A simple method for the synthesis of nanosized Ti$_3$AlC$_2$ powder in NaCl–KCl molten salt

Ling Xu Yang$^{a,b}$, Ying Wang$^{a,b}$, Hai Liang Zhang$^{a,b}$, Hui Jun Liu$^a$ and Chao Liu Zeng$^a$

$^a$Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, People’s Republic of China; $^b$School of Materials Science and Engineering, University of Science and Technology of China, Hefei, People’s Republic of China

**ABSTRACT**

Herein we report, a simple novel method to synthesize nanosized Ti$_3$AlC$_2$ powder from Ti, Al, and C powders in NaCl–KCl molten salt. It is more conducive to the formation of Ti$_3$AlC$_2$ at higher salt/precursor materials ratio and particle size of Ti$_3$AlC$_2$ powder dramatically decreases with increasing mass ratio of the salt to precursor materials. Fine-grained Ti$_3$AlC$_2$ powder is successfully synthesized at 950°C for 5 h or at 1000°C for 2 h with a salt/precursor materials ratio of 10:1. Ti$_3$C$_2$ MXene is also prepared by etching fine-grained Ti$_3$AlC$_2$ precursor in HF solution at 60°C for 2 h.

**IMPACT STATEMENT**

It is the first time that nanosized ternary carbide Ti$_3$AlC$_2$ powder has been synthesized by a simple, high efficiency and relatively low-temperature process.

**1. Introduction**

Titanium aluminum carbide, Ti$_3$AlC$_2$, as one of the most promising advanced ceramics belonging to a member of the so-called MAX phases, has attracted increasing attention in recent years because of its unique combination of both metal and ceramic properties [1]. Like metals, it has excellent electrical conductivity, high thermal conductivity, and high machinability [2]. Like ceramics, it has low thermal expansion coefficient, high melting point, strength, and thermal stability [3]. All of these prominent properties make Ti$_3$AlC$_2$ a potential material for various functional and structural applications.

More importantly, Ti$_3$AlC$_2$ is also a precursor material for preparation of Ti$_3$C$_2$ [4], which is a member of the two-dimensional (2D) materials called MXene and generated by selectively etching element A from MAX phase in aqueous HF solution. Additionally, MXenes have shown great promise in Li–S batteries [5], Li–Na–K–ion batteries [6–9], supercapacitors [10], and catalysts [11] due to its high conductivity and hydrophilicity. Therefore, the synthesis of Ti$_3$AlC$_2$ powder is becoming increasingly important.

Since Ti$_3$AlC$_2$ was firstly synthesized by sintering cold-compacted powder mixtures of Ti, TiAl, Al$_4$C$_3$, and C in pure hydrogen at 1300°C for 20 h [1], many different processes, such as self-propagating high-temperature synthesis [12], combustion synthesis [13], and pressureless sintering [14], have been attempted to synthesize Ti$_3$AlC$_2$ powders in the past two decades [15]. However, the particle size of the prepared Ti$_3$AlC$_2$ powder ranges from a few to dozens of micron. Meanwhile, it is reported that the initial particle size of Ti$_3$AlC$_2$ powder has a decisive influence on kinetics of the selective extraction of Al from Ti$_3$AlC$_2$. In other words, decreasing the Ti$_3$AlC$_2$ particle size would lead to faster conversion of Ti$_3$AlC$_2$ to its 2-D Ti$_3$C$_2$ counterpart [16, 17]. For example, it is reported that at least 24 h is needed for etching Al from Ti$_3$AlC$_2$ powders passed through a 325-mesh...
screen in 49% HF solution at 60°C to prepare 2-D Ti$_3$C$_2$ [18]. Therefore, it is necessary to develop a novel process to synthesize fine-grained Ti$_3$AlC$_2$ powders.

Unsurprisingly, molten salt method, as a relatively low-temperature technique for nanosized carbide synthesis, has attracted increasing interest in recent years [19,20]. In this method, a salt is used as liquid medium, causing faster reactions at relatively lower temperature and reaction completion in shorter time [21]. Up to now, Ti$_3$SiC$_2$ and Cr$_2$AlC have been successfully synthesized by molten salt method [22,23]. Unfortunately, the particle size of the prepared MAX phases is also larger than a few microns. Therefore, it is urgent to decrease the grain size of the obtained Ti$_3$AlC$_2$ powder or explore a novel process to synthesize submicron or nano-sized Ti$_3$AlC$_2$ grains to facilitate faster conversion of Ti$_3$AlC$_2$ to its 2-D Ti$_3$C$_2$ counterpart. The objective of this work is to report on the synthesis of nano-sized Ti$_3$AlC$_2$ powder by molten salt method at a relatively low temperature to obtain a faster conversion of Ti$_3$AlC$_2$ to its 2-D Ti$_3$C$_2$ counterpart.

