Kinetics of aluminum extraction from Ti$_3$AlC$_2$ in hydrofluoric acid

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** Highlights **
- Exfoliation of Ti$_3$AlC$_2$ by immersion in hydrofluoric acid.
- The exfoliation is a time, temperature and initial particle size dependent process.
- Arch-shaped edge morphology of exfoliated Ti$_3$C$_2$ is reminiscent of graphene.

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** Abstract **
Herein we report on the influence of particle size, time and temperature on the kinetics — quantified by X-ray diffraction — of the selective extraction of Al from the ternary layered transition metal carbide, Ti$_3$AlC$_2$, when powders of the latter are immersed in hydrofluoric acid. Transmission and scanning electron microscopy, energy-dispersive X-ray spectroscopy and thermogravimetric analysis were also used to characterize the resulting powders. Increasing the temperature and immersion times, and decreasing the Ti$_3$AlC$_2$ particle size, led to faster conversion of Ti$_3$AlC$_2$ to its 2-D Ti$_3$C$_2$ counterpart. Arch-shaped edges at the ends of some Ti$_3$C$_2$ layers resembled graphene, corroborating the single-sheet structure of exfoliated Ti$_3$C$_2$. The removal of water and/or OH surface groups from Ti$_3$C$_2$ using drying in vacuum was also attempted.

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1. Introduction

Over the last decade, two-dimensional (2-D) materials have attracted increasing attention due to their unique properties, with potential applications in pseudo- and double-layer capacitors [1], lithium batteries [2–4], and transistors [5,6] among many others. The most studied 2-D material is graphene [7]. Other 2-D layered compounds that have been exfoliated include boron nitride [8], transition metal sulfides [9], oxides and hydroxides [10,11], and zeolites [12].

The MAX phases, a group of ternary carbides and nitrides, are a relatively new class of hexagonal-structure (space group P63/mmc) materials with a general formula M$_{n+1}$AX$_n$ ($n = 1–3$), where M is an early transition metal, A is an A-group (mostly groups 13 and 14) element, and X is C and/or N [13–15]. These phases possess an unusual combination of properties, exhibiting some characteristic of ceramics and others of metals. For example, some show resistance to oxidation and corrosion, high thermal stabilities, and are elastically stiff, but at the same time are readily machinable, thermally and electrically conductive, resistant to thermal shock and ductile at elevated temperatures [13,16,17].

One of the most widely studied MAX phases is Ti$_3$AlC$_2$ [18] which was discovered and first synthesized by Pietzka and Schuster [19]. With respect to the MX bonds, the M–A bonds are relatively weak. It follows that in Ti$_3$AlC$_2$, the Al atoms are the most reactive species and can be readily removed from the MAX structure. We have recently shown that immersing Ti$_3$AlC$_2$ powders in a 50% HF solution at room temperature for 2 h resulted in the complete selective etching of the Al layers according to the following reaction [20]:

$$\text{Ti}_3\text{AlC}_2 + 3\text{HF} = \text{AlF}_3 + 3/2\text{H}_2 + \text{Ti}_3\text{C}_2$$  \hspace{1cm} (1)

We further showed that the exfoliated 2-D Ti$_3$C$_2$ layers are most probably terminated with OH and/or F surface groups according to:

$$\text{Ti}_3\text{C}_2 + 2\text{H}_2\text{O} = \text{Ti}_3\text{C}_2(\text{OH})_2 + \text{H}_2$$  \hspace{1cm} (2)

and possibly...
In that paper, we proposed that Ti$_3$C$_2$ may be a member of a much larger family of 2-D metal carbides and/or nitrides that we labeled "MXenes" to emphasize the removal of the A-group element from MAX and, equally importantly, to highlight the commonality of the resulting 2-D structures to graphene. More recently we showed that to be the case by successfully exfoliating, also in HF, the following MAX and, equally importantly, to highlight the commonality of the resulting suspensions were washed several times (Table 1), the resulting suspensions were washed several times and temperatures, as summarized in Table 1.

