

On the Synthesis of Low-Cost, Titanium-Based MXenes

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Abstract

Herein we report methods to synthesize two MAX phases, Ti_2AlC and Ti_3AlC_2 , starting with rutile (TiO_2), graphite and aluminum powders as raw materials. Adjusting the initial ratios of the raw materials led to the synthesis of multi-phase mixtures containing predominantly $Ti_2AlC-Al_2O_3$ or $Ti_3AlC_2-Al_2O_3$. Free-standing Ti_2CT_x and $Ti_3C_2T_x$ MXene films were successfully produced by etching the powders in a solution of hydrochloric acid with pre-dissolved lithium fluoride followed by sonication in water to produce colloidal suspensions of atomically thin MXene flakes. The $Ti_3C_2T_x$ films produced from the lower-cost precursors retained the high electrical conductivity previously reported for this material. Since starting with rutile instead of Ti metal powders reduces the cost of the raw materials by a factor of about 2.6, this new, scalable approach to MXene synthesis is more economical.

Keywords: MAX phase, MXene, ceramics, 2D materials, nanomaterials

I. Introduction

Recently, we discovered a new family of two-dimensional (2D) early transition metal carbides and carbonitrides, that we labeled MXene^{1,2}, because they are derived from the MAX phases. The latter's chemistry is $M_{n+1}AX_n$, where M is an early transition metal, A is an A-group element (mostly groups 13 and 14 elements), X is carbon and/or nitrogen, and $n = 1-3$ ³. The exfoliation process is carried out by selectively etching the A layers with hydrofluoric acid (HF)^{1,2}, or mixtures of lithium fluoride (LiF) and hydrochloric acid (HCl)^{4,5}. The end result are 2D layers of $M_{n+1}X_nT_x$, where T represents surface functionalization by -OH, -F and/or -O groups⁶. These new phases were named MXene to emphasize their MAX phase origin, their 2D graphene-like morphology, and their high electrical conductivities^{7,8}. However, unlike graphene, MXenes are hydrophilic, and are being explored for a host of applications, such as supercapacitors^{4,9,10}, anodes in secondary metal-ion batteries¹¹⁻¹⁴, transparent conductive coatings^{7,15,16}, removal of toxic metal ions from water^{17,18}, and as reinforcements in polymers¹⁹.

Generally, MAX phase powders are made starting with transition metal powders. For example, Ti_2AlC powders – that are fairly expensive – are made starting with Ti powders, and are sold commercially under the trade name MAXTHAL. One obvious strategy to reduce the cost of these powders is to start with TiO_2 instead of Ti. Unfortunately, it is impossible to obtain pure MAX phase powders starting with TiO_2 . Instead, depending on the starting compositions, mixtures of MAX phases, alumina (Al_2O_3) and/or titanium carbide (TiC) are typical-

ly obtained. There have been a few reports in the literature, where TiO_2 -Al-C powder mixtures were used to synthesize MAX-TiC- Al_2O_3 mixtures²⁰⁻²². In such a system, the Al reduces the TiO_2 to form Al_2O_3 ; the Ti then reacts with the C to form TiC and/or the MAX phase. For example, Chen *et al.* obtained Ti_3AlC_2 -TiC- Al_2O_3 multi-phase mixtures by combustion synthesis, during which a compacted pellet composed of TiO_2 , Al and C, in a 3:5:2 molar ratio, was heated to 1500 °C at a rate of 10 K/min and held at temperature for 0.5 h²⁰. Hendaoui *et al.* prepared Ti_2AlC - Ti_3AlC_2 - Al_2O_3 mixtures with aluminothermic reduction of TiO_2 in the presence of C²¹. More recently, Yeh *et al.* synthesized *in situ* Ti_3AlC_2/Al_2O_3 and Ti_2AlC/Al_2O_3 composites by incorporating the thermite reaction of Al with TiO_2 into the SHS system of Ti, Al, and carbon black²³. Even more recently, Cuskelly *et al.* used the same approach to make a large number of MAX phase/ Al_2O_3 composites²².

As noted above, to date, Ti-based MXenes have been synthesized by etching Ti_3AlC_2 (312 composition) and Ti_2AlC (211 composition) powders using HF, aqueous mixtures of LiF and HCl, or ammonium bifluoride. Currently, commercially available Ti_2AlC powders are quite expensive, rendering the corresponding MXenes costly for some bulk applications such as reinforcements in polymer composites. In order to reduce the cost, herein we outline a method for synthesizing MAX-based, multi-phase mixtures, based on the reduction of rutile, TiO_2 using Al as the reducing agent. The product is then converted to pure MXenes by first etching and then separating the MXenes from other unwanted phases.