2. Experimental

A mixture composed of NaCl and KCl in eutectic (supplied by Tianjin Kemiou Chemical Reagent Co., Ltd. Analytical grade) was used as liquid medium, which was firstly dried at 350°C for 24 h to remove moisture. A 1.63 g mixture composed of commercially available powders of Ti (1.20 g, particle size $< 50 \mu$m, purity $> 99.8$%), Al (0.23 g, particle size $< 100 \mu$m, purity $> 99.8$%), and acetylene black (0.20 g, particle size $< 50$ nm, purity $> 99.9$%) with molar ratio of 3Ti/1Al/2C were used as precursor materials, which were weighed and mixed with various mass ratios of the dried NaCl–KCl of 1:1, 1:3, 1:6, and 1:10 in an alumina crucible, respectively. After that, the alumina crucible was placed in a closed stainless steel vertical tubular reactor, and subsequently heated to 950°C holding for 5 h or 1000°C holding for 2 h at a rate of 6°C·min$^{-1}$ under flowing argon ($\sim 30$ mL·min$^{-1}$, purity $> 99.999$%). After completion of prior thermal exposures, the chamber was naturally cooled to room temperature. Then the sample was ultrasonically rinsed with boiling deionized water for several times to remove residual salts. Finally, the obtained sample was dried at 80°C for 12 h for characterization.

The phase constituents of samples were identified by X-ray diffraction (XRD, PANalytical X’Pertpro) with Cu target Kα radiation. The morphology of the sample was characterized by a high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20) and selected-area electron diffraction (SAED). The microstructure of the sample was also characterized by field-emission
scanning electron microscope (FESEM, Inspect F50, FEI Co., Hillsboro, OR, USA).

3. Results and discussion

XRD patterns of samples synthesized from 3Ti/Al/2C precursor powders in eutectic NaCl–KCl molten salt at different salt/precursor materials ratio at 950°C for 5 h are shown in Figure 1. After removing background of XRD patterns, the diffraction intensities of (002) peak of Ti₃AlC₂ (phase a), (002) peak of Ti₂AlC (phase b) and (111) peak of TiC (phase c) were measured, respectively. Therefore, the weight percent of Ti₃AlC₂, Ti₂AlC and TiC is calculated by Equations (1), (2), and (3), respectively, [24]:

\[
\omega_a = \frac{I_a}{I_a + 0.220I_b + 0.084I_c},
\]

\[
\omega_b = \frac{I_b}{4.545I_a + I_b + 0.382I_c},
\]

\[
\omega_c = \frac{I_c}{11.905I_a + 2.619I_b + I_c}.
\]

Figure 2. SEM images of samples synthesized from 3Ti/Al/2C precursor powders in NaCl–KCl molten salt at different salt/precursor materials ratio at 950°C for 5 h (a) 1:1, (b) 3:1, (c) 6:1, (d) 10:1, the corresponding insets show higher magnification micrograph of Ti₃AlC₂ particles and TiC fibers. (e) TEM image and (f) the corresponding SAED pattern of the TiC fiber in Figure 2(b).
The result shows that the desired Ti₃AlC₂ (70.1%) besides TiC(18.4%) and Ti₂AlC (11.5%) impurities are detected when mass ratio of the salt to precursor materials is 1:1 as shown in diffractogram a. Furthermore, the amount of TiC and Ti₂AlC phases reduces while the desired Ti₃AlC₂ increases with increasing mass ratio of the salt to precursor materials as shown in diffractograms b and c, indicating that higher mass ratio of the salt to precursor materials is more conducive to Ti₃AlC₂ formation. When the mass ratio of the salt to precursor materials increases to 10:1, the desired Ti₃AlC₂ (96.7%) and a few TiC (3.3%) are obtained as shown in diffractogram d. These indicate that Ti₃AlC₂ has been successfully synthesized from 3Ti/Al/2C precursor powders in NaCl–KCl molten salt with salt/precursor materials ratio of 10:1 and 6:1 at 950°C for 5 h. Additionally, it is reported that the plate-like and needle-like Ti₃AlC₂ grains have been synthesized at 1300–1500°C and 1300°C, respectively, by traditional [14,15] and molten salt methods [25]. Therefore, the temperature of Ti₃AlC₂ powder synthesized in this work is relatively lower, and the method is simpler and more efficient than that synthesized by traditional and molten salt methods. This may be due to the disproportionation reactions of Ti(II) and Ti(III) species in the molten salt, thus larger content of salts is required [26].

