On the Topotactic Transformation of Ti$_2$AlC into a Ti–C–O–F Cubic Phase by Heating in Molten Lithium Fluoride in Air

Michael Naguib,$^1,^8$ Volker Presser,$^1,^8$ Darin Tallman,$^1$ Jun Lu,$^5$ Lars Hultman,$^5$ Yury Gogotsi,$^1,^8$ and Michel W. Barsoum$^{1,†}$

$^1$Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104

$^5$A. J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania 19104

$^8$Thin Film Physics Division, Department of Physics (IFM), Linköping University, S-581 83, Linköping, Sweden

Herein we report on the formation of a Ti–C–O–F phase via the topotactic transformation of Ti$_2$AlC by immersion in molten lithium fluoride, LiF, at 900°C in air for 2 h. The Al diffuses out of the structure and reacts with LiF to form Li$_3$AlF$_6$. X-ray diffraction, Raman spectroscopy, optical, scanning and transmission electron microscopy, with energy-dispersive spectroscopy, showed the selective etching of Al from the structure and the formation of a cubic, rock-salt, Ti–C–O–F phase. The transformation is topotaxial, involves de-twinning of the hexagonal Ti$_2$AlC structure and results in domains that are of the order of 10 nm. The reaction rate is significantly higher when the reaction is carried out in air than when it is carried out in vacuum.

I. Introduction

The ternary carbides and nitrides with a M$_n$+1AX$_n$ chemistry—where $n = 1$, 2, or 3, M is an early transition metal, A is an A-group element (mostly groups 13 and 14), and X is C or N—represent a family of more than 60 members. These phases are layered hexagonal (space group P6$_3$/mmc), with two formula units per unit cell. In the crystal structure, near close-packed M atom layers are interleaved with layers of group A elements; the X atoms fill the octahedral sites between the former [Fig. 1(a)].

The main motivation of this work was to create two-dimensional, 2-D, M$_n$+1X$_n$ structures by the selective removal of the A-element for a host of potential applications, the most important of which is the use of these materials as anodes in Li-ion batteries. We recently have shown that heating Ti$_3$SiC$_2$ in carburizing atmospheres results in the out-diffusion of Si and the formation of TiC$_x$, the same was observed when heating Ti$_3$SiC$_2$ in molten Al. Heating to relatively high temperatures under vacuum also results in decomposition of the MAX phase into the binary carbide and an A-group rich liquid. Examples include the heating of Ti$_2$InC to 800°C under vacuum, and the decomposition of Ti$_3$SiC$_2$ thin films in vacuum. Zhau et al.,$^{10}$ studied the crystallographic relations between Ti$_3$SiC$_2$ and TiC and found that removing Si from Ti$_3$SiC$_2$, resulted in the formation of a cubic substoichiometric transition metal carbide (TiC$_{0.67}$).

More germane to this paper is previous work in which we showed that when Ti$_3$SiC$_2$ was immersed in molten cryolite (Na$_3$AlF$_6$) at 960°C in air, it converted to a cubic rock-salt phase with a composition of Ti(C$_{0.5}$Si$_{0.5}$). The transformation was topotactic, and occurred by the outward diffusion Si [Fig. 1(b)] and the de-twinning of alternate Ti$_3$C$_2$ layers [Fig. 1(c)]. We also presented some evidence that the vacancies, in the resulting Ti$_3$C$_2$ phase, were partially ordered. Herein we report on a similar transformation of Ti$_2$AlC into a TiC$_{0.5+\delta}$ phase—rich in oxygen and fluorine—when the former is immersed in molten lithium fluoride, LiF, at 900°C.

II. Experimental Procedure

Both powder (>92 vol%, −325 mesh, Sandvik-Kantthal, Hallsthammar, Sweden) and bulk Ti$_2$AlC samples were used. The processing details of making the bulk Ti$_2$AlC samples can be found elsewhere.$^{12}$ In short, a stoichiometric mixture of Ti, Al$_2$C$_3$ (99%, Alfa Aesar, Ward Hill, MA), and graphite (99%, Alfa Aesar) powders was mixed and hot-pressed for 4 h under vacuum at 1600°C under a load corresponding to a stress of 40 MPa. The resulting sample was predominantly single phase and fully dense.