In short, it is impossible to make Ti_3AlC_2 or Ti_2AlC powders from TiO_2 without the presence of other ex-

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traneous phases such as Al_2O_3 and TiC . While the latter phases are undesirable when fabricating MAX phases, they pose much less of a problem if the end result is to synthesize MXenes, since these impurity phases can be readily separated from the MXenes when LiF/HCl is the etchant, together with a mild sonication treatment. The purpose of this work is to synthesize Ti_3AlC_2 and Ti_2AlC -containing powders starting with TiO_2 , exfoliate them into Ti-based MXenes, and compare the properties of free-standing MXene films derived from the composite MAX and pure MAX powders.

II. Materials and Methods

To fabricate the MAX-containing powders, powders of TiO_2 (Alfa Aesar, 99.5 %, 45 μm), aluminum (Alfa Aesar, 99.5 %, < 44 μm), and graphite (Alfa Aesar, 99 %, < 74 μm) were mixed in the following stoichiometric ratios with the goal of synthesizing Ti_3AlC_2 and Ti_2AlC , respectively, according to the following reactions:



The powder mixtures – henceforth referred to as 3–5–2 and 6–11–3 were ball-milled for 10 h, heated at 10 K/min, under flowing argon, Ar, in a tube furnace up to 1500 °C and held at temperature for 2 h before furnace cooling. Preliminary results indicated that TiC was also produced. In order to decrease the TiC content, the following mixtures were also heated to 1500 °C for 2 h: 3 TiO_2 -5.1Al-1.9C and 3 TiO_2 -5.1Al-1.8C, henceforth referred to as 3–5–1.9 and 3–5–1.8, respectively.

For comparison, predominantly single-phase Ti_2AlC and Ti_3AlC_2 were also synthesized. The former was prepared by ball-milling titanium (Alfa Aesar, 99 %), aluminum (Alfa Aesar, 99.5 %), and graphite (Alfa Aesar, 99 %) powders in a 2.0 : 1.1 : 1.0 molar ratio and heated at a rate 10 K/min, under flowing Ar, in a tube furnace to 1400 °C and held at that temperature for 4 h. Ti_3AlC_2 was prepared according to previous reports⁴.

The sintered compacts were first broken up using a hammer, and then converted to powders using a TiN-coated milling bit. The resulting products were sieved through a 400 mesh sieve to produce a powder with a particle size < 38 μm , respectively.

To convert the MAX-containing precursors to MXenes, 1 g of the sieved 6–11–2.7, 6–12.3–2.7, and pure Ti_3AlC_2 powders was slowly added into a solution of 10 mL of 12 M hydrochloric acid, HCl (Technical Grade, Fisher Scientific, Fair Lawn, NJ, USA), with 1 g of LiF pre-dissolved (98.5 %, Alfa Aesar, Ward Hill, MA, USA) and magnetically stirred at 35 °C for 24 h. In the case of pure Ti_2AlC , 1 g of the sieved powders were added to 10 mL of 6 M HCl with 0.66 g of LiF pre-dissolved instead. Afterwards the etched powder mixtures were washed three times with 6 M HCl to remove residual LiF salts. Next the mixtures were washed with distilled water, centrifuged (3500 rpm x 2 min.), and the supernatant was decanted. This process was repeated five times until the supernatant reached a pH of approximately 6. In order to further separate the MXenes from the other extraneous phases present,

the above products were shaken in 50 mL distilled water, sonicated in an ice-cooled bath sonicator for 0.5 h under a constant bubbling of Ar gas through the suspension, and followed by centrifugation at 3500 rpm for 1 h. Given that the extraneous phases do not form colloidal solutions, but the MXenes do, the supernatant resulting from sonication and centrifugation is a solution containing only delaminated MXene flakes. These colloidal MXene suspensions were subsequently vacuum-filtered onto a nanoporous polypropylene (PP) membrane (Celgard 3501, Celgard LLC, Charlotte, NC, USA) to fabricate free-standing MXene films. The resulting films were easily be peeled off from the PP membranes for further analysis.

