughening TiC ceramic materials are SiC, WC, C, and CNTs. Due to its strong covalent bond and low self-diffusion coefficient (6.98 cm²/s), the sintering temperature of TiC ceramics needs to be controlled above 2000 °C to achieve complete densification [11], but the high temperature will make the grains grow wildly, this will have a fatal impact on the fracture toughness and bending strength of the whole material. It is reported that the addition of SiC can significantly reduce the sintering temperature and promote mass diffusion [12]. TiC-SiC ceramics were prepared by Cabrero et al. [13] using SPS sintering method at 1800 °C, and its relative density reached 99.23%, and its vickers hardness reached an astonishing 31 GPa, it may be due to the fact that SiC itself is a hard phase, and the pinning effect of SiC inhibits the aggregation of TiC grains [14]. Carbon fiber has many interesting properties, such as high-temperature forbearance, high tensile strength and stiffness, and low weight [15], these properties have attracted much attention in aerospace and civil engineering. M. Sribalaji et al. [16] prepared the TiC-2wt.%CNT composite ceramics by adding carbon nanotubes to the TiC matrix. The fracture toughness of iC-2wt.%CNT composite ceramics reached 8.1 MPam²/3, which is much higher than that of TiC ceramics. In the past studies, metals (Ni [17], Co [18], Al [19]) or alloys (Ni-Mo) [20] were usually used as sintering binders. Generally speaking, the lower melting point of these metals or alloys would
have an adverse effect on the high temperature properties of composites [21], but the addition of metal carbides could effectively improve the high temperature properties of composites. Cheng et al. [22] reported a kind of WC reinforced TiC matrix composite ceramic. With the increase of WC content, the fracture toughness of the composite reached 6.3 MPam$^{1/2}$. WC effectively inhibits the grain growth through pinning, which keeps the grain size at a low level (2.1 nm) after sintering, and the mechanical properties will not decay at 2000 °C [23,24]. Direct reduction of TiO$_2$ and C is the main method to prepare TiC at present. The disadvantages are that the product is prone to large agglomeration, and there are unreacted raw materials and other phenomena. Nguyen et al. [11] reported a method of strengthening TiC composite ceramic materials with nano-diamond. It was found that carbon elemental substance effectively limited the occurrence of grain boundary slip, holes and creep, and free carbon elemental substance consumed the residual TiO$_2$ in the process of preparing TiC, reduced the bonding of weak interfaces, and improved the bending strength of TiC matrix composites by 30%. Although there are many reports on improving the mechanical properties of TiC ceramics, the review of carbide reinforced titanium carbide ceramics has not been reported, in particular, there are few reports on the mechanism of carbide reinforcement.

In this work, we carefully summarized the research status and existing problems and future development trend of titanium carbide ceramics, and discussed the influence of second phase particles, fibers and carbon nanotubes on the microstructure and mechanical properties of titanium carbide ceramics as well as the toughening mechanism, aiming to provide some useful guidance for researchers in this field.

2. Properties of TiC Based Ceramics

TiC is a kind of important inorganic nonmetallic material and typical transition metal carbide. As shown in Table 1, its crystal structure includes microscopic ionic bonds, metal bonds and covalent bonds. It has the same cubic structure and face-centered cubic crystal structure as NaCl crystal, so it has the advantages of high melting point (3140 ± 90 °C), large elastic modulus, high hardness, good corrosion resistance and excellent electrical and thermal conductivity. TiC is mainly used as raw material for manufacturing TiC-based ceramics. It is also used as a reinforcing agent for manufacturing various metal matrix composites, or as an anti-wear agent for wear-resistant coatings. Its application involves many fields such as machining, surface engineering, powder metallurgy and electronic industry.