**2.2. Synthesis of exfoliated Ti$_3$C$_2$**

Non-sieved Ti$_3$AlC$_2$ powders were immersed in HF solutions for various times and temperatures, as summarized in Table 1.

In order to study the effect of particle size on the exfoliation kinetics, one experiment involved the separation of powders into three fractions using sieves with openings of 38 μm and 53 μm. The fraction that passed through the 53 μm, but was retained by the 38 μm openings — i.e. the average particle size was ≈ 45 μm — was immersed in HF for 2 h at room temperature.

In all cases, after immersion in the solution for predetermined times (Table 1), the resulting suspensions were washed several times using deionized water and centrifuged to separate the powders. The latter were then dried under mechanical vacuum at 100 °C for 22 h. The pure, dried samples were placed in capped glass vials and stored under ambient conditions.

**3. Results and Discussion**

**3.1. Exfoliation kinetics**

The diffractograms of the treated powders (Fig. 1a) show three peaks at 2θ ≈ 39 ° that corresponds to the (104) peak of Ti$_3$AlC$_2$. This peak diminishes with increasing temperature and time, disappearing altogether above 50 °C and after 15 h, respectively, indicating the etching of the Al from the structure [20]. Concomitantly, the intensity of the (002) diffraction peak at 2θ = 9°—which corresponds to the basal planes of the 2-D Ti$_3$C$_2$-based layers, most likely terminated with OH groups—increases. The fact that this peak shifts to lower angles, compared to the (002) peak of non-exfoliated Ti$_3$AlC$_2$ is evidence for the expansion along [0001], as the Al is replaced by OH or F [20]. Because of the relatively wide particle size distribution range (from hundreds of nano- up to tens of micro-meters with a ~75 wt.% fraction for particles within the 1–20 μm size range) and diffusion-limited etching, the expansion was not uniform. Consequently, the position of the (002) MXene peaks varied slightly from sample to sample resulting in different values of c-lattice parameters (Table 1).

A calibration curve (Fig. 2b) was plotted using the XRD results (Fig. 2a) of samples with known ratios of fully reacted to unreacted...
Ti$_3$AlC$_2$. Polynomial fitting of the calibration curve (shown as solid line in Fig. 2b) yields:

$$y = \frac{1}{C_0} x^{0.013} \cdot \frac{1}{2} x^2;$$

where $y$ is the weight fraction of Ti$_3$C$_2$ and $x$ is the intensity ratio of the Ti$_3$AlC$_2$ (104) peak to the Ti$_3$C$_2$(OH)$_2$ (002) peak. Using this calibration curve, we determined $y$ for each run shown in Fig. 1 and plotted it as functions of temperature and time in Fig. 3a. Here again, clearly, the degree of exfoliation increases with increasing times and temperature. At temperatures above 50°C, complete exfoliation of Ti$_3$AlC$_2$ with HF occurs after 2 h. At room temperature (RT), the process can take as much as 15 h.

The powders with particle sizes larger than 38 µm but less than 53 µm were completely exfoliated by stirring in a 50% aqueous HF at RT for 2 h. However, these conditions were insufficient to exfoliate particles larger than 53 µm. Assuming the reaction is diffusion controlled, this implies a diffusion coefficient of $\approx 10^{-13}$ m$^2$ s$^{-1}$.

