X-ray Photoelectron Spectroscopy of Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_z$, and TiC Provides Evidence for the Electrostatic Interaction between Laminated Layers in MAX-Phase Materials

Lars-Ake Näslund,* Per O. Å. Persson, and Johanna Rosen

Abstract: The inherently nanolaminated Ti$_3$AlC$_2$ is one of the most studied MAX-phase materials. MAX-phases consist of two-dimensional $M_{n+1}X_n$-layers (e.g., Ti$_3$C$_2$-layers) with strong internal covalent bonds separated by weakly interacting A-layers (e.g., Al-layers), where the repetitive stacking of the $M_{n+1}X_n$-layers and the A-layers suggests being the foundation for the unusual but attractive material properties of the MAX-phases. Although being an important parameter, the nature of the bonding between the Ti$_3$C$_2$-layers and the Al-layers in Ti$_3$AlC$_2$ is through electrostatic attraction facilitated by a charge redistribution of the delocalized electrons from the Ti$_3$C$_2$-layers to the Al-layers. This charge redistribution is facilitated by the weak interaction between the Ti$_3$C$_2$-layers and the Al-layers in Ti$_3$AlC$_2$ is through electrostatic attraction facilitated by a charge redistribution of the delocalized electrons from the Ti$_3$C$_2$-layers to the Al-layers. This charge redistribution is of the same size and direction as between Ti atoms and Al atoms in TiAl alloy. This finding opens up a pathway to predict and improve MAX-phase materials properties through A-layer alloying, as well as to predict new and practically feasible MXene compounds.

1. INTRODUCTION

MAX-phases are a group of ternary compounds with the general composition $M_{n+1}AX_n$ ($n = 1, 2, 3$), where M is an early transition metal, A is an A-group element (mainly group 13 or 14), and X is carbon (C) or nitrogen (N). Today, we can find more than 150 reported synthesized MAX-phases, materials that possess characteristics of both metals and ceramics. The MAX-phases are inherently nanolaminated materials of a metal carbide or nitride ($M_{n+1}X_n$-layers) separated by monolayers of A-atoms (A-layers). The $M_{n+1}X_n$-layer consists of $n + 1$ M-monolayers and $n$ X-monolayers stacked in an alternated sequence where the first and the last $M$-monolayers form the interfaces toward the A-layers on each side of the $M_{n+1}X_n$-layer. The bond between the $M_{n+1}X_n$-layers and the A-layers is relatively weak, and through selective etching of the A element, using a suitable etchant, it is possible to exfoliate MAX-phases to form two-dimensional (2D) $M_{n+1}X_n$ ($n = 1, 2, 3$) materials. These 2D materials are known as MXene, and until today, there are about 30 different MXene compounds reported. Both the MAX-phase materials and the MXene compounds have interesting and tunable properties. Some of the MAX-phases show, for example, high resistance of corrosion and oxidation, good electrical and thermal conductivities, and have high stiffness and low tendency to deform under the influence of mechanical stress. The MXene compounds have characteristics of being a 2D material and have shown great promise in a host of applications, not the least of which is in energy storage. All of these properties can be modified by the selection of the M, A, and X elements and, in the case of the MXene compounds, also the termination species $(T_z)$ on the $M_{n+1}X_z$-surfaces. It is common to add the $T_z$ to the MXene formula, i.e., $M_{n+1}X_zT_z$ ($n = 1, 2, 3$), to emphasize the importance of the termination species for the MXene properties.