The ideal crystal structure model of TiC$_x$ (x = 1) is shown in Figure 2. It can be seen that the TiC$_x$ (x = 1) unit cell has a typical face-centered cubic structure, and the smaller carbon atoms occupy the octahedral gap position of Ti atom face-centered cubic lattice. However, structural defects inevitably exist in actual crystals, so that each atom in TiC cannot strictly occupy the ideal lattice node position, forming a non-stoichiometric compound TiC$_x$ (x is the stoichiometric ratio of C to Ti atoms) [25], as shown in Figure 2b. Figure 3 shows that TiC$_x$ mainly presents polyhedral, octahedral, hexagonal, spherical, dendrite, and petal morphology, its physical and chemical properties are closely related to its morphology [26]. When the molar ratios of C to Ti are 0.6, 0.7, and 1.4, respectively. The morphologies of TiC$_x$ crystal are octahedral, truncated octahedral and nearly spherical, and spherical, respectively [27]. When x is between 0.5 and 0.8, the lattice constant of TiC$_x$ increases with the increase of x, but decreases with the increase of carbon content, as pointed out by Zarrinfar et al. [28] research shows that the morphology of TiC$_x$ can be changed from octahedral to layered hexagon by adding trace boron in Al-Ti-C system [29], and with the increase of Al content, the size of TiC$_x$ can be reduced rapidly, the morphology of TiC$_x$ can be changed from block to octahedral [30]. When x is increased from 0.5 to 1.0, the morphology of TiC$_x$ gradually changes from octahedral to truncated octahedral to spherical [31]. It was that Zhang et al. [32] designed the Cu-Ti-C system, they found that the molar ratio of C/Ti has a significant effect on the morphology of TiC$_x$. Meng et al. [33] synthesized the TiC$_x$ by using laser cladding technology, the morphology of TiC$_x$ mainly
includes dendritic, petal-like, spherical or spherical-like, needle-like, and some irregular shapes, so the morphology of TiCx is closely related to the synthesis method.

![Figure 2. Crystal structure model of TiC: (a) Ideal crystal structure. (b) Defect crystal structure.](image)

![Figure 3. Typical morphologies of TiCx: (a) polyhedron shape, (b) cuboctahedron shape, (c) octahedron shape, (d) truncated octahedron shape, (e) hexagonal shape, (f) petaloid shape, (g) dendritic shape, (h) spherical shape.](image)

At present, the preparation methods of TiC include direct reaction method [34] and carbothermal reduction method [35]. Direct reaction method is a method of directly reacting titanium and carbon to form TiC. The chemical reaction formula is:

\[ \text{Ti} + \text{C} = \text{TiC} \]

The direct reaction method is an exothermic reaction, so the self-propagating reaction can occur without high temperature, but the purity of the product is not high, and there will be unreacted titanium powder and carbon powder deposition, which will affect the mechanical properties of the material. Carbothermal reduction is a relatively mature technology for preparing TiC powder. The reaction equation is:

\[ \text{TiO}_2 + 3\text{C} = \text{TiC} + 2\text{CO} \]

Carbothermal reduction has the advantages of simple process and cheap raw materials, but it is easy to cause TiO2 residue, which will have a negative impact on the toughening of TiC in the future.
Table 1. Some properties parameters of carbide ceramics [36–40].

<table>
<thead>
<tr>
<th>Attribute</th>
<th>TiC</th>
<th>ZrC</th>
<th>NbC</th>
<th>HfC</th>
<th>TaC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>FCC</td>
<td>FCC</td>
<td>FCC</td>
<td>FCC</td>
<td>FCC</td>
</tr>
<tr>
<td>Space group</td>
<td>Fm-3m 225</td>
<td>Fm-3m 225</td>
<td>Fm-3m 225</td>
<td>Fm-3m 225</td>
<td>Fm-3m 225</td>
</tr>
<tr>
<td>Lattice parameters (nm)</td>
<td>a = 0.46000,</td>
<td>b = 0.46000,</td>
<td>a = 0.44000,</td>
<td>a = 0.46410,</td>
<td>a = 0.44460,</td>
</tr>
<tr>
<td></td>
<td>c = 0.46000,</td>
<td>c = 0.46000,</td>
<td>c = 0.46000,</td>
<td>c = 0.46410,</td>
<td>c = 0.44460,</td>
</tr>
<tr>
<td>Resistivity (µΩ·cm)</td>
<td>68</td>
<td>63</td>
<td>74</td>
<td>109</td>
<td>30</td>
</tr>
<tr>
<td>Thermal conductivity (W/m·K)</td>
<td>21</td>
<td>20.5</td>
<td>14</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Theoretical density (g/cm³)</td>
<td>4.94</td>
<td>6.73</td>
<td>7.6</td>
<td>12.7</td>
<td>14.3</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>3140</td>
<td>3540</td>
<td>3500</td>
<td>3890</td>
<td>3880</td>
</tr>
<tr>
<td>Theoretical density (g/cm³)</td>
<td>4.94</td>
<td>6.73</td>
<td>7.6</td>
<td>12.7</td>
<td>14.3</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (10⁻⁶ K⁻¹)</td>
<td>7.74</td>
<td>6.7</td>
<td>6.65</td>
<td>12.7</td>
<td>14.3</td>
</tr>
<tr>
<td>Modulus of elasticity (GPa)</td>
<td>241</td>
<td>220</td>
<td>170</td>
<td>209</td>
<td>232</td>
</tr>
<tr>
<td>Fracture toughness (GPa)</td>
<td>451</td>
<td>480</td>
<td>338</td>
<td>300-400</td>
<td>470-540</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>240-400</td>
<td>400</td>
<td>250-350</td>
<td>600-700</td>
<td></td>
</tr>
</tbody>
</table>