Roughly 10 g of Ti$_2$AlC powder was mixed with ≈30 g of LiF powder (99%, Alfa Aesar) and heated to 900°C for 2 h in air in a platinum, Pt, crucible. After cooling, the resultant powder was investigated by X-ray diffraction (XRD) with a powder diffractometer (Siemens D500, Bruker AXS, Karlsruhe, Germany) using CuK$_\alpha$ radiation, and a step scan of 0.02° and 1 s per step. When possible, Si powder (99%, Alfa Aesar) was used as an internal standard. To induce preferred orientation, the reacted powders were cold-pressed to a stress of 1 GPa into ≈300 μm thin, 2.5 cm diameter disks.

Bulk samples were also immersed in molten LiF at 900°C for 2 h. Upon cooling, the samples were cleaned by gently grinding off the solidified salt, and their surfaces investigated by XRD. The bulk samples were also cross-sectioned, mounted, ground, and polished—down to 1 μm—and observed under an optical microscope, OM, (SMAP0: Leica Microsystems Inc., Bannockburn, IL) and a scanning electron microscope, SEM, (Supra 50 VP, Zeiss, Oberkochen, Germany) using CuK$_\alpha$ radiation, and a step scan of 0.02° and 1 s per step. When possible, Si powder (99%, Alfa Aesar) was used as an internal standard. To induce preferred orientation, the reacted powders were cold-pressed to a stress of 1 GPa into ≈300 μm thin, 2.5 cm diameter disks.

$^8$Author to whom correspondence should be addressed. e-mail: barsoumm@drexel.edu

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Germany) equipped with an energy-dispersive spectrometer, EDS, (Oxford Inca X-Sight, Oxfordshire, U.K.).

Raman spectroscopic investigation of the samples was carried out with an inVia Raman microspectrometer (Renishaw plc, Gloucestershire, U.K.) using an Ar-ion laser (488.0 nm) and a grating with 1800 lines/mm. This corresponds to a spectral resolution of 1.8 cm$^{-1}$ and a spot size of 0.7 μm in the focal plane. Two transmission electron microscopes, TEM, (JEOL JEM-2010F and JEM 2010, Akishima, Japan) operating at 200 kV were used to characterize the reacted powders. The EDS analysis in the TEM was carried out using an ultrathin window X-ray energy-dispersive spectrometer, EDAX (EDAX, Mahwah, NJ). The as-processed material was characterized using a TEM (FEI, Tecnai G2 TF20UT FEG, Eindhoven, the Netherlands) with EDS analysis.

The Vickers microhardness, at 10 N, of the reaction layer was also measured using a microhardness tester (LECOM 400, LECO Corp., St. Joseph, MI).

### III. Results and Discussion

The XRD pattern of the unreacted powders [Fig. 2(a)] show only peaks belonging to LiF and Ti$_2$AlC, with a small amount of TiC present as an impurity in the starting Ti$_2$AlC powder. After treatment, the Ti$_2$AlC peaks disappear and are replaced by broad peaks whose positions [dashed lines in Figs. 2(b)–(d)] correspond to those of TiC. Using the Scherrer formula, the average grain size after treatment is estimated to be 10 ± 3 nm. The XRD pattern of the treated powders show additional peaks for LiF and Li$_3$AlF$_6$. The TiC lattice parameters are 4.29 ± 0.02 Å for the powders [Figs. 2(c) and (d)] and 4.30 ± 0.03 Å for the bulk [Fig. 2(b)]. Note that the XRD pattern of the bulk sample shows much less ancillary phases.

The OM images of the bulk-reacted samples [Figs. 3(a)–(c)], show a ≈200–400 μm thick reaction zone. At higher magnification, of an area comprising the interface between the reacted and unreacted zones [Fig. 3(b)], it is clear that the grain boundaries in the former are better delineated. The grain boundaries in the reacted region appear as if they had been etched, when, in fact they had not been.

The topotactic nature of the reaction is also incontrovertible. After the reaction, the original sharp corner [top left in Fig. 3(a)] of the bulk sample is preserved, and the grains do not change shape upon reaction.

The etching effect can also be seen in SEM micrographs [Fig. 4(a) and top inset]. A higher magnification SEM micrograph [bottom inset in Fig. 4(a)] shows that the exfoliation of the basal planes is occurring at a quite fine scale indeed.

