Carbon reduction of Ti3AlC2 phase for TiC nanosheet production

Baoyan Liang*a, Zhen Dai†, Wangxi Zhang*a,‡, Qisong Li†, Dongming Niu†, Yanli Zhang‡, Mingli Jiao*, Li Yang* and Xiaoyan Guan*

*Materials and Chemical Engineering School, Zhongyuan University of Technology, Zhengzhou, P.R. China; †National and Local Joint Laboratory of Engineering of Diamond Technology, Zhengzhou, P.R. China; ‡Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, P.R. China

ABSTRACT
In this study, we investigated the formation of TiC nanosheets from carbon black and Ti3AlC2 mixtures in NaCl-KCl eutectic salt. The effects of raw material ratio, molten salt ratio, and heating temperature on TiC formation were studied in detail. Results show that carbon black may enhance the decomposition of amounts of Ti3AlC2 at 1,100°C by heat treatment without salt addition, while molten salt plays key roles in the total decomposition of Ti3AlC2 and the formation of TiC nanosheets at 1,000°C. Higher heating temperature and excess carbon black benefits the synthesis of high content TiC. The as-synthesized TiC nanosheets are approximately 15 nm thick and 80–220 nm long. We propose a possible reaction mechanism that governs TiC formation in molten salts and explain the observations based on kinetic considerations.

1. Introduction
Titanium carbide (TiC) is an important ceramic material [1–3] with high hardness, good chemical corrosion resistance, high melting point, good high temperature stability, good corrosion resistance and acceptable thermal conductivity. TiC has potential applications in many fields, such as aerospace, cutting tools, nuclear reactors and so on [4–6]. The poor toughness [7,8] of ceramic materials seriously limits their application, so their strengthening and toughening is the first problem to be solved. It is a promising method to disperse two-dimensional graphene sheets into ceramic matrix, which can effectively strengthen and toughen ceramic materials [9–12]. However, the bonding ability between graphene and ceramic matrix is weak, and there is strong van der Waals force between two-dimensional graphene, which easily leads to matrix agglomeration. These limits the application of ceramic additives to a great extent. Compared with graphene materials, 2D TiC nanosheets have higher hardness, chemical stability and oxidation resistance, so it is expected to become a new type of high-efficiency strengthening and toughening material for ceramic materials. However, to date, the main method of preparing TiC nanosheets is the template method [13,14]. Although this method can produce TiC on a large scale, it is complicated and time consuming. Therefore, it is necessary to explore effective methods to synthesize 2D TiC nanomaterials.

In the previous sintering preparation of MAX phase matrix composites, we found that the presence of carbon source in the reaction environment substantially promotes the low-temperature decomposition of the MAX phase. For example, in the previous research [15], when Ti3SiC2/diamond (10 wt.%) composite was prepared by spark plasma sintering, the results showed that the use of fine-grained diamond (5 μm) could promote the decomposition of Ti3SiC2 at a low temperature and generate numerous fine TiC grains. Several studies [16,17] also found that the thermal stability of MAX phase materials (such as Ti3SiC2 or Ti3AlC2 materials) is very sensitive to solid carbon source or carbon-containing atmosphere (such as CO). Carbon materials can promote the decomposition of MAX phase materials at a low temperature and generate numerous fine titanium carbide particles. In these reports, the formation of 2D titanium carbide MX materials was not found mainly because the reaction temperature of heat treatment or sintering is higher (usually higher than 1,300°C).

The molten salt method is a simple way to synthesize anisotropic powders with specific components at a low temperature and in a short time [18]. In the molten-salt-assisted method, one or several metal salts with a low melting point are used as reaction medium in the reaction, and the heating temperature is controlled above the melting point of metal salts. Molten salt has the properties of high-temperature stability, low viscosity, and high ion mobility. When the temperature rises above the melting point of the molten salt, the structure of the reactants rearranges and diffuses rapidly in the molten salt medium, and the
product particles gradually nucleate and grow. Using the liquid tension of high-temperature molten salt, the molten salt method is often employed to prepare ceramic powders with sheet morphology, such as Bi2NbO5SF [19] and Si3N4 [20] materials.