3. Effects of Secondary Phase on Microstructure and Mechanical of TiC

TiC has attracted wide attention because of its excellent physical and chemical properties, but its intrinsic brittleness greatly limits its development in practical applications. Three TiC matrix strengthening methods (particle toughening, whisker toughening, carbon nanotube toughening) and key experimental data are listed in Table 2. The effects of preparation process and carbide type on hardness and density of TiC-based composites are shown in Figure 4. As shown in Figure 4a, the relative density of the overall material shows an upward trend with the addition of SiC. However, when the SiC content exceeds 20%, the relative density will decrease. Figure 4c shows that the addition of SiC has little effect on the overall hardness when SiC content is lower than 10%. With the increase of SiC content, the hardness value shows a polarization trend, which may be affected by sintering temperature. Figure 4b,d show the effect of sintering temperature on the mechanical properties of composites. Lower sintering temperature will make sintering incomplete, the bending strength is always at a low level, and the sintered grain size and sintering temperature always keep a single positive correlation. Excessive sintering temperature will lead to grain coarsening, so the mechanical properties of the matrix will also show a downward trend at higher temperature. The image shows that the best sintering temperature is between 1800 °C and 1900 °C.

Table 2. Effects of preparation process and carbide type on mechanical properties of TiC-based composites.

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>Processing Conditions</th>
<th>Material Particle Size (µm)</th>
<th>Relative Density (%)</th>
<th>Vickers Hardness (GPa)</th>
<th>Fracture Toughness (MPa m¹/²)</th>
<th>Flexural Strength (Mpa)</th>
<th>Modulus of Elasticity (GPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>SPS, 1600/10/50</td>
<td>-</td>
<td>96.1</td>
<td>25.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (10 mol.%)</td>
<td>-</td>
<td>97.3</td>
<td>25.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (25 mol.%)</td>
<td>-</td>
<td>97.1</td>
<td>18.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (50 mol.%)</td>
<td>SPS, 1700/10/50</td>
<td>0.6</td>
<td>96.5</td>
<td>23.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (10 mol.%)</td>
<td>-</td>
<td>96.4</td>
<td>23.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (25 mol.%)</td>
<td>0.4</td>
<td>96.4</td>
<td>17.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (50 mol.%)</td>
<td>0.23</td>
<td>91.1</td>
<td>16.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC</td>
<td>SPS, 1800/10/50</td>
<td>1</td>
<td>94.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (10 mol.%)</td>
<td>-</td>
<td>96.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (25 mol.%)</td>
<td>0.5</td>
<td>96.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (50 mol.%)</td>
<td>0.33</td>
<td>95.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC</td>
<td>SPS, 1900/10/50</td>
<td>1</td>
<td>98.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (10 mol.%)</td>
<td>-</td>
<td>96.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (25 mol.%)</td>
<td>0.7</td>
<td>96.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (50 mol.%)</td>
<td>0.39</td>
<td>95.4</td>
<td>24.4</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC</td>
<td>SPS, 1800/5/75</td>
<td>0.9</td>
<td>95.4</td>
<td>24.4</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (10 mol.%)</td>
<td>0.54</td>
<td>97.2</td>
<td>21.7</td>
<td>2.2</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (25 mol.%)</td>
<td>0.4</td>
<td>97.3</td>
<td>23.7</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiC-SiC (50 mol.%)</td>
<td>0.27</td>
<td>97.3</td>
<td>31.3</td>
<td>3.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

References:
[13], [14], [41], [42]
Table 2. Cont.