The EDS of the area delineated by the vertical rectangle in Fig. 4(a) is shown in Fig. 4(b). The concentration profiles confirm that the affected zone is depleted in Al, and is rich in F and O. The average chemistry of the outermost layer—delineated by the horizontal rectangle in Fig. 4(a) translates to ≈TiC$_{0.5}$O$_{0.4}$F$_{0.5}$Al$_{0.1}$. In the unaffected area, EDS confirmed the 211 chemistry, viz. Ti$_2$Al$_{0.96}$O$_{0.92}$. This result in turn increases our confidence that the C-levels reported herein are more or less accurate. The Al concentration is slightly higher near the surface, most probably due to contamination with Li$_3$AlF$_6$ goes through a minimum in the center of the reacted layer, and increases to ≈25 at.% in the bulk. The opposite is true of the O and F concentrations.

Figure 5(a) shows a TEM micrograph of a TiC$_x$ flake. The lacy nature of the flake with fine cracks and delaminations and kink bands—again at the nanoscale—are obvious. The EDS of that area [Fig. 5(b)] shows the presence of Ti, C, O, and F, but little to no Al. Twinned domains with respect to the TiC matrix is indicated in the selected area diffraction (SAD) pattern as shown in Fig. 5(c).

Figure 6(a) shows a HRTEM image of a heavily twinned region. Figures 6(b) and (c) are higher magnifications of regions outlined by rectangles in Fig. 6(a). A closer inspection of the lattice in Fig. 6(a) reveals the presence of several twin boundaries. While some twin boundaries have perfect coherency [c.f. Fig. 6(b)], most are incoherent and consist of atom columns with a dumbbell appearance as in a stacking fault while maintaining coherency with the lower and upper parts of the twinned material across the boundary [c.f. Fig. 6(c)]. Some of the incoherent twin boundaries are terminated in the basal plane by partial dislocations indicated, in the left lower portion of Fig. 6(a), by inverted Ts.

When the Raman spectra of Ti$_2$AlC [Fig. 7(a)], Ti$_3$AlC$_2$ [Fig. 7(b)], and a grain in the reacted zone [Figs. 7(c)] are compared, the following observations are salient: (i) for the most part, the peaks at $\omega_3$ and $\omega_4$ disappear after reaction; (ii) the peaks $\omega_3$ and $\omega_5$ appear to merge, down-shift to a frequency $\omega_5$, at about 617 cm$^{-1}$ shown by the dashed vertical line in Fig. 7; and (iii) the peaks after reaction are considerably wider. The Raman spectrum [Fig. 7(d)] of the edge of a grain that appeared partially reacted [colored grain in Fig. 3(b)] contains peaks belonging to both Ti$_2$AlC and those of the reaction product.

The Vickers’ microhardness of the reacted layer was 3 ± 0.2 GPa.
Fig. 3. Cross-sectional OM micrographs of polished, bulk Ti$_2$AlC sample after LiF treatment for 2 h at 900°C in air, (a) low magnification, showing reaction layer and sharp corner after reaction. (b) Raman mapping in the affected zone; point (1) represents pure Ti$_2$AlC, point (2) highly affected MAX [cf. Fig. 7(c)], and point (3) represents partially transformed 211 [cf. Fig. 7(d)]. The green (partially transformed) and red (fully transformed) colors correspond to the degree of transformation. (c) High magnification OM image showing etched-like grains.

Fig. 4. (a) Cross-sectional SEM micrograph of a bulk sample after the LiF treatment. Top inset shows higher magnification of reacted area. Lower inset, an even higher magnification of the same region; (b) EDS line mapping along the vertical rectangle in (a), the vertical line is divides the graph into two parts; etched and unetched.)
From the EDS and XRD results, it is reasonable to conclude that the following simplified reaction occurs when Ti$_2$AlC is immersed in molten LiF:

\[
0.5 \text{Ti}_2\text{AlC} + 3.44 \text{LiF} + 0.72 \text{O}_2 = \\
\text{TiC}_{0.5}\text{O}_{0.4}\text{F}_{0.5}\text{Al}_{0.1} + 0.5 \text{Li}_3\text{AlF}_6 + \text{Li}_2\text{O}
\] (1)

This reaction is simplified in that it assumes the Ti:C ratio to be 2:1 when it is not (see below). It also assumes that the O:F:Al ratios to be fixed, when in fact, these values differ from grain to grain. At this juncture, it is important to note the important role that oxygen plays in this reaction. At \(\approx 20\,\mu\text{m}\), the reaction layer formed when a bulk sample was heated in a vacuum hot press (not shown) for 8 h is significantly thinner than the one that formed in air after 2 h at the same temperature [Fig. 3(a)]. These results are not surprising as it is well established that oxygen plays a key role when metals react with fluoride salts.\(^{14}\)