The MAX-based powders and MXene films were characterized with a powder x-ray diffractometer (Rigaku SmartLab, Tokyo, Japan) using CuK_α radiation ($\lambda = 1.54$ Å). Samples were examined on a scanning electron microscope (SEM, Carl Zeiss Supra 50VP) equipped with an energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments) to obtain cross-sectional micrographs of the free-standing films and measure the chemical compositions of various samples.

Electrical resistivity measurements were performed on free-standing MXene films in a nitrogen-filled glove-box (< 500 ppm O_2) using a Keithley 2634B SYSTEM Sourcemeter in a linear 4-point probe configuration with a probe spacing of 2.3 mm. The reported resistivity values and error indicate the arithmetic mean and standard deviations, respectively, of five measurements.

III. Results and Discussion

After heating the 3–5–2 mixture to 1500 °C for 1 h, the XRD patterns (Fig. 1a.i) evidenced peaks for Ti_3AlC_2 , Al_2O_3 and TiC . When the 3–5–1.9 and 3–5–1.8 compositions were used instead, the TiC content decreased as shown, respectively, in Figs. 1a.ii and 1a.iii. These results are consistent with former work on producing $\text{Ti}_3\text{AlC}_2/\text{TiC}-\text{Al}_2\text{O}_3$ composites starting with TiO_2 , Al, and C powders^{21,22}.

In an attempt to further increase the Ti_3AlC_2 content, a 3–5.5–1.8 mixture was heated to 1500 °C for 1 h. In this case, peaks belonging to Al_3Ti appeared, while those for Ti_3AlC_2 almost disappeared (Fig. 1a.iv). Hence, there is a limit to how much the relative C-content can be reduced, before Al_3Ti is formed at the expense of Ti_3AlC_2 .

Fig. 1b.i shows a typical XRD pattern of the reaction products obtained when a 6–11–3 mixture was heated to 1500 °C for 2 h. In this case, the formed phases are Ti_2AlC , Ti_3AlC_2 and Al_2O_3 . To prepare powders containing a majority of Ti_2AlC or Ti_3AlC_2 , adjustments to the Al and C contents in the raw materials were made. Figs. 1b.ii and 1b.iii show, respectively, the XRD patterns of the reaction products when the starting composition ratios, 6–11–2.7 and 6–12.3–2.7, were heated to 1500 °C and held for 2 and 4 h, respectively. From these results, it is clear that relatively pure $\text{Ti}_2\text{AlC}-\text{Al}_2\text{O}_3$ with some impurities of Ti_3AlC_2 and TiC and $\text{Ti}_3\text{AlC}_2-\text{Al}_2\text{O}_3$ mixtures with some impurities of Ti_2AlC and TiC were synthesized starting with these compositions, respectively. While Rietveld refinement was attempted to quantify the phase composition, a good diffraction pattern could not be calculated based on

these four phases due to the presence of unidentifiable impurities, marked as “?” on Fig. 1b.

At this juncture it is important to note that all compositions, when removed from the furnace, showed clear signs of combustion synthesis, such as a hollowed center surrounded by a sintered, deformed ring. In general, the products of combustion reactions can show compositional variations between different experiments despite identical starting ratios of reactants.

We note in passing that, like Hendaoui *et al.*²¹, we found that decreasing the Al-content was beneficial to the formation of Ti_2AlC , while increasing the Al-content, was beneficial to the formation of Ti_3AlC_2 . These caveats notwithstanding, these powders were, in turn, used as precursors to synthesize their respective MXenes.

Colloidal suspensions obtained after etching and sonicating the 6–11–2.7 and 6–12.3–2.7 mixtures and further diluting them with water are shown in Fig. 2a. Typically, colloidal suspensions with concentrations of 2–3 mg/mL were obtained. Flexible, free-standing films (Fig. 2b–c) were obtained by filtering the colloidal suspensions of the 6–12.3–2.7 mixture. In Fig. 2d, an SEM micrograph of the cross-section of the film shown in Fig. 2b–c shows the dense re-stacking of delaminated MXene flakes during vacuum filtration. MXene films with similar morphology were also obtained from the 6–11–2.7 composite powders.