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>Processing Conditions (°C/Min/MPa)</th>
<th>Material Particle Size (µm)</th>
<th>Relative Density (%)</th>
<th>Vickers Hardness (GPa)</th>
<th>Fracture Toughness (MPa m¹/²)</th>
<th>Flexural Strength (MPa)</th>
<th>Modulus of Elasticity (GPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>HP, 2000/120/90</td>
<td>28.16</td>
<td>98.44</td>
<td>2111 (HV 0.5kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[43]</td>
</tr>
<tr>
<td>TiC-SiCw (10 vol.%)</td>
<td>SPS, 1900/7/40</td>
<td>-</td>
<td>95.1</td>
<td>22.8</td>
<td>468.4</td>
<td>-</td>
<td>-</td>
<td>[44]</td>
</tr>
<tr>
<td>TiC-WC (5 vol.%)</td>
<td>HP, 2000/120/90</td>
<td>28.16</td>
<td>98.4</td>
<td>2111 (HV 0.5kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[45]</td>
</tr>
<tr>
<td>TiC-SiCw (5 vol.%)</td>
<td>SPS, 1900/7/40</td>
<td>-</td>
<td>95.1</td>
<td>22.8</td>
<td>468.4</td>
<td>-</td>
<td>-</td>
<td>[44]</td>
</tr>
<tr>
<td>TiC-SiC (10 vol.%)</td>
<td>SPS, 1900/7/40</td>
<td>-</td>
<td>95.1</td>
<td>22.8</td>
<td>468.4</td>
<td>-</td>
<td>-</td>
<td>[44]</td>
</tr>
<tr>
<td>TiC–WC (5 vol.%)</td>
<td>SPS, 2100/10/40</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (30 vol.%)</td>
<td>SPS, 2100/15/-</td>
<td>-</td>
<td>92.2</td>
<td>2729 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (50 mol.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>99.1</td>
<td>3214 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (10 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (3.5 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (5 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (10 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (3.5 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (5 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (10 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (3.5 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (5 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>TiC–WC (10 wt.%)</td>
<td>SPS, 2100/10/-</td>
<td>-</td>
<td>98.1</td>
<td>3068 (FV 0.1kg)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
</tbody>
</table>

3.1. Effect of Particle Phase on TiC Matrix Composites

According to previous studies, we found that the microstructure of pure TiC is not single-phase [58]. When non-stoichiometric TiCx is formed, some carbon atoms leave the stoichiometric TiC structure and deposit in the matrix [59–61]. Besides, SiC will decompose into silicon and carbon at high temperature, according to the observation of high temperature and high pressure behavior of SiC. Therefore, the influence of carbon on the whole composites is also an important research direction [62–64]. Figure 5b shows the fracture picture obtained by Nguyen et al. [50] adding 5 wt.% carbon black to TiC matrix. The addition of carbon fills most pores of TiC matrix [65] (Figure 4a), a relative density of nearly 100% was obtained, and the vickers hardness is increased by 3%. This may be due to the fact that carbon is a kind of soft phase, which can destroy the hardness of the matrix, but the higher relative density counteracts the negative effect, so the hardness of the composites is kept at the same level as that of the whole TiC [66]. In addition, the flexural strength of the composites has been improved by an astonishing 30%, from the original 504 MPa to 658 MPa [67]. In addition to the above-mentioned increase in relative density, this result may also be due to the fact that free carbon can effectively eliminate TiO₂ [68],...
so TiC can form strong bonds [69]. In contrast, the existence of TiO$_2$ will produce weak interface bonding, which is the preferred region for crack propagation [70].

