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ORIGINAL REPORT

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A simple method for the synthesis of nanosized Ti_3AlC_2 powder in NaCl–KCl molten salt

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ABSTRACT

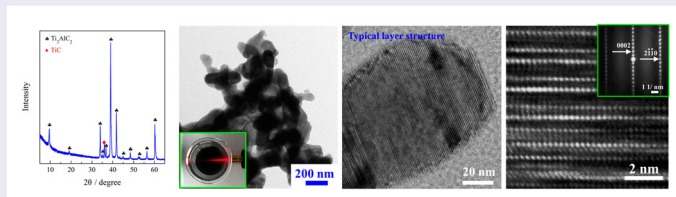
Herein we report, a simple novel method to synthesize nanosized Ti_3AlC_2 powder from Ti, Al, and C powders in NaCl–KCl molten salt. It is more conducive to the formation of Ti_3AlC_2 at higher salt/precursor materials ratio and particle size of Ti_3AlC_2 powder dramatically decreases with increasing mass ratio of the salt to precursor materials. Fine-grained Ti_3AlC_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_3C_2 MXene is also prepared by etching fine-grained Ti_3AlC_2 precursor in HF solution at 60°C for 2 h.

ARTICLE HISTORY

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KEYWORDS

Ternary carbide; Ti_3AlC_2 ; nanosized powder; molten salt; microstructure



IMPACT STATEMENT

It is the first time that nanosized ternary carbide Ti_3AlC_2 powder has been synthesized by a simple, high efficiency and relatively low-temperature process.

1. Introduction

Titanium aluminum carbide, Ti_3AlC_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_3AlC_2 a potential material for various functional and structural applications.

More importantly, Ti_3AlC_2 is also a precursor material for preparation of Ti_3C_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- and K-ion batteries [6–9], supercapacitors [10], and catalysts

[11] due to its high conductivity and hydrophilicity. Therefore, the synthesis of Ti_3AlC_2 powder is becoming increasingly important.

Since Ti_3AlC_2 was firstly synthesized by sintering cold-compacted powder mixtures of Ti, TiAl, Al_4C_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_3AlC_2 powders in the past two decades [15]. However, the particle size of the prepared Ti_3AlC_2 powder ranges from a few to dozens of micron. Meanwhile, it is reported that the initial particle size of Ti_3AlC_2 powder has a decisive influence on kinetics of the selective extraction of Al from Ti_3AlC_2 . In other words, decreasing the Ti_3AlC_2 particle size would lead to faster conversion of Ti_3AlC_2 to its 2-D Ti_3C_2 counterpart [16, 17]. For example, it is reported that at least 24 h is needed for etching Al from Ti_3AlC_2 powders passed through a 325-mesh

screen in 49% HF solution at 60°C to prepare 2-D Ti_3C_2 [18]. Therefore, it is necessary to develop a novel process to synthesize fine-grained Ti_3AlC_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_3SiC_2 and Cr_2AlC 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_3AlC_2 powder or explore a novel process to synthesize submicron or nano-sized Ti_3AlC_2 grains to facilitate faster conversion of Ti_3AlC_2 to its 2-D Ti_3C_2 counterpart. The objective of this work is to report on the synthesis of nano-sized Ti_3AlC_2 powder by molten salt method at a relatively low temperature to obtain a faster conversion of Ti_3AlC_2 to its 2-D Ti_3C_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 μm , purity > 99.8%), Al (0.23 g, particle size < 100 μm , 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 ($\sim 30 \text{ mL} \cdot \text{min}^{-1}$, 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 $K\alpha$ 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