Based on the above analysis, we consider using nano carbon black to decompose the composition of the MAX phase at a low temperature to obtain MX materials and introduce molten salt synthesis technology to realize the directional growth of the MX phase and obtain MX nanosheets.

In this paper, Ti3AlC2, the representative material of the MAX system, is selected as the object of carbon reduction molten salt treatment. The TiC nanosheets material is synthesized by molten salt heat treatment of carbon black–Ti3AlC2 system. The effects of the presence or absence of molten salt, amount of molten salt, raw material ratio, and heating temperature of carbon black and Ti3AlC2 on the phase composition and morphology of the products are also studied.

2. Experimental procedure

Carbon black (30 nm in average) was purchased from Daosheng Chemical (Shanghai) Co., Ltd. Ti3AlC2 powder (~74 µm, 99.0% purity) was purchased from Laizhou Kai Ceramic Materials Co., Ltd. Anhydrous NaCl and KCl (analytical purity) were purchased from Tianjin Zhiyuan Chemical Plant Co., Ltd. Multilayer graphene (95% purity, 5–10 layers) powders were purchased from Suzhou Carbon Technology Co., Ltd. Nano graphite (99.9% purity, 40 nm in average) powders were purchased from Beijing Dejindaok.co., Ltd. Multiwalled carbon nanotube (95.0% purity, 20–40 nm) powders were purchased from CAS Chengdu Organic Chemistry Co., Ltd. Al (99% purity, 55 µm in average) powders were purchased from Beijing Xingrongyuan Technology Co., Ltd.

Table 1 lists the raw material formulas. The raw material powders were mixed for 1 h using a grinder. The mixed powders were then loaded into graphite crucible, closed, and placed in a vacuum carbon tube furnace. First, they were heated to 700°C in a vacuum, and Ar was added to protect them. Then, they were heated to different temperatures for 1.5 h and cooled down with the furnace. The heat-treated samples were washed repeatedly with distilled water and alcohol, and finally dried and ground. The specimens obtained at different heat treatment temperatures were named as Tm (m = 0, 1, 2, 3, 4, 5, 6)–temperature (1,000, 1,050, and 1,100).

The as-synthesized samples were characterized by X-ray diffraction (XRD, D/MAX-2500PC) and field-emission scanning electron microscopy (FE-SEM, Quanta 250 FEG).

3. Results and discussion

Figure 1 shows the original morphology of Ti3AlC2. Figure 1 (a) shows that it has a size of approximately 20–50 µm. The typical lamellar morphology of Ti3AlC2 can be clearly observed from Figure 1 (b).

The effect of different carbon sources (carbon black, nano graphite, graphene, and carbon nanotubes) on the reduction of Ti3AlC2 was studied. Figure 2 shows the XRD patterns of the molten salt products obtained.
by using different carbon sources at 1100°C for 1.5 h. The mass ratio of molten salt to raw material was 4. The mole ratio of carbon black to Ti3AlC2 was 1. Figure 2 shows that when carbon nanotubes, multilayer graphite, and nano graphite were used as raw materials, a small amount of Ti3AlC2 was not reduced. In addition, the part Al decomposed by Ti3AlC2 existed in the form of simple substance, and the other part was oxidized to Al2O3. Carbon black can promote the complete decomposition of Ti3AlC2, and the decomposed Al existed in the form of simple substance. The results in Figure 2 show that the effect of carbon black promoting the decomposition of Ti3AlC2 was the best, and the byproduct obtained from the decomposition was Al simple substance, which was easy to remove. Moreover, the price of carbon black was much lower than that of other nano carbon sources, which was also conducive to the industrial promotion of this process. Therefore, in the following study, we will use carbon black as carbon source to reduce Ti3AlC2 materials.