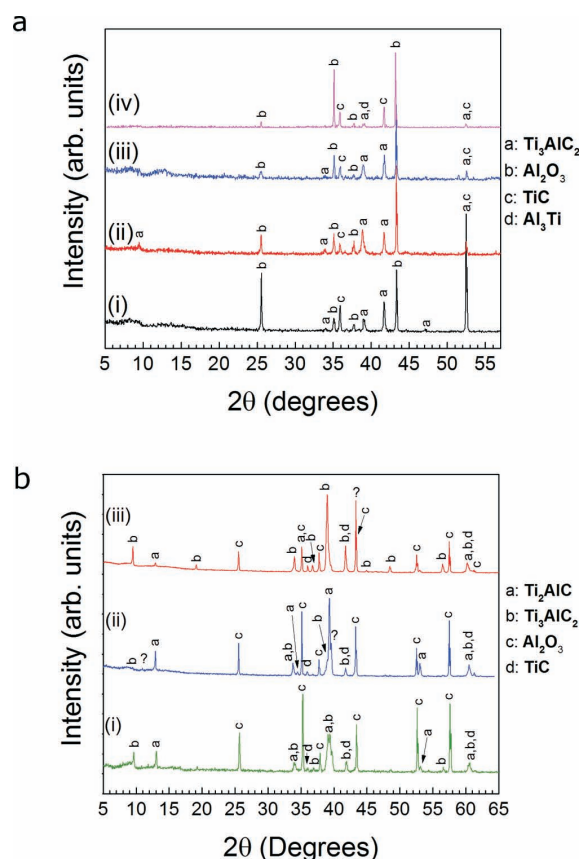


Fig. 1: Powder XRD patterns of (a) mixtures of, (i) $3\text{TiO}_2\text{-}5\text{Al-}2\text{C}$, (ii) $3\text{TiO}_2\text{-}5.1\text{Al-}1.9\text{C}$, (iii) $3\text{TiO}_2\text{-}5.1\text{Al-}1.8\text{C}$ and, (iv) $3\text{TiO}_2\text{-}5.5\text{Al-}1.8\text{C}$ reaction at $1500\text{ }^\circ\text{C}$; and (b) Powder XRD patterns of starting compositions, (i) $6\text{TiO}_2\text{-}11\text{Al-}3\text{C}$, (ii) $6\text{TiO}_2\text{-}11\text{Al-}2.7\text{C}$ and, (iii) $6\text{TiO}_2\text{-}12.3\text{Al-}2.7\text{C}$ after reaction at $1500\text{ }^\circ\text{C}$.

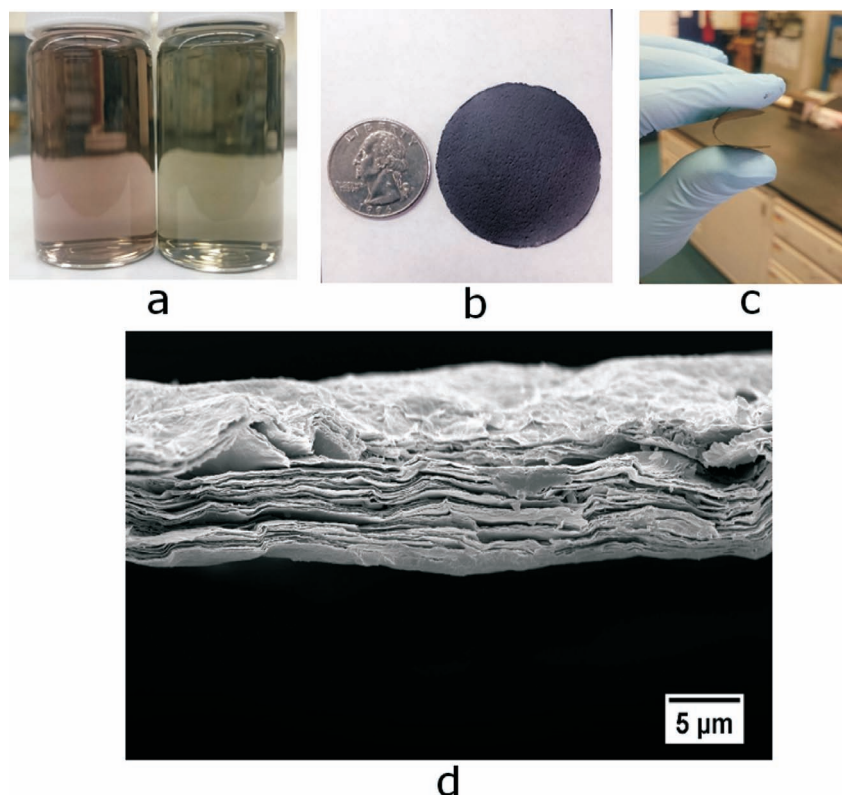


Fig. 2: (a) Diluted suspensions of delaminated MXene starting with the 6–11–2.7 (left) and 6–12.3–2.7 (right) composite powders; (b) free-standing film produced by vacuum filtration of MXene synthesized from the 6–12.3–2.7 precursor; (c) the same film bent to show flexibility; (d) SEM image of a typical $\text{Ti}_3\text{C}_2\text{T}_x$ MXene film's cross-section.