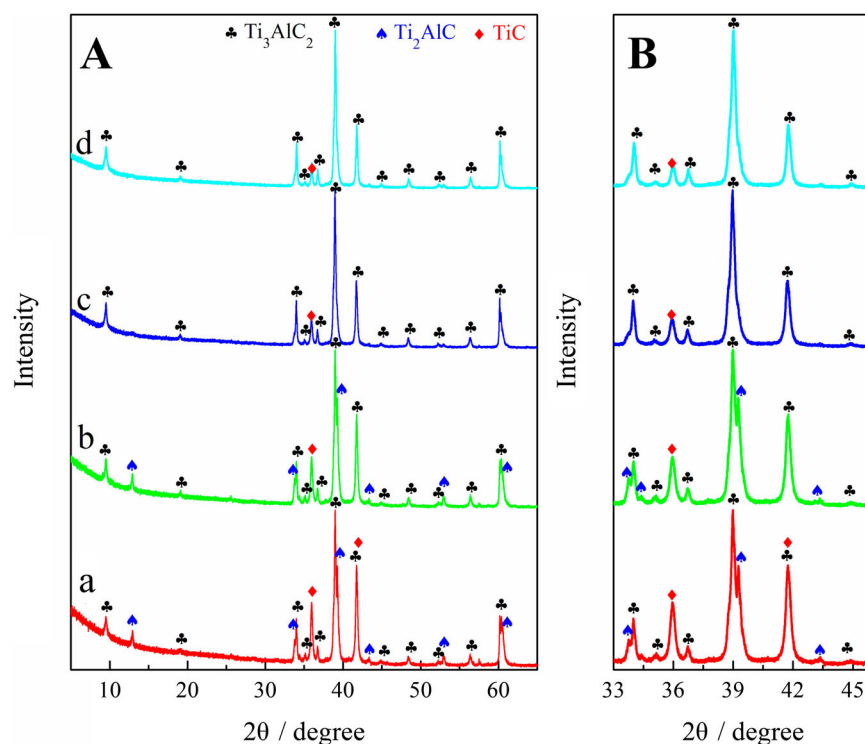


Figure 1. XRD patterns (A) and the detailed XRD patterns (B) of samples synthesized from 3Ti/Al/2C precursor powders in NaCl–KCl molten salt at different salt/precursor materials ratio at 950°C for 5 h (a) 1:1, (b) 3:1, (c) 6:1, (d) 10:1.

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 Ti_3AlC_2 (phase a), (002) peak of Ti_2AlC (phase b)

and (111) peak of TiC (phase c) were measured, respectively. Therefore, the weight percent of Ti_3AlC_2 , Ti_2AlC and TiC is calculated by Equations (1), (2), and (3), respectively, [24]:

$$\omega_a = \frac{I_a}{I_a + 0.220I_b + 0.084I_c}, \quad (1)$$

$$\omega_b = \frac{I_b}{4.545I_a + I_b + 0.382I_c}, \quad (2)$$

$$\omega_c = \frac{I_c}{11.905I_a + 2.619I_b + I_c}. \quad (3)$$

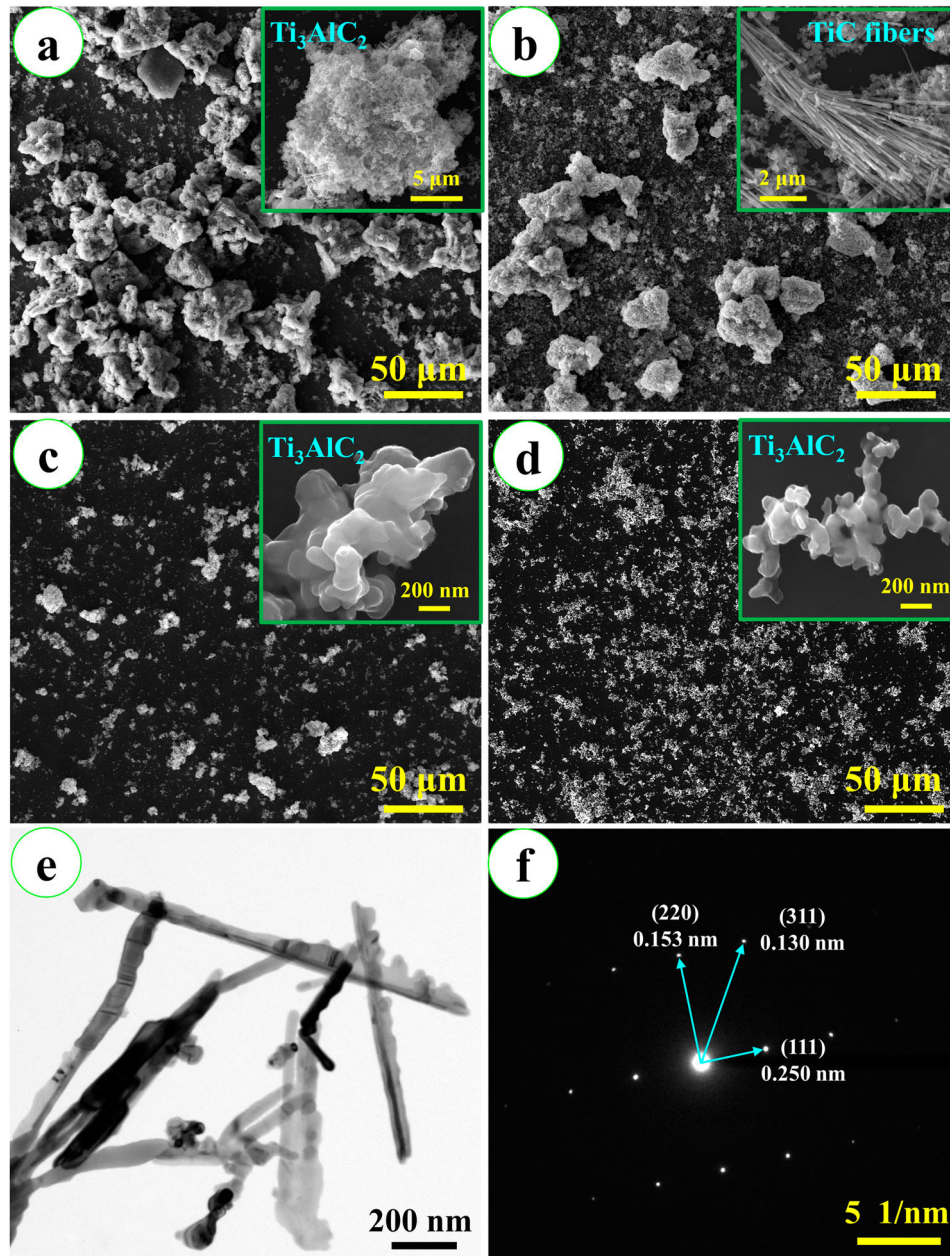


Figure 2. SEM images of samples synthesized from 3Ti/Al/2C precursor powders in NaCl–KCl molten salt at different salt/precursor materials ratio at 950°C for 5 h (a) 1:1, (b) 3:1, (c) 6:1, (d) 10:1, the corresponding insets show higher magnification micrograph of Ti_3AlC_2 particles and TiC fibers. (e) TEM image and (f) the corresponding SAED pattern of the TiC fiber in Figure 2(b).

The result shows that the desired Ti_3AlC_2 (70.1%) besides TiC (18.4%) and Ti_2AlC (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 Ti_2AlC phases reduces while the desired Ti_3AlC_2 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 Ti_3AlC_2 formation. When the mass ratio of the salt to precursor materials increases to 10:1, the desired Ti_3AlC_2 (96.7%) and a few TiC (3.3%) are obtained as shown in diffractogram d. These indicate that Ti_3AlC_2 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 Ti_3AlC_2 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 Ti_3AlC_2 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 Ti_3AlC_2 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 Ti_3Al (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 Ti_3AlC_2 powder is obtained by the reaction of the dispersed TiC , Ti_3Al (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