Figure 3(a) shows the XRD patterns of T01000 obtained without salt addition. Figure 3(a) shows that Ti3AlC2 decomposes gradually with the increase of heating temperature. The main decomposition product is TiC with other impurities such as TiAl and Al0.64Ti0.36. The Ti3AlC2 decomposition rate of T01100 can be simply calculated as 91.7% by formula [21]. The results show that carbon black can induce the decomposition of a large amount of Ti3AlC2 at a low temperature and form TiC, TiAl, and Al0.64Ti0.36.

Figure 3(b)–(c) show the SEM image of T01100. The low-magnification SEM in Figure 3(b) shows that the sample is composed of several micron-sized powder particles. The high magnification in Figure 3(c) shows that these powder particles are aggregates composed of numerous nanoparticles (60–200 nm). However, nanosheet morphology cannot be observed. Therefore, in the absence of molten salt, carbon black only can induce the decomposition of large amounts of Ti3AlC2 at a low temperature but will not form TiC nanosheets.

Figure 4 shows the (a) XRD patterns and (b) SEM images of the heat-treated product obtained by the molten salt synthesis of single-phase Ti3AlC2 powders at 1100°C. Figure 4(a) shows that a small amount of Ti3AlC2 is decomposed to form TiC and Al. The decomposition of Ti3AlC2 can also be promoted in a molten salt environment. However, compared with carbon black, as shown in Figure 3 (a), its promoting effect is much worse. Figure 4 (b) shows that the larger Ti3AlC2 particles become loose. Its surface has many fine particles. Figure 4 (c) demonstrates that a large number of fine TiC nanosheets are formed on the surface of Ti3AlC2 particles.

Based on the above research, carbon black can remarkably promote the decomposition of Ti3AlC2 to obtain fine TiC nanoparticles. Molten salt can promote the decomposition of some Ti3AlC2 and obtain TiC nanosheets. Therefore, in the following sections, molten salt heat treatment on carbon black and Ti3AlC2 mixed powder is carried out to obtain TiC nanosheets.

The amount of molten salt is an important factor in molten salt synthesis, which has a substantial influence on the purity and morphology of the target product [18–20]. Figure 5 shows the XRD patterns of several samples with different amounts of molten salt. Figure 5 (a) shows that the main phase of T11000 is TiC, weak Al3Ti and Al5Ti3 diffraction peaks are observed, and
the peaks of Ti3AlC2 disappeared. However, samples with higher amounts of molten salt (T21000 and T31000) have stronger Ti3AlC2 peaks in the XRD spectra. These results show that low molten salt amounts can promote the complete decomposition of Ti3AlC2 and produce a small amount of TiAlx compound impurities at 1,000°C. The decomposition of Ti3AlC2 is inhibited by a high salt content.

Figure 5(b) shows the XRD patterns of three samples obtained at 1,050°C. The XRD pattern of T11050 is the same as that of T11000. The main phase is TiC and contains a small amount of Al and TiAlx compounds. The XRD spectra of T21050 and T31050 approximate that of T11050. Their main phase is TiC, and a small amount of Al, and TiAl are obtained. The results show that increasing the temperature can promote the remarkable decomposition of Ti3AlC2 in samples with a high molten salt content.

Increasing the temperature can promote the complete decomposition of Ti3AlC2 in samples with a high molten salt content. When the temperature rises to 1,050°C, Ti3AlC2 in T21050 and T31050 are completely decomposed. The main phase of the three products is TiC, and the second phase is Al and TiAlx compounds. When the temperature is further increased to 1,100°C, the main phase of T11100 is TiC, and a small Al by-product is observed. However, T21100 and T31100 composed of single-phase TiC, showing that single-phase TiC can be obtained by using a sample with a high molten salt ratio at 1,100°C.