The crack deflection image of TiC-SiC (50 vol.%) composites is shown in Figure 6a. We can clearly observe the crack deflection phenomenon, which is the main reason for improving fracture toughness [71]. By observing the fracture picture of TiC-SiC (Figure 5c), it can be found that fine silicon carbide particles are located on the grain boundary of coarse TiC particles, the pinning effect of silicon carbide inhibits the growth of TiC particles (The mechanism of pinning is shown in Figure 7). When the crack propagates and reaches the submicron grain size of TiC or SiC, a crack propagating in a plane of particle ($\alpha_p$ (thermal expansion of particle) > $\alpha_m$ (thermal expansion of matrix)) will be first deflected (compressive stress hoop axis in the matrix is normal to the crack propagating plane). As the crack traverses further around the particle it can be subsequently attracted to the particle interface (tensile radial stress axis), it is difficult for the crack to pass through the particles, and the crack will deflect and propagate along the grain boundary of SiC and TiC [50]. Luo [72] and Wang [73] et al. also attributed the crack deflection to the residual stress caused by the difference of thermal expansion coefficient and elastic modulus between SiC and TiC.

Figure 4. Effects of preparation process and carbide type on hardness and density of TiC-based composites. (a) Quantitative relationship between relative density and sintering additive dosage, (b) Vickers hardness and grain size of TiC based ceramics at different testing temperature, (c) Quantitative relationship between Vickers hardness and additive content, (d) Relative density and bending strength of TiC based ceramics at different testing temperature.
Figure 5. SEM images of Particle reinforced TiC Composites (a) TiC-WC, (b) TiC-C, (c) TiC-SiC, (d) TiC-SiC-WC.

Figure 6. High magnification finite element scanning electron microscope image. (a) Picture of crack deflection in TiC-50 vol.% SiC, (b) Picture of crack deflection in TiC-3.5 wt.% WC.
Foong et al. [52] investigated the effect of WC particles on the whole TiC. Research found that the hardness of the whole material can be increased by 8% with the addition of WC, which can be caused by a variety of reasons. Firstly, the small thermal conductivity (25 W/(m·k)) of TiC leads to a large temperature gradient [74], the addition of tungsten carbide (100 W/(m·K)) can promote the uniform distribution of temperature [75]. As a secondary carbide, tungsten carbide can also improve the wettability and sintering property of titanium (carbon, nitrogen)-based cermet, and inhibit the grain growth [76]. The smaller size of WC has played a dispersion strengthening role on the matrix, making the matrix structure uniform and refined, as shown in Figure 6b. The average grain size of the composites decreased by 28%, and the smaller grain size resulted in higher hardness [77]. Secondly, the addition of WC will form (Ti, W) C solid solution with a higher hardness than pure TiC phase, so the hardness of composites will be improved, which has been found in other works [78].

The addition of WC greatly improved the fracture toughness of the materials [22]. The fracture toughness of the composites reached 6.3 MPam$^{1/2}$ when 3.5 wt.% WC was added at 1600 °C. The increase in fracture toughness is due to the deflection and bridging of cracks along or around the (Ti, W) C phase [79]. As shown in Figure 7b, the residual stress caused by thermal mismatch ensures the crack deflection or bridging between TiC particles along the (Ti, W) C phase. Besides, we can still find some residual pores in the images of TiC-WC composites after cracking, as shown in Figure 5. The formation of pores may be related to the trapped gas phase (CO) produced during hot pressing [80–85].

The toughening mechanism of particle reinforced TiC-based ceramics is shown in Figure 8. Due to the mismatch of thermal expansion coefficient and elastic modulus between TiC and the second phase ($\Delta \alpha = -2.6 \times 10^{-6} \, ^{\circ} \text{C}^{-1}$, $E = 451$ GPa), resulting in a residual fluid net tension in the second phase particles. The second phase particles will be subjected to both circumferential compression and radial tension. Figure 8a shows that when cracks move around the particles, they will be attracted to the surface of the particles (tensile radial stress axis). Figure 8b,c show the tensile state of grain boundary phase and grain phase, respectively, so the main modes of particle phase reinforcement are from intergranular to transgranular [86] and crack deflection.