Assuming the densities of the Ti$_2$AlC, LiF, TiC$_{0.5}$O$_{0.4}$F$_{0.5}$Al$_{0.1}$, Li$_3$AlF$_6$, and Li$_2$O to be, respectively, 4.11, 2.64, 4.93, 2.87, and 2.01 Mg/m$^3$, the molar volume change of reaction 1 is only approximately \(-2\%\). This mild volume change...
change explains why, for the most part, the reaction occurs with minimal cracking. This is most convincingly seen at the corner of the sample [Fig. 3(a)]. Typically, when reaction volume changes are high, cracks nucleate at sharp corners. Their absence herein thus confirms the small volume changes on reaction. The fine cracks and the etching of the grain boundaries, on the other hand, is consistent with the small volume shrinkage, calculated based on Eq. (1).

The lattice constant of the TiC\_x present in the bulk sample prior to LiF treatment, is 4.33 Å, which corresponds to an x of ≈1.15. The lattice parameter of the newly formed cubic phase, however, is 4.29 Å in the case of the powders and 4.30 Å in case of the bulk sample. Why the values are different is not clear at this time, but is most probably due to the presence of oxygen, fluorine and or carbon deficiency. For example, Zainulin et al.\textsuperscript{16} and Lvrenko et al.\textsuperscript{17} showed that the incorporation of O in the TiC lattice decreased the lattice parameter of the latter.

The full width at half maximum, FWHM, of the resulting phase peaks is significantly wider than that of the unreacted TiC in the starting Ti\_2AlC powder. Using the Scherer formula,\textsuperscript{13} we estimate the average grain size to be ≈10 nm. The fact that all peaks—not just the (111) peaks—are broadened after reaction, implies that the reaction results in the breakdown of the original grains, in both the a and c directions of the original structure.

The HRTEM results [Figs. 5, and 6(a)] confirm the nanoscale of the resulting grains.

The angles (θ and β) between the twinned planes in the HRTEM micrographs [Fig. 6(c)] are ~138° and 110°, respectively. These values are close to those one would predict from the Ti\_2AlC structure [Fig. 1(b)] viz. ~132° and 111°, respectively. Both sets of values are also in agreement with the angles (θ' and β') in the SAD pattern [Fig. 5(c)] that are ~70° and 39°, respectively (viz. θ' ≈ 180°–0°, β' ≈ 180°–0°).

As important, the SAD results showed two sets of spots with an angle of 39° between them. This angle is consistent with the de-twinning of the hexagonal structure upon the formation of the cubic phase. In this sense, these results are in complete agreement with previous work.\textsuperscript{11} How the de-twinning of few layers in one direction and others in the opposite direction occurs remains a mystery. The reasons for the de-twinning, however, is clear. TiC does not form twins readily because its stacking fault energy is quite high. Our finding of the stacking fault nature of the twin boundary in TiC during de-twinning [Fig. 6(c)] sheds important new light to our understanding of de-twinning in this system. The stacking fault, with associated partial dislocations, if glissile could explain the de-twinning. Another possibility is the presence of thin intergrown TiC platelets in the initial Ti\_2AlC sample. Liu et al.\textsuperscript{18} showed that these platelets exist in Ti\_2AlC with the following orientation: (0001)Ti\_2AlC// (111)TiC. It is thus possible that the transformation of the Ti\_2AlC into the cubic phase results in de-twinning with two directions, one for the initial TiC and the second for transformed Ti\_2AlC. In addition, it was reported that inducing “A” element (as Si) in TiC results in microtwins,\textsuperscript{19} and so, some microtwins may exist in the TiC platelets from the beginning before the reaction.