Figure 6 shows the SEM images of (a)(b) T11000, (c) T11050, (d) T21050, (e) T31050, (f) T11100, (g) T21100, and (h) T31100. Figure 6(a) shows that T11000 is composed of many flocculent large particles. The surface of these large particles is composed of many nanosheets and a small amount of irregular block crystals. XRD (Figure 7) and EDS (Figure 7) confirm that the nanosheets are TiC, and the bulk crystals are TiAlx phase. In addition, the average thickness of these nanosheets is about 15 nm, and the length is about
80–220 nm, as shown in Figure 6(b). TiC nanosheets are obtained by carbon-black-induced Ti3AlC2 by molten salt treatment. After heating to 1,050°C and 1,100°C, T11050 and T11100 are also composed of amounts of TiC nanosheets, as shown in Figure 6(c) and (f). However, T2 and T3 samples are mainly composed of numerous TiC nano grains, with sizes ranging from 50 nm to 400 nm. A small amount of TiC nanosheets can be observed.

The XRD and SEM results show that heating temperature plays a decisive role in the decomposition of Ti3AlC2. Increasing the temperature can promote the complete decomposition of Ti3AlC2 to form TiC, Al, and other TiAlx compounds. The molten salt ratio is very important for the formation of TiC nanosheets. TiC nanosheets can be obtained at a low molten salt ratio, whereas TiC nanoparticles can be obtained at a high molten salt ratio.

Therefore, the flux/raw material ratio of 4:1 was used in the following study on the effect of raw material ratio on the TiC formation. The as-synthesized TiCx could be non-stoichiometric, and the deviation range of this stoichiometric ratio was probably very large [22–24]. The composition range of TiCx is x = 0.4–1.1. We consider several cases in which the carbon content deviates from the stoichiometric ratio. Figure 8(a) shows the XRD patterns of T41000, T51000, and T61000. Figure 8(a) shows that when the carbon black content is lowest (X = 0.5), the diffraction peak intensity of Ti3AlC2 is relatively high. However, when the carbon content in the sample is slightly higher (X = 1.1), the main phase in the T51000 product is TiC, and a small amount of Al and TiAlx impurity is observed. Tiny amounts of Ti3AlC2 do not decompose when the carbon content is seriously excessive (X = 1.5), and Al, Al3Ti, TiAl, and Al0.64Ti0.36 are contained in T61000.

The Ti3AlC2 diffraction peak of T41050 is evidently weakened, and the Ti3AlC2 peak in T61050 completely disappears when the temperature is further increased to 1,050°C. Increasing the temperature may enhance the decomposition of Ti3AlC2. Compared with the XRD pattern of T51000, that of T51050 has almost no change.

The main phase of T51100 is TiC with the temperature increasing to 1,100°C, a small amount of Al is observed, and T61100 is composed of single-phase TiC. Compared with the XRD pattern of T41050, that of T41100 has almost no change.

The above results show that the change of carbon content alters the chemical balance and promotes the
decomposition of Ti3AlC2 to TiC. Moreover, at 1,100°C, the increase of carbon content will promote the synthesis of single-phase TiC. Based on the above analysis, we speculate that TiC and Al are the main products obtained by the carbon reduction of Ti3AlC2. Then, Al reacts with a small amount of Ti3AlC2 to form TiAlx compounds at a low temperature.

Figure 9 shows the FE-SEM images of (a) T51000, (b) T61000, (c) T51050, (d) T61050, (e) T51100, and (f) T61100. Figure 9(a) shows that T51000 has relatively few TiC nanosheets. Other samples are mainly composed of TiC nanosheets.

The TEM images in Figure 10 show that the nanosheets have an average thickness of 2 nm and a length of 70–150 nm.