3.2. Effect of Whiskers on TiC Matrix Composites

As we all know, relative density, sintering temperature and microstructure are important factors affecting the mechanical properties of ultra-high temperature ceramic composites, which have been reported repeatedly by many researchers. It is impossible to obtain compact whole ultra-high temperature materials at relatively low sintering temperature, and too high sintering temperature will lead to over-growth of grains and some other crystal defects, which will have a negative impact on the mechanical properties of materials.

Figure 7. Schematic diagram of particle reinforced TiC matrix (a) pinning effect, (b) refinement effect.

Figure 6. High magnification finite element scanning electron microscope image.
The above conclusion is also valid for SiC\textsubscript{W}, which has been confirmed by the research results of Fattahi et al. [44]. The effects of SiC\textsubscript{W} content on microstructure of TiC-SiC\textsubscript{W} composite ceramics are shown by Figure 9a–c. According to the results of Figure 4a, we found that the relative density of TiC-SiC\textsubscript{W} composites increased almost linearly with the increase of SiC\textsubscript{W}. The residual pores in the original samples are mainly located at the triple joints. With the increase of SiC\textsubscript{W} content, more and more diffusion bonds are formed on the high diffusion path between TiC particles, which is beneficial to densification. Secondly, the activation of liquid phase sintering is also beneficial to the uniform filling of micro pores in the densification process. Cross sectional image shows that the sintered TiC-SiC\textsubscript{W} samples is incomplete at sintering temperature of 1800 °C (Figure 9d), and there are pores in the microstructure. When the sintering temperature is 2000 °C, the grain growth is obvious and the pore size is obviously enlarged, as shown in Figure 9f. In contrast, TiC-SiC\textsubscript{W} samples has a uniform equiaxed fine grain structure and high density when sintered at 1900 °C, as shown in Figure 9e.

![Diagram](image-url)

**Figure 8.** (a) Mechanism of crack deflection, (b) Fracture mode of grain boundary phase, (c) Transgranular fracture mode.

![Images](image-url)

**Figure 9.** Microstructure of TiC-SiC\textsubscript{W} composite ceramics. (a) TiC, (b) TiC-20\%SiC\textsubscript{W}, (c) TiC-40\%SiC\textsubscript{W}. (d) TiC-10\%SiC\textsubscript{W} sintered at 1800 °C, (e) TiC-10\%SiC\textsubscript{W} sintered at 1900 °C, (f) TiC-10\%SiC\textsubscript{W} sintered at 2000 °C.
Jiang et al. [87] proved that the greater the carbon-titanium ratio, the higher the hardness. Carbon vacancies in TiC_\text{x} with low carbon-titanium ratio will accelerate the diffusion of interstitial elements to TiC_\text{x}. With the increase of SiC_\text{w} content, carbon atoms are easier to penetrate from SiC phase to TiC_\text{x} phase, and non-stoichiometric TiC_\text{x} gradually develops towards a complete stoichiometric compound. Therefore, with the increase of SiC_\text{w}, the overall hardness of composites shows an upward trend, this method of enhancing hardness has great application potential in cutting tools industry. The existence of SiC_\text{w} also plays a positive role in the flexural strength of TiC-SiC_\text{w} composites. The flexural strength of TiC-SiC_\text{w} composites with 20\% SiC_\text{w} reached 644 MPa, which is because when the crack propagates to the whisker, the crack is bridged by the whisker, and the closing stress is added to the surface of the crack to prevent the crack from propagating, so as to play the role of toughening, as shown in Figure 10a. Moreover, due to the high modulus of SiC_\text{w}, the whisker in the matrix is difficult to crack through. The crack will generally bypass the whisker and the crack will be deflected, which will also improve the modulus of the matrix, as shown in Figure 10b. SiC_\text{w} can effectively improve the flexural strength of the specimen, but too high content of SiC_\text{w} will be counter-productive, which is due to the formation of a large number of brittle Ti_3SiC_2 phase in the interface between TiC and SiC_\text{w}. Because high concentration of SiC_\text{w} will cluster during sintering, it is an urgent need to introduce new interface materials in the future.

Figure 10. Whisker toughening mechanism (a) pull-out and bridging, (b) crack deflection.