Theoretical studies have suggested that the key to the unusual material properties of the MAX-phases is, at least in part, the strong covalent bonding within the $M_{n+1}X_n$-layer facilitated by the weak interaction between the $M_{n+1}X_n$-layer and the A-layer. The weak interaction between the $M_{n+1}X_n$-layers and the A-layers is also the basis of the method employed to synthesize MXene, i.e., removing the A-layers with a suitable etchant without disrupting the bonds in the...
$M_{n+1}X_n$-layers.\textsuperscript{5–7,14} Despite being an important parameter, there are only a few theoretical/experimental studies reported on this topic,\textsuperscript{13,15–21} and a fundamental understanding of the interaction between the $M_{n+1}X_n$-layers and the A-layers is not yet established. Calculations of partial density of states indicate bonding between Ti 3d and Al 3p in Ti$_3$AlC$_2$, see, e.g., Zhou et al.\textsuperscript{13} The strength and nature of this bonding have generally been suggested to be weak and even of weak covalent character;\textsuperscript{15,20} however, conclusive evidence thereof remains to be presented.

The aim of the present work is to increase our understanding of the interaction between the $M_{n+1}X_n$-layers and the A-layers in $M_{n+1}AX_n$-phases. With an expanded knowledge about this interaction, it might be possible to predict and improve the properties of a MAX-phase through modifications of the A-layers, e.g., through alloying\textsuperscript{22,23} or introducing A$_2$-layers,\textsuperscript{24,25} as well as to predict and facilitate the synthesis of novel MXenes. So far, most synthesized MXene compounds originate from MAX-phases with aluminum (Al) as the A element, although they can also be produced from, e.g., a MAX-phase-related material, $M_{n+1}AX_n$-phase, where the A$_2$-layer is a gallium (Ga) bilayer.\textsuperscript{26}

In this work, we have investigated Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_y$, and TiC by employing X-ray photoelectron spectroscopy (XPS), which provides element-specific information on the electronic structure of the examined components. Through XPS, it is thus possible to gain information about the chemical environment around the probed element, including the nature of the bonding to the nearest-neighbor atoms. XPS measurements on Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_y$ have been performed previously.\textsuperscript{16,17,27,28} Nevertheless, in this study, we have provided extra attention to the binding energy calibration, which is essential in the characterization of the weak interactions between the laminated layers. It is ensured that the XPS binding energy scale is calibrated with the same care and method for all samples, including the reference samples, since comparison with XPS databases and literature values might not be relevant, especially if they are obtained from XPS spectra that are not calibrated or calibrated using the adventitious C 1s of carbon contamination.\textsuperscript{29,30}

In our study, presented herein, we compare a MAX-phase with Al as the A element (Ti$_3$AlC$_2$) with its corresponding MXene compound (Ti$_3$C$_2$T$_y$), three-dimensional (3D) cubic MX (TiC), and 99.95% commercially pure aluminum (Al-1050). The results will not only describe the bonding characters between the $M_{n+1}X_n$-layers and the A-layers in $M_{n+1}AX_n$-phases but also explain why selective etching of A elements can be of great challenge for some MAX-phases and, in addition, provides a method to screen MAX-phases for the synthesis of practically feasible MXene compounds.

2. METHODS

2.1. Samples Preparation. Thin films of Ti$_3$AlC$_2$ were deposited on c-axis-oriented sapphire substrates of 10 × 10 cm$^2$ surface area using direct current magnetron sputtering (DC-MS) in an ultrahigh-vacuum (UHV) system. The depositions were performed using elemental Ti, Al, and C targets with diameters of 75, 50, and 75 mm, respectively. Prior to deposition, the substrates were preheated inside a deposition chamber at 780 °C for 1 h. While keeping the substrates at 780 °C, the Ti and C targets were ignited with powers of 92 and 142 W, respectively, for 30 s, forming incubation layers of TiC before the Al target was ignited at a power of 26 W. The sample holder, which held six substrates, was continuously rotating at 30 rpm for uniform deposition. The duration of sputtering the three targets was 10 min, which produced Ti$_3$AlC$_2$ films about 30 nm thick. The thin-film TiC was obtained separately when the Al target was not ignited.