3.2. Resistivity results

Changes in the sheet resistivities of cold pressed MXene discs as a function of etching time are shown in Fig. 3b. A dramatic increase of resistivity was observed during the first 2 h of reaction. This is due to the replacement of the Al layers, that are metallically bonded, with more insulating oxygen or OH ligands, which are presumably covalently bonded to the Ti$_3$C$_2$ layers and interact only via weak hydrogen and/or van der Waals bonds. Following the sudden increase, no large changes are observed for the next 8 h. However after 10 h of etching, another increase in resistivity is observed. These results are not too surprising since MXenes are expected to have good in-plane, but poor out of plane, conductivities. The results

![Fig. 1. Diffractograms obtained after etching Ti$_3$AlC$_2$ powders a 50% HF solution as a function of (a) temperature after 2 h and (b) time at room temperature. The diffractograms at the bottom of each panel show the XRD patterns of Ti$_3$C$_2$(OH)$_2$ (black lines) and Ti$_3$AlC$_2$ (red lines) previously predicted by Density functional theory (DFT)-based geometry optimizations [from Ref. [20]]; XRD pattern of TiOF$_2$ (PDF No. 08-0060). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 2. (a) Diffractograms of cold pressed mixtures of Ti$_3$AlC$_2$/Ti$_3$C$_2$ of known ratios used to generate the calibration curve shown in (b). Percentage values indicate weight fraction of Ti$_3$C$_2$ in the powder mixture; (b) Ti$_3$C$_2$ weight fraction vs. the (104) peak for Ti$_3$AlC$_2$/002) peak of Ti$_3$C$_2$, intensity ratio. These results were used to generate the results shown in Fig. 3a.](image2)
also suggest that a MXene percolation threshold was reached after the first 2 h of etching. Based on the results of Fig. 3a, 2 h of etching corresponds to \( \sim 60 \) wt.\% of \( \text{Ti}_3\text{C}_2 \). The reason for the second increase in resistivity is not entirely clear, but is probably caused by the slow oxidation of the MXene powder as it resides longer in the etching solution. Another possible reason is the formation of an insulating titanium oxyfluoride (\( \text{TiOF}_2 \)) phase. The presence of this phase is confirmed by the presence of an XRD peak at 23.6° corresponding to a major (100) peak of \( \text{TiOF}_2 \) (Fig. 2b). These comments notwithstanding, it is important to note that these results are preliminary and more work is needed before a good understanding of the effects of etching on transport properties is reached.

### 3.3. Microstructural study

Fig. 4a shows a typical SEM image of an as-received \( \text{Ti}_3\text{AlC}_2 \) particle. After treatment, the resulting particles are clearly exfoliated (Fig. 4b). At this stage, the \( \text{Ti}_3\text{C}_2 \) layers are presumably joined together only by weak van der Waals or hydrogen forces. This was indirectly confirmed by recent Li intercalation studies [22].

TEM micrographs of sonicated samples confirmed that it was possible to separate the 2-D \( \text{Ti}_3\text{C}_2 \) layers into electron transparent sheets (Fig. 5a). Interestingly, the TEM images also showed evidence for nano-arches at the edges of the exfoliated \( \text{Ti}_3\text{C}_2 \) planes (Fig. 5b and c). Similar folding of single graphitic layers which result in the formation of zipped edges — that are quite similar to those shown here — has been previously reported [23,24]. The mechanism of edge termination was explained by the van der Waals cohesion of the graphene sheets [25]. Fig. 5c shows the formation of separated domains of \( \text{Ti}_3\text{C}_2 \) sheets, presumably due to capillary and electrostatic forces arising after the removal of Al layer and the drying of the samples. A schematic for how this process could occur is shown in Fig. 5d.

### 3.4. Thermogravimetric analysis

According to reaction 1, the theoretical weight loss after exfoliation should be \( \approx 13.9 \) wt. %. However, if reaction 2 is operative, then a 3.6% overall weight gain is expected. Experimentally there was roughly no weight change (yield \( \approx 100\% \)) after reaction with HF. The actual value is most probably higher because of material loss during washing and drying of the powders. This is consistent with the formation of \( \text{Ti}_3\text{C}_2(\text{OH})_2 \) and consistent with the conclusion that the overall reaction yield is high [21]. The latter, in turn, implies that little or no \( \text{Ti}_3\text{C}_2(\text{OH})_2 \) dissolves in the HF. We note, in passing, that this is not always the case; for example, when \( \text{Ti}_2\text{AlC} \) powders are immersed in 50% HF for extended periods they readily dissolve [21]. This is not the case, however, at lower HF concentrations. It follows that to produce \( \text{Ti}_2\text{C} \)-based MXenes, a 10-h treatment in 10% HF is required to dissolve the Al from \( \text{Ti}_2\text{AlC} \), without dissolving the \( \text{Ti}_2\text{C} \) layers.