3.3. Effect of Carbon Nanotubes on TiC Matrix Composites

Sribalaji et al. [36] found that the carbon nanotubes (CNTs) can decompress in the composites and form wide nano-graphene ribbons (GNR) in situ. As shown in Figure 11, the addition of CNTs will increase the relative density of the composites, which may be because CNTs improve the thermal conductivity of the composites and the in-situ formation of GNR. In addition, the pinning effect of carbon nanotubes also plays a role in grain refinement to a certain extent. A similar conclusion was obtained by Bakshi et al. [88] in TaC-CNTs experiments. Although the addition of carbon nanotubes significantly improves the relative density of the whole composite material. However, the hardness shows a downward trend, which is due to the fact that CNTs phase is not harder than the matrix, and grain slip may occur during indentation. Nieto et al. [89] also reported that the same phenomenon occurred in graphene in TaC.
The bridging of GNR is also related to its high thermal conductivity, the wide GNR formed in situ has a high interface area, as shown in Figure 12a. Therefore, the crack propagation through GNR needs to consume more fracture energy, which is due to the high elastic modulus of GNR. As shown in Figure 12b, cracks are difficult to propagate through GNR, and generally it will propagate around GNR [90]. The results show that with the increase of crack propagation path, more and more energy will be consumed in the process of crack propagation [91]. So, the fracture toughness of TiC monolithic materials is improved from 3.1 MPam$^{1/2}$ to 7.4 MPam$^{1/2}$, which is close to 138%. This kind of report is also common in other ultra-high temperature ceramic composites [92,93]. The deflection and bridging effects of carbon nanotubes on matrix cracks are shown in Figure 12, when the crack propagates near the CNTs, due to the high modulus of CNTs, it cannot be penetrated by the crack, and some cracks will bypass it, resulting in crack deflection (Figure 12d). For some CNTs with specific distribution, the cracks will be bridged by CNTs, and the closing stress is added to the crack surface, and the crack propagation is prevented, which plays a role in toughening (Figure 12c). Two toughening modes of CNTs and GNR are shown in Figure 13. The bridging and deflection of carbon nanotubes are shown in Figure 13a,b. Due to the excellent thermal conductivity of CNTs, some TiC grains have partially re-melted during sintering, CNTs are embedded in TiC grains, crack propagation is greatly hindered. The crack propagation is also hindered by the fine grain region and high-density region of the matrix material.

Figure 11. Fe-SEM images of spark plasma sintering. (a) GNR and CNT pull out, (b) GNR grain wrapping, (c) GNR bending and, (d) GNR sliding during GNR and CNT pull-out.
The hardness of TiC is affected by the ratio of carbon to titanium. The higher the ratio of carbon to titanium, the higher the hardness of TiC matrix. However, with the addition of 5% carbon black, the hardness value only increased by 3%. Due to the limitation of TiC preparation method, TiC matrix contains some unreacted TiO\textsubscript{2}, and the reaction between

**Figure 12.** High magnification finite element scanning electron microscope image. (a,b) crack bridging and deflection of TiC CNT, (c,d) crack bridging and deflection of TiC GNR.

**Figure 13.** Toughening mechanism of gnts (a) pull-out and slipping, (b) bridging and crack deflection.

**4. Summary and Outlook**

The processing method involved in this paper is mainly HP and SPS (Table 2). These two methods can shorten the processing time and achieve high relative density. However, high temperature and high pressure will damage the integrity of additives. Therefore, reasonable selection of additives is an important step in the development of high temperature composites. SiC\textsubscript{W} can effectively control the grain growth in the sintering process by pinning, and the addition of carbon can effectively fill most of the pores of TiC matrix, and increase the relative density of TiC matrix from 95.3% to nearly 99%. But there is no breakthrough in bending strength because a new brittle phase is formed at the interface between TiC and SiC\textsubscript{W}. This may be caused by the sintering method, so it is very important to find a new sintering method and break the limitations of the existing sintering process.