Thick-film Ti$_3$C$_2$T$_y$ samples were prepared through immersion of the DC-MS-obtained Ti$_3$AlC$_2$ in 10% concentrated HF(aq) (Sigma-Aldrich, Stockholm, Sweden) for 1 h at room temperature (RT) and were thereafter rinsed in deionized water and ethanol. The formation of Ti$_3$C$_2$T$_y$ was confirmed through the increase in the c lattice parameter, as observed in the diffractograms shown in Figure 1 (the XRD was performed quickly to reduce the sample exposure to the laboratory atmosphere). The size of the XRD peak shift depends on the obtained spacing between the Ti$_3$C$_2$ layers when the Al-layers are removed in the HF(aq) etching process.\textsuperscript{11}

The amount of impurities, such as TiO$_2$ and Al$_2$O$_3$ and contamination, such as hydrocarbon and alcohol compounds, was kept as low as possible. For example, the obtained DC-MS Ti$_3$AlC$_2$ and TiC samples were removed from the UHV system first after cooling down to RT and were exposed to the atmosphere as brief as possible. The Ti$_3$C$_2$T$_y$ samples were prepared immediately and thereafter placed in the XPS instrument shortly after the etching process was performed.

In addition to Ti$_3$AlC$_2$, this study also includes the following MAX-phases: Ti$_3$AlC, V$_3$AlC, Nb$_3$AlC, (Cr,Mn)$_3$AlC, Mo$_2$GaC, and the MAX-phase related material Mo$_2$GaC$_x$. Ti$_3$AlC was commercially obtained (3-ONE-2, Voorhees, NJ), Nb$_3$AlC was synthesized by M. W. Barsoum et al. from the Department of Materials Science and Engineering, Drexel University, Philadelphia.\textsuperscript{31} Mo$_2$GaC$_x$, Mo$_2$GaC, and (Cr,Mn)$_3$AlC were synthesized as thin films through magnetron sputtering deposition.\textsuperscript{25,32}

2.2. Material Characterization. XPS experiments for F 1s, O 1s, Ti 2p, C 1s, and Al 2p were performed with the AXIS Ultra$^{\text{MD}}$ system from Kratos Analytical Ltd. using monochromatic Al Kα radiation and a pass energy ($E_{\text{pass}}$) of 20 eV. The samples were placed in an analyzer chamber with the surface normal in the direction along the electron lens toward the electron energy analyzer and with the incident X-ray at an angle of 45° relative to the surface normal, which provided an analysis area of $300 \times 700 \mu m^2$ on the surface with a photoelectron acceptance angle of ±15°.
The binding energy scale of all XPS spectra, presented herein, was carefully calibrated against the Fermi edge \( E_F \), which was set to a binding energy of 0.00 ± 0.02 eV. The overall energy resolution obtained for the XPS spectra presented in this report was better than 0.3 eV (see Table 1), as determined through differentiation of the intensity over the Fermi edge. Normalization of all spectra was performed at the binding energy for the Ag 3d5/2 was 368.33 ± 0.02 eV, and the Ti 2p, C 1s, and Al 2p peak positions were determined through curve fitting of each spectrum. The binding energies for other components, such as the TiO2 components in the Ti 2p spectra, the Al2O3 components in the Al 2p spectra, and the graphite-like (C–C), hydrocarbons (CHx), alcohol (C–OH), and carboxyl (COO) components in the C 1s spectra, are on the other hand determined within ±0.1 eV. In the O 1s spectra, the TiO2 components and the adsorbed O on Ti3C2T, could be determined within ±0.05 eV, while features at higher O 1s binding energies were determined within ±0.1 eV.