The mechanism of Ti₃AlC₂ formation is proposed as follows: a small quantity of Ti powder is firstly dissolved to form Ti(II) and Ti(III) species when the temperature of the salt reaches 700°C [27,28]. Then, nanosized TiC and Ti₃Al (or TiAl) particles will be in-situ synthesized by the reaction between Ti atoms, which come from disproportionation reactions of Ti(II) and Ti(III) species, and C and Al atoms on the surface of acetylene black and Al [19], respectively. Finally, the desired Ti₃AlC₂ powder is obtained by the reaction of the dispersed TiC, Ti₃Al (or TiAl), and acetylene black particles in molten salt.

SEM images of samples obtained from 3Ti/Al/2C precursor powders in NaCl–KCl molten salt at different salt/precursor materials ratio at 950°C for 5 h are shown in Figure 2. Results indicate that particle size of the

![Figure 3.](image-url)
Ti$_3$AlC$_2$ powder dramatically decreases with increasing mass ratio of the salt to precursor materials as shown in Figure 2(a), (b), (c), and (b). In addition, TEM image of the fiber in the inset of Figure 2(b) is also characterized as shown in Figure 2(e). The corresponding diffraction spots of the fiber are indexed to (111), (220) and (311) plane of cubic TiC as shown in Figure 2(f), suggesting that TiC fibers are formed with salt/precursor materials.

**Figure 4.** (a) TEM image of Ti$_3$AlC$_2$ powder obtained from 3Ti/Al/2C precursor materials in NaCl–KCl molten salt with a salt/precursor materials ratio of 10:1 at 1000°C for 2 h, the inset shows Tyndall scattering effect for the suspension of Ti$_3$AlC$_2$ nanoparticles in deionized water; (b) TEM and (c) HRTEM images of the typical layer structure on the cross-section of a fine-grained Ti$_3$AlC$_2$ particle; (d) TEM and (e) HRTEM images of the layered atomic stacking on the surface of a fine-grained Ti$_3$AlC$_2$ particle; (f) A SAED pattern of Ti$_3$AlC$_2$ along the [01\text{T}0] zone axis.
ratio of 1:1 and 3:1. This is in agreement with XRD results shown in Figure 1. Additionally, although Ti$_3$AlC$_2$ powder, with some impurities, have also been synthesized with salt/precursor materials ratio of 1:1, 3:1, and 6:1, some nano-crystals of Ti$_3$AlC$_2$ are sintered together and they cannot be separated as shown in insets of Figure 2(a) and (c). However, Ti$_3$AlC$_2$ powder with a mean particle size of $\sim$ 100 nm is successfully synthesized at 950°C for 5 h when the mass ratio of the salt to 3Ti/Al/2C precursor materials is 10:1 as shown in the inset of Figure 2(d). To the best of our knowledge, the particle size of Ti$_3$AlC$_2$ powder synthesized in this work is much smaller than that synthesized by traditional [14,15] and molten salt methods [25], which have been reported that plate-like and needle-like Ti$_3$AlC$_2$ grains with a size of 5–10 and 5 μm were synthesized, respectively.

In order to decrease the synthesis time, the NaCl–KCl salt and 3Ti/Al/2C precursor powders with mass ratio of 10:1 without ball milling were mixed in an alumina crucible, and then heated to 1000°C holding for 2 h to synthesize Ti$_3$AlC$_2$ powders. Typical SEM image and XRD pattern of the product obtained are shown in Figure 3(a) and (b), respectively. Results show that Ti$_3$AlC$_2$ has also been successfully synthesized with a salt/precursor materials ratio of 10:1 at 1000°C for 2 h. Additionally, Ti$_3$AlC$_2$ powders with similar size and purity are obtained both at 950°C for 5 h (shown in Figures 2(d) and 1(d)) and 1000°C for 2 h (shown in Figure 3(a) and (b)). These results indicate that the temperature and dwell time do not have an apparent effect on grain growth of the Ti$_3$AlC$_2$ synthesized with a salt/precursor materials ratio of 10:1 in the temperature range 950–1000°C dwell for 2–5 h.