The above results show that TiC nanosheets can be obtained by the carbon reduction of Ti3AlC2 phase by molten salt heat treatment. Carbon black and molten salt heat treatment are used to synthesize TiC nanosheets for the first time. However, to date, the main method of preparing TiC nanosheets is the template method [13,14]. Although this method can produce TiC on a large scale, it is complicated and time consuming. In addition, Ti3AlC2 is one representative material of the MAX phase. This method of carbon reduction of Ti3AlC2 to synthesize TiC nanosheets can be applied to other MAX phase materials, such as Ti2AlC and Cr2AlC.

We investigated the synthesis mechanism of TiC nanosheets by carbon reduction of Ti3AlC2. First, we calculated the Gibbs free energy (ΔG) values of possible chemical reactions in the system at different temperatures using the thermodynamic data of Ti-Al-C system provided in Ref [25,26], as shown in Figure 11. We selected TiAl and TiAl3 as the representatives for thermodynamic calculation in the following study due to the wide variety of Ti-Al compounds. Then, based on the experimental results and thermodynamic calculation results, we discussed the formation mechanism of TiC.

The thermal decomposition reaction of MAX phase can be described as Mn+1AXn→Mn+1Xn + A [16]. This decomposition mode can be attributed to the high activity of A element, which is due to the much weaker binding between M and A than between M and X. The carbon-induced thermal decomposition reaction of Ti3AlC2 can be attributed to the following equation:

\[
C + Ti_3AlC_2 = 3TiC + Al
\]  

(1)

The XRD results of heat treatment products obtained at 1,100°C verify the decomposition mechanism, as shown in Fig. 5(c) and 8(c). However, the XRD experimental results at lower temperatures show that different TiAl phases are formed in the products. The decomposition of titanium aluminum carbon is not so simple. The literature [17] pointed that the direct decomposition of Ti3AlC2 can be induced by C material, and Ti3AlC2 is decomposed to Ti3C2 and Al. Ti3C2 is a metastable phase, which can be further decomposed into Ti3C2 and Ti. Finally, Ti and Al can
react to form various TiAl compounds, such as TiAl3 and TiAl. The reaction Formulas (2) (3) are shown as follows:

\[ Ti_3AlC_2 = Ti_3C_2 + Al \]  \hspace{1cm} (2)

\[ Ti_3C_2 = Ti_{3-x}C_2 + xTi \]  \hspace{1cm} (3)

Figure 11 shows that the \( \Delta G \) values of Reactions (1) and (2) are less than zero, indicating that both reactions will occur spontaneously. However, the absolute value of Reaction (1) is much larger than that of Reaction (2), indicating that it is easier to carry out.

According to these two reaction paths, amounts of Al can be formed. Then, Al may react with Ti3AlC2, Ti, and carbon black as follows:

\[ 2Al + Ti_3AlC_2 = Al_3Ti + 2TiC \]  \hspace{1cm} (4)

\[ Ti + 3Al = TiAl3 \]  \hspace{1cm} (5)

\[ Ti + Al = TiAl \]  \hspace{1cm} (6)
Al + C = Al₄C₃ \hspace{1cm} (7)

The Ti obtained by reaction (3) can also react directly with carbon black to form TiC.

\[
Ti + C = TiC
\]  \hspace{1cm} (8)

Figure 11 shows that the ΔG values of Reactions (4)–(8) are all less than zero, and these reactions can be spontaneous. From the thermodynamic point of view, TiC is more stable than TiAlₓ and Al₄C₃. TiAlₓ and Al₄C₃ will transform to TiC with the increase of temperature.

The results of literature study [27] on Al-Ti₃AlC₂ system show that Al₄C₃ is very unstable at a high temperature and will react with TiAl₃ to form TiC and Al.

\[
3TiAl₃ + Al₄C₃ = 3TiC + 13Al
\]  \hspace{1cm} (9)
Figure 9. FE-SEM images of (a) T51000, (b) T61000, (c) T51050, (d) T61050, (e) T51100, and (f) T61100.