Spanier et al.\textsuperscript{20} have shown that the peaks at ω\textsubscript{1}–ω\textsubscript{4} [Figs. 7(a) and (b)], are due to vibrations of the Al atoms in Ti\_2AlC or Si atoms in Ti\_SiC\_2. It is thus not surprising that these peaks disappear after the reaction, with the etching away of the Al layers. [Fig. 7(c)]. The peaks at ω\textsubscript{5} and ω\textsubscript{6} are due to the vibrations of the C-atoms; those peaks do not appear in the 211 MAX structure, they only appear in the 312 and 413 phases. It is thus not unreasonable to assume that the peak ω\textsubscript{7} at 617 cm\textsuperscript{-1} [Fig. 7(c)] that emerges after reaction—is also related to the vibration of the C-atoms. This peak can be assumed to be due to the merging of peaks ω\textsubscript{5} and ω\textsubscript{6} and their downshifting due to the presence of ordered vacancies on the Al-sublattice [Fig. 1(b)]. Such downshifting has been observed in Raman spectra of very thin layers of inorganic layered compounds.\textsuperscript{21} Furthermore, line broadening and the spectral shifts in the Raman spectra are consistent with structural deterioration and loss of crystallinity as evidenced from the broadened XRD profiles. Indeed, less affected grains [Fig. 7(d)] show narrower linewidths. The nature of the peak at ω\textsubscript{8} [Fig. 7(d)] remains unclear at this time, but is most probably related to defects—most probably vacancies. What role that F and O atoms play in the Raman spectra, and where they reside remains unclear and is beyond the scope of this work.

In cubic TiC\_x with random vacancies, the (111) plane's intensity is higher than that of the (200) planes.\textsuperscript{15} In the reaction product formed herein, these peak intensities are reversed. This reversal was previously ascribed to vacancy ordering, and there is no reason to believe that the situation herein is any different.

The hardness of near stoichiometric TiC is ≈30 GPa,\textsuperscript{22} the microhardness of the oxicarbide is even higher.\textsuperscript{17} Reducing the C-content to 0.58, viz. TiC\_0.58, reduces the hardness to ~12 GPa.\textsuperscript{23} Given that the hardness of the reaction layer produced herein is 3 ± 0.2 GPa, it is unlikely that the vacancies are not ordered. As far as we are aware, this is by far the lowest hardness value ever reported for TiC\_x. This comment notwithstanding, one reason for the lower hardness has to be the presence of the very fine delaminations parallel to the original basal planes of Ti\_2AlC [Fig. 5(a) and lower inset in Fig. 4(a)], which can be taken as another manifestation of ordering. More importantly, these powders differ from conventional TiC\_x in that, they have sufficient ductility/plasticity to allow them to be cold-pressed into free-standing thin disks that can be easily handled.

The material described herein, viz. two-dimensional Ti–C–O–F nanoparticles, offers a large number of prospective applications, especially when considering that the MAX phase precursor can be manufactured in various forms, such as powder, monolithic materials, thin films, etc. With a low surface energy, oxyfluorcarbides have recently been shown to be useful as anti-stain coatings.\textsuperscript{24} This nano Ti–C–O–F phase may also be used as an absorbent for environmental pollutants.\textsuperscript{25} While the carbon content results in optically nontransparent samples, and therefore the low polarizability of oxyfluorides cannot be used, the material's high Lewis acidity\textsuperscript{26} may enable a wide range of catalyst applications. Further given the unique photocatalytic properties of TiO\_2 doped with carbon,\textsuperscript{27,28} the novel Ti–C–O–F nanophase reported herein may be utilized as bi-functional, opto-
Li₃AlF₆. The vacancies in the resulting structure are partially Al. Oxygen plays a crucial role in the reaction and it is likely contains significant amounts of O and F and small amounts of Al. Further investigation of this new structure is required.

IV. Conclusions

When Ti₂AlC is immersed in molten LiF at 900°C for 2 h in air, a topotactical transformation is induced that results in the formation of a TiC cubic phase where x ≈ 0.5, that contains significant amounts of O and F and small amounts of Al. Oxygen plays a crucial role in the reaction and it is likely that without it, the reaction would not proceed. The Al diffuses out of the structure and reacts with LiF to form Li₃AlF₆. The vacancies in the resulting structure are partially ordered. Direct HRTEM evidence for de-winning of the Tiₙ₋₁Cₙ blocks is also presented. The volume change on reaction is small. We conclude from this study that Ti₂AlC cannot be used in molten halide salts, and more specifically, LiF (especially in the presence of oxygen).

The combination of the ordered vacancies, which, in turn, offer possibilities of exfoliation, together with the nanoscopic structure and novel chemistry, viz. Ti–C–O–F, suggest many potential uses; uses that could span the gamut from photocatalysis to energy storage in batteries or supercapacitors, among others.

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