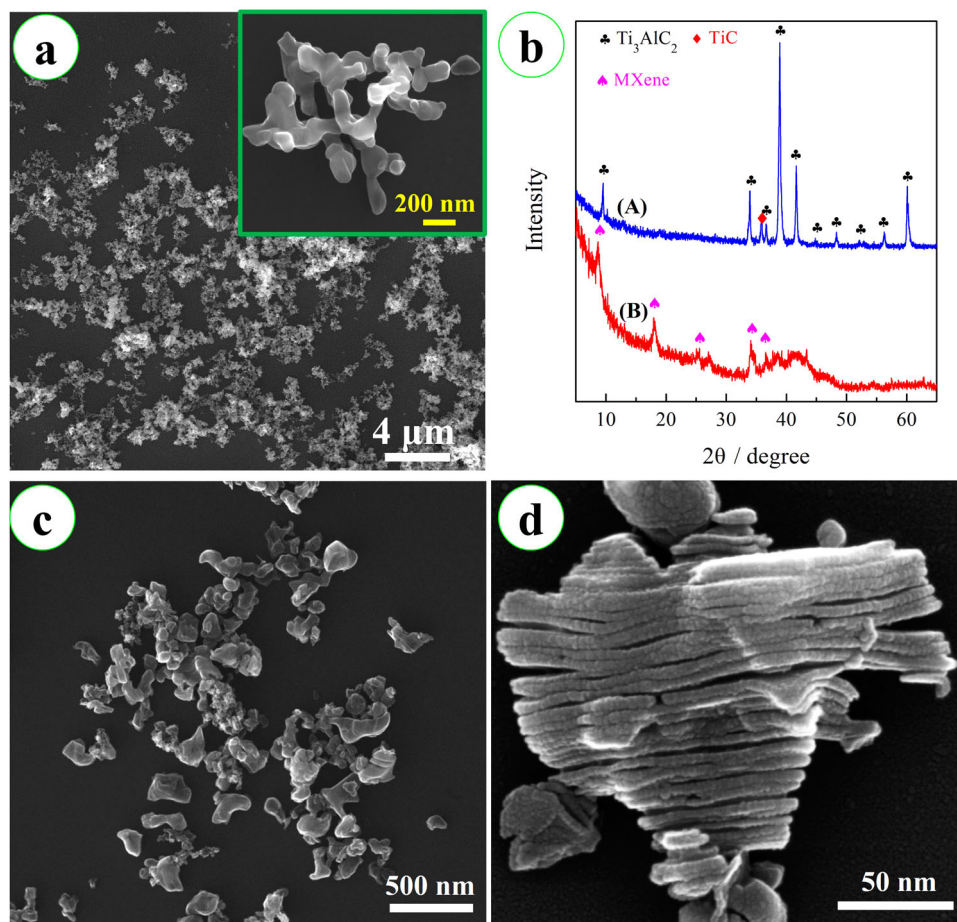


Figure 3. (a) SEM image of Ti_3AlC_2 powder obtained from 3Ti/Al/2C precursor powders in NaCl–KCl molten salt with a salt/precursor materials ratio of 10:1 at 1000°C for 2 h, the inset shows higher magnification micrograph of Ti_3AlC_2 particles; (b) XRD patterns of Ti_3AlC_2 powder before (A) and after (B) 40% HF etching at 60°C for 2 h; (c) SEM and (d) Higher magnification SEM images of Ti_3AlC_2 powder after 40% HF etching at 60°C for 2 h.