Figure 10. The TEM images of T61050 sample.
Carbon black was also observed in this study. Thus, the TiAlx phase will react with carbon to form TiC and Al.

\[
3\text{Al}_2\text{Ti} + 2\text{C} = \text{TiC} + 2\text{Al} \quad (10)
\]

\[
\text{TiAl} + \text{C} = \text{TiC} + \text{Al} \quad (11)
\]

Figure 11 shows that the ΔG values of reactions (9) (10) (11) are small or zero, and the absolute values are large; thus, these reactions can easily be spontaneous. Al4C3 and TiAlx compounds are only intermediate products, which will eventually be transformed into TiC and Al.

The above analysis shows that carbon black plays a major role in the decomposition and transformation of Ti3AlC2 into TiC at a low temperature, and the decomposition of Ti3AlC2 is further promoted by introducing molten salt. Why does carbon and molten salt treatment substantially promote Ti3AlC2 decomposition?

The results in Figure 8 strongly prove that carbon black is a reactant rather than a catalyst. Assuming that carbon black is the reactant, the mole ratio of carbon black and Ti3AlC2 when they fully react to form 3TiC and Al is 1:1, which we consider the normal value. Figure 8 shows that the main phase of the products is TiC when the content of carbon black is normal or excessive. When the content of carbon black is half the normal value, amounts of Ti3AlC2 still exist in the products. In addition, if carbon black is the catalyst, then a large number of carbon black nanoparticles will be found in the product (the mole ratio of carbon black to Ti3AlC2 is 0.5–1.5). However, carbon black could not be observed in any SEM or TEM image, as shown in Figure 3 (b)–1 (c), 6, 9, and 10). Therefore, we infer that carbon black acts as a reagent.

For the reaction system without molten salt, the Al byproduct may hinder the contact of carbon black with other unreacted Ti3AlC2, which is equivalent to the “protective layer” of unreacted Ti3AlC2 material. Al also reacts with Ti3AlC2 to form Al3Ti. The existence of Al3Ti further hinders the contact between carbon black and Ti3AlC2, inhibiting the decomposition of Ti3AlC2.

The heat treatment of Al and Ti3AlC2 mixed powder in a molten salt environment was carried out to verify the above inference. Figure 12(a) shows the XRD patterns of the product obtained by the molten salt heat treatment (the mass ratio of molten salt to raw material was 4) of equimolar Al and Ti3AlC2 powders at 1100°C for 1.5 h. Figure 12(a) shows that the product was composed of Al3Ti, TiC, and Al2O3. Figure 12(b) shows that TiC grains in the product were equiaxed, and the size was approximately 0.22–1 μm. The above results show that TiC grains developed into nanoparticles rather than nanosheets when Ti3AlC2 grains coexisted with molten salt and Al. In addition, the product powder was agglomerate, which was much more compact than the porous structure of the molten salt products of C-Ti3AlC2 system (Figure 6).

Molten salt promotes Ti3AlC2 decomposition because it provides a liquid environment and greatly enhances the diffusion and dissolution of elements. Al easily migrates from the reaction zone. Carbon black can rapidly diffuse to the unreacted part of Ti3AlC2, accelerating the decomposition of Ti3AlC2.

However, the increase of molten salt content is not conducive to the formation of TiC nanosheets because it will inevitably increase the precipitation distance of Al from raw materials. This situation will certainly prolong the existence time of Al in the molten salt system, such that the synthesized TiC will be in liquid Al melt for a longer time.
TiC is easy to develop into nanoparticles under the action of Al. Generally, TiC formed in Al-Ti-C system [28,29] is equiaxed, that is, the morphology of TiC is granular. The existence of Al inhibits the directional growth of TiC. Therefore, the products without molten salt in this study and the decomposition products of Ti3AlC2 induced by carbon reported in the literature [17] are all granular TiC, as shown in Figure 3(c).

Based on the above analysis, an excessive molten salt content is conducive to the formation of TiC particles.