Fig. 6a shows the weight losses of exfoliated powders that were previously dried in air at room temperature for 72 h. Fig. 6b shows the same for powders held under mechanical vacuum at 120 °C for 24 h. The total weight loss for the former was 7.4%, with respect to the original sample weight; for the latter it was 4.5%. In both cases,
the weight loss between 40 and 200 °C can be attributed to the removal of superficial and interstitial water and/or HF residue from the MXene surfaces [26–28]. Weight losses above 200 °C could result from the dehydroxylation of the remaining isolated OH groups bonded to the Ti-terminated surface [29]. It can be also attributed to the elimination of physisorbed water embedded between the layers [26, 30]. In both cases, weight losses in this range are roughly the same (around 2.6 wt.%). This result is not too surprising since both samples were dried at temperatures below 200 °C. At temperatures >450 °C, no significant weight change was observed in the TGA curves (only ~0.4 wt.%), which demonstrates that most volatile species were eliminated at temperatures below this threshold.

Comparing the weight losses of samples dried at RT and at 120 °C, in the 30–120 °C temperature range (Fig. 6a and b), one can estimate the amount of gas product produced as a result of drying the sample under mechanical vacuum at 120 °C for 24 h. Assuming evaporation of water alone (no HF release), calculations showed evaporating of ~0.0007 mol of water per 1 g of exfoliated Ti3C2 due to drying. This amount of water represents ~16.7 wt.% of the overall weight loss taking place between 40 and 500 °C.

As noted above, the weight loss in the 200–450 °C temperature range that could be attributed to the dehydroxylation of the OH groups is ≈2.6%, viz. 1/6 of what it should have been had the initial composition been Ti3C2(OH)2. Why this is the case is not entirely clear at this time, but is most probably due to the presence of fluorine termination. EDX of the exfoliated samples dried at room temperature showed that the Ti:C:O:F atomic ratios are 35:25:15:25. In other words, the exfoliated structure can be written as ≈Ti2.94C2F2O0.55(OH)0.65. Assuming the complete removal of OH surface groups due to treatment at 450 °C, the theoretical weight loss of this composition should be 4.9%, a value that is much closer to the experimentally measured 2.6 wt.%. It follows that the less than expected weight loss can be ascribed to the presence of F. Another possibility is the oxidation of the MXene composition to form crystalline titanium oxide, a phase that we know forms if MXene samples are heated to 600 °C in air. Another possibility is the partial substitution of carbon by oxygen in the Ti3C2 structure, as happens in cubic TiC [31].

Note that if the formal valences of the elements are chosen to be: Ti = +4, C = −4, etc., Ti2.94C2F2O0.55(OH)0.65 is electrically neutral.
neutral. In other words, the formula assumed is electrically neutral and is more consistent with the weight loss and EDX results.

4. Conclusions

In this work three main parameters that are important in the extraction of Al from Ti3AlC2 in 50 wt.% HF, viz: time, temperature and initial particle size are identified. Drying of the sample at 120°C, under a mechanical vacuum, results in the removal of superficial and partially interstitial water molecules, but not OH groups. Assuming evaporation of only water molecules, \( \approx 0.0007 \) mol of water per 1 g of exfoliated Ti3C2 evaporates due to the drying under these conditions. Exfoliated MXenes show morphologies that are reminiscent of graphene such as the formation of arch-shaped edges.

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