The hardness of TiC is affected by the ratio of carbon to titanium. The higher the ratio of carbon to titanium, the higher the hardness of TiC matrix. However, with the addition of 5% carbon black, the hardness value only increased by 3%. Due to the limitation of TiC preparation method, TiC matrix contains some unreacted TiO\textsubscript{2}, and the reaction between
carbon black and TiO$_2$ produces CO, which increases the porosity of matrix. Therefore, the research on residual gas will be a key direction in the future.

The metal carbide WC and TiC matrix formed solid solution and formed strong metallurgical bonding, so that the fracture toughness of the rechecked material reaches an amazing 7.4 MPam$^{1/2}$, and the bending strength is increased from the initial 410 MPa to 491 MPa. It may be that the WC phase is also toughened by the mismatch of elastic modulus and thermal expansion coefficient with the matrix. The mechanical properties of TiC-WC material will not decrease obviously even at high temperature, it is the most potential thermal protection structural material in the future. Therefore, it is an important trend to introduce new phases and explore the properties of ternary or quaternary composites in the future.

The bridging and pull-out of SiC$_w$ and CNTs consumes more fracture energy, inhibits crack diffusion, and improves fracture toughness and flexural strength. However, SiC$_w$ clusters occur at high temperature, losing its original morphology, and the improvement of mechanical properties is very limited. CNTs are also damaged at high temperature, which cannot meet the theoretical requirements of experimental design. Therefore, it is necessary to introduce suitable interfacial materials and build interphase coatings on the surface of whiskers or fibers to protect them from being damaged.

The straw burning process of TiC high temperature ceramics is mainly affected by temperature, time, pressure, and raw material size. Coordinating the relationship between these factors and exploring efficient preparation methods will also be a focus of future research.

**Author Contributions:** Conceptualization, Y.Z.; Methodology, Y.Z., H.M., and T.F.; validation, Y.Z., F.S. and K.C.; Formal analysis, J.W. and F.S.; Investigation, H.W., H.M. and K.C.; Resources, Y.Z.; Data curation, Y.Z., H.M., T.T. and T.L.; Writing—original draft preparation, Y.Z., H.M. and K.C.; Writing—review and editing, Y.Z. and H.M.; Visualization, K.C. and H.M.; Supervision, Y.Z.; Project administration, Y.Z.; Funding acquisition, Y.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Anhui Province Science Foundation for Excellent Young Scholars (No. 2108085Y19) and the National Natural Science Foundation of China (No. 51604049).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data sharing is not applicable to this article.

**Acknowledgments:** The authors wish to acknowledge the contributions of associates and colleagues at Anhui University of Technology. The financial support of the National Key Research and Development Program of China.

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

**References**

2. Zhang, Y.Y.; Yu, L.H.; Fu, T.; Wang, J.; Shen, F.Q.; Cui, K.K. Microstructure evolution and growth mechanism of Si-MoSi$_2$ composite coatings on TZM (Mo-0.5Ti-0.1Zr-0.02C) alloy. *J. Alloys Compd.* 2022, 894, 162403.
3. Zhang, Y.Y.; Cui, K.K.; Fu, T.; Wang, J.; Shen, F.Q.; Zhang, X.; Yu, L.H. Formation of MoSi$_2$ and Si/MoSi$_2$ coatings on TZM (Mo-0.5Ti-0.1Zr-0.02C) alloy by hot dip silicon-plating method. *Ceram. Int.* 2021, 47, 23053–23065. [CrossRef]


38. He, R.; Li, K.; Liu, Q. High-temperature phase composition, crystal stabilisation, and interfacial diffusion of (NbC-ZrC)/SiC double-layer coated C/C composites enduring the oxyacetylene flame. *Corros. Sci.* 2021, 188, 109541. [CrossRef]


46. Fattahi, M.; Asl, M.S.; Delbari, S.A.; Namini, A.S.; Ahmadi, Z.; Mohammadi, M. Role of nano-WC addition on microstructural, mechanical and thermal characteristics of TiC-SiCw composites. *Int. J. Refract. Met. Hard Mater.* 2020, 90, 105248. [CrossRef]


72. Luo, Y.; Li, S.; Wei, F. Fabrication and mechanical evaluation of SiC-TiC nanocomposites by SPS. Mater. Lett. 2004, 58, 150–153. [CrossRef]