The co-existence of carbon black and molten salt ensures that Ti3AlC2 is completely transformed into TiC nanosheets and Al at a low temperature. Based on the above analysis, we propose a possible reaction mechanism that carbon black induces Ti3AlC2 decomposition to form TiC nanosheets in a molten salt environment. Figure 13 illustrates that carbon black is first adsorbed on the Ti3AlC2 surface and fully contacts the Ti3AlC2, as shown in Figure 13(a). Then, carbon black induces the decomposition of Ti3AlC2 to form TiC and Al, as shown in Figure 13(b). Afterward, some Al reacts with Ti3AlC2 to form AlTi3 and TiC, as shown in Figure 13(c). Finally, AlTi3 reacts with C to form TiC and Al. TiC grains develop into nanosheets, as shown in Figure 13(d).

4. Conclusions

In this study, TiC nanosheets were prepared from carbon black and Ti3AlC2 by molten salt heat treatment. The effects of molten salt content, raw material ratio, and heat treatment temperature on Ti3AlC2 decomposition, TiC yield, and morphology were studied in detail. The results of XRD, SEM, EDS, and TEM analyses revealed the following:

a) Carbon black can promote the decomposition of Ti3AlC2 at a low temperature (1,000°C) and obtain many nano TiC particles. Carbon black can promote
the complete decomposition of Ti3AlC2 by using molten salt heat treatment, resulting in a large number of TiC nanosheets and a small amount of TiAl phase impurities.

b) The addition of less molten salt can promote the complete decomposition of Ti3AlC2 at 1,000°C. However, the Ti3AlC2 in the sample with a higher amount of molten salt can be completely decomposed when the temperature rises to 1,050°C.

c) Serious deviation from raw material ratio is not conducive to Ti3AlC2 decomposition.

Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

This work was supported by the National Natural Science Foundation of China [51864028, 51973246, 51805557]; Program for Science and Technology Innovation Talents in Universities of Henan Province [19HASTIT024]; Key scientific research projects of colleges and universities in Henan Province [18A430033].

References

[1] Gu Y, Liu J, Xu F, et al. Pressureless sintering of titanium carbide doped with boron or boron carbide. J Eur Ceram Soc. 2017;37(2):539–547.
[2] Magnus C, Kwanman T, Rainforth W. Dry sliding friction and wear behaviour of tic-based ceramics and consequent effect of the evolution of grain buckling on wear mechanism. Wear. 2019;422423(3):54–67.
[3] Upadhyaya G. Materials science of cemented carbides—an overview. Mater Des. 2001;22(6):483–489.
[4] Bagheri S, Vajdi M, Moghanlou F. Numerical modeling of heat transfer during spark plasma sintering of titanium carbide. Ceram Int. 2019;46(6):7615–7624.

[5] Khodaei M, Yaghobizadeh O, Baharvandi H, et al. Effects of different sintering methods on the properties of SiC-TiC, SiC-TiB2 composites. Int J Refract Met Hard Mater. 2018;70:19–31.

[6] Fattahi M, Asl M, Delbari S, et al. Role of nano-WC addition on microstructural, mechanical and thermal characteristics of TiC–SiCw composites. Int J Refract Met Hard Mater. 2020;105248.

[7] Xia Z, Curtin W. Tough-to-brittle transitions in ceramic-matrix composites with increasing interfacial shear stress. Acta Mater. 2000;48(20):4879–4892.

[8] Kelly J, Denny I. Stabilized zirconia as a structural ceramic: an overview. Dent Mater. 2008;24(3):289–298.

[9] Sherrell P, Mattevi C. Mesoscale design of multifunctional 3D graphene networks. Mater Today. 2016;19(8):428–436.

[10] Zhang X, Zhao Z, He C. The superior mechanical and physical properties of nanocarbon reinforced bulk composites achieved by architecture design-A review. Prog Mater Sci. 2020;113:100672.