XRD diffractograms of MXene films produced from the 6–11–2.7 and 6–12.3–2.7 powders are shown in Fig. 3a and b, respectively. The characteristic broadening and shifting of the basal {001} peaks to lower angles for both films unambiguously confirms the conversion of MAX phase to MXene. The c -lattice parameters – calculated as two times the d_{002} spacing – of the pure $\text{Ti}_3\text{C}_2\text{T}_x$ films (25.4 Å) and those derived from the 6–12.3–2.7 precursor (26.1 Å) show good agreement. Similarly, good agreement is found between the c -lattice parameters of pure Ti_2CT_x films (23.4 Å) and those derived from 6–11–2.7 precursors (22.0 Å). While these small differences may be attributed to small variations in the amount of water between the MXene layers⁴, the reason for the considerably broader (002) peak of MXenes produced from 6–11–2.7 mixtures is not clear at this time.

The absence of the (110) peaks of Ti_2AlC and Ti_3AlC_2 near 61° for the diffractograms of the free-standing films also confirms that sonication delaminates the MXene flakes into atomically thin sheets, which then have a turbostratic arrangement upon restacking during vacuum filtration. Moreover, the absence of any peaks associated with Al_2O_3 , TiC , or other impurity phases in the 6–11–2.7 and 6–12.3–2.7 precursors, confirm that the sonication and centrifugation process easily separates MXene from these unwanted phases.

The room temperature electrical resistivities of $\text{Ti}_3\text{C}_2\text{T}_x$ films made starting with pure Ti_3AlC_2 powders and those derived from the 6–12.3–2.7 mixture were compared. At $220 \pm 10 \mu\Omega\cdot\text{cm}$ the resistivity of the former was lower than the $380 \pm 100 \mu\Omega\cdot\text{cm}$ of the latter. Thus, the $\text{Ti}_3\text{C}_2\text{T}_x$ films made with the 6–12.3–2.7 low-cost precursors are ~70 % more resistive than films made from pure Ti_3AlC_2 . The reason for the increased resistance is unclear at this time and requires further work. However, when our results are compared to previous results in Table 1, it is clear that our values, including those for films made from the low-cost precursors, fall within the range of what has been published previously^{7,8}. It follows that this new approach to make Ti-based MXenes results in films whose transport properties are not too different from ones made with significantly cleaner precursors.

Using 2015 prices, Cuskelly *et al.*²² estimated that the cost of the elemental reactants needed to produce one ton of Ti_3AlC_2 , is $\approx \$11\,500$. Instead, producing it according to Eq. 1, would cost about \$4 350 per ton. Given that cost is probably the most important driver in whether a material is commercially used or not, this reduction in the cost of raw materials by a factor of 2.6 bodes well for these new 2D materials. Moreover, it is crucial to note that if the MAX phases can be produced by SHS alone, as reported by Yeh *et al.*, then the attendant cost would be further significantly reduced²³. Note however, that to maintain the combustion, Ti powder was added to the starting mixture²³. It follows that a comparison of the cost of heating the powders to 1500°C without Ti – as done in this work – versus combustion at room temperature with some Ti, would have to be carried out to determine which is more economical. Another fruitful area of research would be to pre-heat the powder mixture used herein to temperatures be-

low 1500°C before igniting them. Under those conditions it may be possible to ignite the powders and maintain the combustion, while using no, or smaller, amounts of Ti.