Ti_3AlC_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

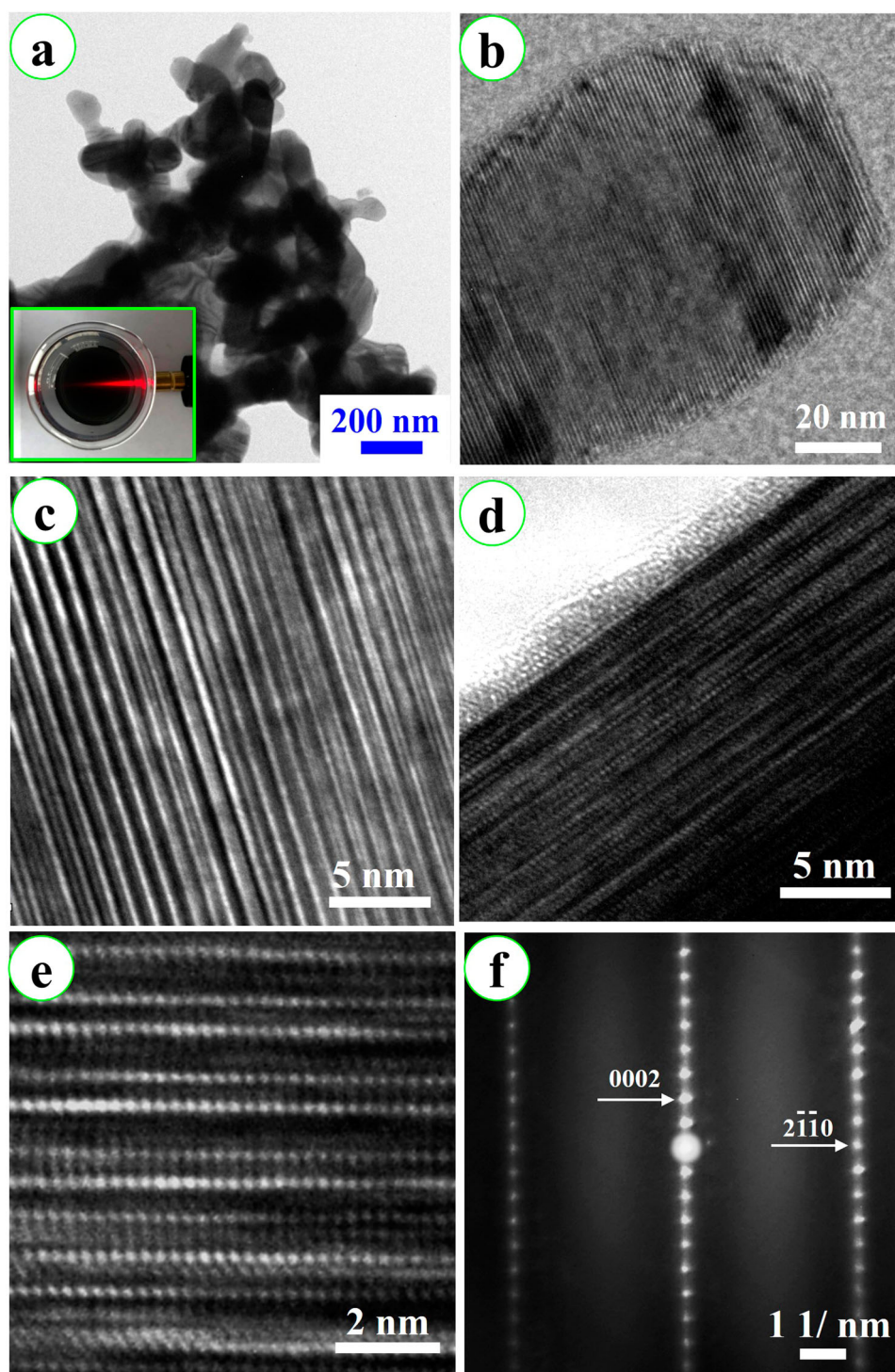


Figure 4. (a) TEM image of Ti_3AlC_2 powder obtained from 3Ti/Al/2C precursor materials in NaCl–KCl molten salt with a salt/precursor materials ratio of 10:1 at 1000°C for 2 h, the inset shows Tyndall scattering effect for the suspension of Ti_3AlC_2 nanoparticles in deionized water; (b) TEM and (c) HRTEM images of the typical layer structure on the cross-section of a fine-grained Ti_3AlC_2 particle; (d) TEM and (e) HRTEM images of the layered atomic stacking on the surface of a fine-grained Ti_3AlC_2 particle; (f) A SAED pattern of Ti_3AlC_2 along the $[01\bar{1}0]$ zone axis.