[11] Gao C, Peng P, Peng S, et al. Carbon nanotube, graphene and boron nitride nanotube reinforced bioactive ceramics for bone repair. Acta Biomater. 2017;61:1–20.

[12] Chen F, Yan K, Sun J, et al. From the research state of the thermal properties of graphene reinforced ceramics to the future of computer simulation. Ceram Int. 2020;46(11):18428–18445.

[13] Chen T, Li M, Seunghyun S, et al. Biotemplate preparation of multilayered TiC nanoflakes for high performance symmetric supercapacitor. Nano Energy. 2020;71:104549.

[14] Chen K, Bao Z. Synthesis and characterization of carbide nanosheets by a template-confined reaction. Journal of Nanopart Res. 2013;15(9):1141.

[15] Liang B, Zhang W, Feng Y. Microstructure and grinding property of Ti3SiC2/diamond composites fabricated by spark plasma sintering. Mater Sci Eng Powder Metall. 2017;22:399–406.

[16] Racault C, Langlais F, Naslain R, et al. Solid-state synthesis and characterization of the ternary phase Ti3SiC2. J Mater Sci. 1994;29(13):3384–3392.

[17] Gai J, Chen J, Zhang H, et al. Synthesis of Al2O3 whiskers by heat treating bulk Ti3AlC2 in a carbon-containing environment. Mat Lett. 2016;167:73–76.

[18] Selloni A, Carnevale P, Car R, et al. Localization, hopping, and diffusion of electrons in molten salts. Phys Rev Lett. 1987;59(7):823–826.

[19] Wang J, Li J, Wang K, et al. Controlled synthesis of Bi2NbO5F plates with exposed [010] facet by molten salt method and their photocatalytic mechanism insights. Journal of Alloys and Compounds. 2019;776:586–593.

[20] Chai Z, Ding J, Deng C, et al. Ni-catalyzed synthesis of hexagonal plate-like alpha silicon nitride from nitridation of Si powder in molten salt media. Adv Powd Tech. 2016;27(4):1637–1644.

[21] Wang C, Zhou A, Qi L, et al. Quantitative phase analysis in the Ti–Al–C ternary system by X-ray diffraction. Powder Diffr. 2005;20(3):218–223.

[22] Lopacinski M, Puszynski J, Lis J. Synthesis of Ternary Titanium Aluminum Carbides using self-propagating high-temperature synthesis technique. J Am Ceram Soc. 2001;84(12):3051–3053.

[23] Wang X, Zhou Y. Oxidation behavior of Ti3AlC2 at 1000–1400 °C in air. Corros Sci. 2003;45(5):891–907.

[24] Wang X, Zhou Y. Stability and selective oxidation of Aluminum in Nano-Laminate Ti3AlC2 upon heating in Argon. Chem Mater. 2003;15(19):3716–3720.

[25] Chen Y, Chu M, Wang L, et al. First-principles study on the structural, phonon, and thermodynamic properties of the ternary carbides in Ti–Al–C system. Phys Status Solidi A. 2011;208(8):1879–1884.

[26] Ye DL, Hu JH. Practical inorganic thermodynamic data book. second ed. Beijing: Metallurgical industry press; 2002.

[27] Wang W, Gauthier-Brunet V, Bei G, et al. Powder metallurgy processing and compressive properties of Ti3AlC2/Al1−x composites. Mater Sci Eng A. 2011;530:168–173.

[28] Samer N, Andrieux J, Gardiola B, et al. Microstructure and mechanical properties of an Al–TiC metal matrix composite obtained by reactive synthesis. Compos Part A Appl Sci. 2015;72:50–57.

[29] Jerome S, Ravisankar B, Mahato P, et al. Synthesis and evaluation of mechanical and high temperature tribological properties of in-situ Al–TiC composites. Tribol Int. 2010;43(11):2029–2036.