In order to confirm that small particle size would lead to faster conversion of Ti$_3$AlC$_2$ to its 2-D Ti$_3$C$_2$ counterpart, the Ti$_3$AlC$_2$ precursor powder, shown in Figure 3(a), was etched in 40% HF at 60°C for 2 h. XRD patterns of Ti$_3$AlC$_2$ powder before (A) and after (B) etching in 40% HF at 60°C for 2 h are shown in Figure 3(b). SEM image and typical accordion-like morphology of the obtained product are also shown in Figure 3(c) and (d), respectively. In addition, although some nano-crystals of Ti$_3$AlC$_2$ are slightly attached together before HF etching as shown in Figure 3(a), single crystal of Ti$_3$C$_2$ is obtained after HF etching as shown in Figure 3(c), which may be due to the grain boundary corrosion during HF etching. These results indicate that nanosized Ti$_3$C$_2$ MXene is prepared by etching Ti$_3$AlC$_2$ precursor in 40% HF at 60°C for 2 h. However, it is reported that at least 24 h is needed for Ti$_3$AlC$_2$ powders passed through a 325-mesh screen (particle size < 45 μm) in 49% HF solution at 60°C to prepare Ti$_3$C$_2$ MXene [18]. Therefore, the obtained nanosized Ti$_3$AlC$_2$ powder is much easier to be etched by HF solution in a short period of time at same conditions. The present result is in agreement with the result reported that smaller particle sizes of the Ti$_3$AlC$_2$ can effectively reduce the required etching duration and/or HF concentration [17].

Figure 4 displays the representative microstructure of Ti$_3$AlC$_2$ nanoparticles obtained from 3Ti/Al/2C precursor materials in NaCl–KCl molten salt with a salt/precursor materials ratio of 10:1 at 1000°C for 2 h. The result indicates that particle size of Ti$_3$AlC$_2$ is $\sim$ 100 nm as shown in Figure 4(a). The inset of Figure 4(a) shows the Tyndall scattering effect for the suspension of Ti$_3$AlC$_2$ nanoparticles in deionized water, which suggests that the Ti$_3$AlC$_2$ nanoparticle was a colloidal solution with high hydrophilicity and dispersibility. Additionally, TEM and HRTEM images of fine-grained Ti$_3$AlC$_2$ nanoparticle with typical layer structure are also displayed in Figure 4(b) and (c). The obvious lattice fringes reveal that the Ti$_3$AlC$_2$ powder is fine-grained. The layered atomic stacking on the surface of the obtained Ti$_3$AlC$_2$ powder can also be clearly identified by TEM and HRTEM images as shown in Figure 4(d) and (e), respectively. Furthermore, A SAED pattern of Ti$_3$AlC$_2$ along the [01̅0̅] zone axis is also displayed in Figure 4(f), which further confirms that the Ti$_3$AlC$_2$ powder is synthesized. In fact, as far as we know, it is first time that nanosized Ti$_3$AlC$_2$ powder has been synthesized, and the obtained nanosized Ti$_3$AlC$_2$ powder is more easily etched by HF solution in a short period of time at similar conditions [17,29].

4. Conclusions

A simple, high efficiency and relatively low-temperature process for preparation of nanosized Ti$_3$AlC$_2$ powder has been developed by using Ti, Al, and C elemental powders as precursor materials without ball milling in NaCl–KCl molten salt. It is more conducive to the synthesis of Ti$_3$AlC$_2$ at higher mass ratio of the salt to precursor materials and particle size of the Ti$_3$AlC$_2$ powder dramatically decreases with increasing mass ratio of the salt to precursor materials. The homogenous nanosized Ti$_3$AlC$_2$ powder is successfully synthesized at 950°C for 5 h or 1000°C for 2 h with a salt/precursor materials ratio of 10:1. In addition, the obtained nanosized Ti$_3$AlC$_2$ powder is characterized by high crystallinity and has high hydrophilicity, therefore nanosized Ti$_3$C$_2$ MXene is also easier to be prepared by etching the fine-grained Ti$_3$AlC$_2$ precursor in 40% HF solution at 60°C for 2 h. In addition, due to the highly defined morphology of Ti$_3$C$_2$, the application of Ti$_3$C$_2$ as a promising electrode material in supercapacitors will be explored in our future work.
Disclosure statement
No potential conflict of interest was reported by the authors.

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