ratio of 1:1 and 3:1. This is in agreement with XRD results shown in Figure 1. Additionally, although Ti_3AlC_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_3AlC_2 are sintered together and they cannot be separated as shown in insets of Figure 2(a) and (c). However, Ti_3AlC_2 powder with a mean particle size of ~ 100 nm is successfully synthesized at 950°C for 5 h when the mass ratio of the salt to $3\text{Ti}/\text{Al}/2\text{C}$ 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_3AlC_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_3AlC_2 grains with a size of 5–10 and $5\text{ }\mu\text{m}$ were synthesized, respectively.

In order to decrease the synthesis time, the NaCl-KCl salt and $3\text{Ti}/\text{Al}/2\text{C}$ 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_3AlC_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_3AlC_2 has also been successfully synthesized with a salt/precursor materials ratio of 10:1 at 1000°C for 2 h. Additionally, Ti_3AlC_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_3AlC_2 synthesized with a salt/precursor materials ratio of 10:1 in the temperature range $950\text{--}1000^\circ\text{C}$ dwell for 2–5 h.

In order to confirm that small particle size would lead to faster conversion of Ti_3AlC_2 to its 2-D Ti_3C_2 counterpart, the Ti_3AlC_2 precursor powder, shown in Figure 3(a), was etched in 40% HF at 60°C for 2 h. XRD patterns of Ti_3AlC_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_3AlC_2 are slightly attached together before HF etching as shown in Figure 3(a), single crystal of Ti_3C_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_3C_2 MXene is prepared by etching Ti_3AlC_2 precursor in 40% HF at 60°C for 2 h. However, it is reported that at least 24 h is needed for Ti_3AlC_2 powders passed through a 325-mesh screen (particle size $< 45\text{ }\mu\text{m}$) in 49% HF solution at 60°C to prepare Ti_3C_2 MXene [18]. Therefore, the obtained nanosized Ti_3AlC_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_3AlC_2 can effectively reduce the required etching duration and/or HF concentration [17].

Figure 4 displays the representative microstructure of Ti_3AlC_2 nanoparticles obtained from $3\text{Ti}/\text{Al}/2\text{C}$ 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_3AlC_2 is ~ 100 nm as shown in Figure 4(a). The inset of Figure 4(a) shows the Tyndall scattering effect for the suspension of Ti_3AlC_2 nanoparticles in deionized water, which suggests that the Ti_3AlC_2 nanoparticle was a colloidal solution with high hydrophilicity and dispersibility. Additionally, TEM and HRTEM images of fine-grained Ti_3AlC_2 nanoparticle with typical layer structure are also displayed in Figure 4(b) and (c). The obvious lattice fringes reveal that the Ti_3AlC_2 powder is fine-grained. The layered atomic stacking on the surface of the obtained Ti_3AlC_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_3AlC_2 along the $[01\bar{1}0]$ zone axis is also displayed in Figure 4(f), which further confirms that the Ti_3AlC_2 powder is synthesized. In fact, as far as we know, it is first time that nanosized Ti_3AlC_2 powder has been synthesized, and the obtained nanosized Ti_3AlC_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_3AlC_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_3AlC_2 at higher mass ratio of the salt to precursor materials and particle size of the Ti_3AlC_2 powder dramatically decreases with increasing mass ratio of the salt to precursor materials. The homogenous nanosized Ti_3AlC_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_3AlC_2 powder is characterized by high crystallinity and has high hydrophilicity, therefore nanosized Ti_3C_2 MXene is also easier to be prepared by etching the fine-grained Ti_3AlC_2 precursor in 40% HF solution at 60°C for 2 h. In addition, due to the highly defined morphology of Ti_3C_2 , the application of Ti_3C_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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