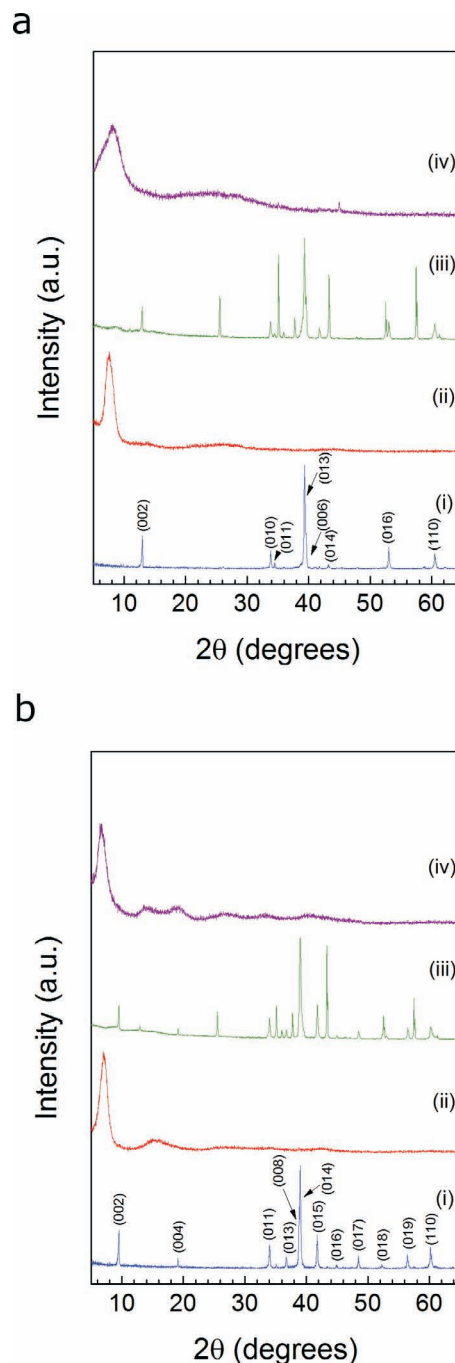


Fig. 3: (a) XRD patterns of, (i) pure Ti_2AlC , (ii) Ti_2C film made from pure Ti_2AlC , (iii) 6–11–2.7 powders and, (iv) film made from 6–11–2.7 powders and, (b) XRD patterns of (i) pure Ti_3AlC_2 , (ii) Ti_3C_2 film made from pure Ti_3AlC_2 , (iii) 6–11–2.7 powders, and (iv) film made from 6–11–2.7 powders.

These comments notwithstanding, it is important to further characterize the MXenes produced with our method in order to confirm that their properties are comparable to those made starting with Ti powders. If the same approach can be used to produce other MAX compositions starting with their oxides, as nicely demonstrated by Cuskelly *et al.*²² quite recently, these powders could again be converted to MXenes at substantially reduced costs.

Table 1: Electrical resistivity of $\text{Ti}_3\text{C}_2\text{T}_x$ synthesized in this work compared to those reported in literature

Sample	Resistivity ($\mu\Omega\cdot\text{cm}$)	Reference
Roll-cast thick film $\text{Ti}_3\text{C}_2\text{T}_x$	667	4
Spin-coated $\text{Ti}_3\text{C}_2\text{T}_x$	152	7
Isolated single flake $\text{Ti}_3\text{C}_2\text{T}_x$	1111	8
Epitaxial thin film $\text{Ti}_3\text{C}_2\text{T}_x$	176	15
Vacuum-filtered film from pure Ti_3AlC_2	220±10	This work
Vacuum-filtered film from 6–12.3–2.7	380±100	This work

Lastly, as noted above, there is a high probability that our powders ignited during processing. The latter is a double-edged sword. On the positive side, it reduces the thermal energy needed to make the powders, rendering them ultimately cheaper to fabricate. On the negative side, unless great care is taken in mixing the powders, and in how they are arranged in the furnace, the surface-to-volume ratio of the powder bed, heating rate, etc., the reproducibility of the final products can vary from batch to batch. It is acknowledged that a detailed study of this issue could have been carried out here, but the results would have had little practical import since every furnace has a different configuration. This is especially true in this case if or when the process is scaled up to an industrial scale. Such considerations have to be tackled during the latter process and are certainly beyond the scope of this paper.

IV. Summary and Conclusions

Powder compacts partially containing Ti_2AlC and Ti_3AlC_2 were successfully synthesized using the aluminothermic reduction of TiO_2 in the presence of C. When the latter powders were immersed in LiF/HCl solution at 35 °C for 24 h, MXene-containing powders were produced. The MXenes were readily separated from other phases present, such as Al_2O_3 and TiC , by simply delaminating the MXenes powders into atomically thin sheets and filtrating the supernatant. Comparable electrical resistivities for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene derived from the lower-cost $\text{Ti}_3\text{AlC}_2/\text{Al}_2\text{O}_3$ precursors versus that made from pure Ti_3AlC_2 were also found. In principle, the methods outlined herein should greatly reduce the cost of producing MXenes.

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