2.4. XPS Spectrum Curve Fitting. The background contributions are represented by functions, which were subtracted from the XPS spectra before curve fitting. The curve fitting of the O 1s, Ti 2p, C 1s, and Al 2p XPS spectra for Ti3AlC2, Ti3C2T, TiC, and Al-1050 was performed using asymmetric Gaussian–Lorentzian curves. All four samples possess metallic conductivity, i.e., they all have delocalized electrons. These free-moving electrons can flow toward the created photoelectron core holes with the purpose to screen them and will, thus, interact with the escaping photoelectrons, i.e., reducing the kinetic energy of the photoelectrons, which will appear as tails on the high binding energy side of the photoelectron main intensity peaks. The Ti–C components in the Ti 2p and C 1s spectra and the Al components in the Al 2p spectra were therefore represented by asymmetric Gaussian–Lorentzian curves with tails toward higher binding energies. The TiO2 and the Al2O3 components, which are isolators and therefore do not have free-moving electrons, were best fitted by Gaussian–Lorentzian curves with small tails; oxidized Ti and Al are not only present on the surface but also embedded in the Ti3AlC2 and TiC samples, e.g., in grain boundaries, and some of the Ti 2p and Al 2p photoelectrons from TiO2 and Al2O3 impurities must then penetrate and interact with the conductive Ti–C materials before they escape the sample. The carbon-based and oxygen-based contamination at the surfaces, i.e., the noncarbide components C–C, CHx, C–OH, and COO in the C 1s spectra and a hydroxide (OH) component in the O 1s spectra, were fitted by symmetric Gaussian–Lorentzian curves.

The 2p feature of a component consists of two peaks, which is because of the atomic spin–orbit interaction that splits the 2p XPS features into two peaks, 2p3/2 and 2p1/2. Two examples of 2p3/2 and 2p1/2 spin–orbit split are shown in the Ti 2p and Al 2p XPS spectra of Ti metal and Al metal, respectively, presented in Figure 2. The intensity ratio between the 2p3/2 and 2p1/2 XPS peaks is 2:1, and it is therefore important to include a restriction in the curve fitting procedure that keeps the XPS intensity ratio equal to 2:1 for the two p-orbital components. It was therefore included in the curve fitting procedure that the integrated intensity for the curve that corresponds to the Ti 2p3/2 component must be twice as large as the corresponding integrated curve intensity for the Ti 2p1/2 component. The curve fitting parameters of the 2p3/2 and 2p1/2 XPS peaks, obtained for the Ti 2p and Al 2p spectra shown in Figure 2, are presented in Table 2.

### Table 1. Energy Resolution in the XPS Study of Ti3AlC2, Ti3C2T, TiC, and Commercial Pure Al Metal

| compound | resolution [eV] |
|----------|----------------|
| Ti3AlC2  | 0.28 ± 0.04    |
| Ti3C2T   | 0.22 ± 0.02    |
| TiC      | 0.26 ± 0.02    |
| Al       | 0.26 ± 0.08    |
| Al high resolution | 0.17 ± 0.03   |

All spectra were obtained using \( E_{pass} = 20 \) eV, except for the Al high-resolution spectrum, which was obtained using \( E_{pass} = 10 \) eV. The Al 2p3/2 and 2p1/2 spin–orbit split of 0.4 eV is resolved with this resolution.

2.3. XPS Binding Energy Calibration. To be able to compare features in the obtained XPS spectra, it is important to calibrate the binding energy scale using a consistent procedure. In this work, the binding energy scale of all XPS spectra was calibrated against \( E_F \) of each sample; Fermi levels of all samples were aligned with the electron energy analyzer. The accuracy of the \( E_F \) being equal to 0.00 ± 0.01 eV using the following procedure. The photoelectron intensity over the \( E_F \) of the Ag reference sample was differentiated, and because of the line shape of the \( E_F \), the differentiated intensity curve shows a peak with the shape of a Gaussian function. The center of the Gaussian-shaped peak defines the 0 eV binding energy reference point and could be determined within ±0.01 eV accuracy. The \( E_F \) values of all samples were thereafter shifted in binding energy to fit the \( E_F \) of the well-calibrated Ag reference sample. Through this procedure, the binding energy scale of all XPS spectra was calibrated within ±0.02 eV accuracy.

The Ag 3d3/2 was also recorded before the measurements of Ti3AlC2, Ti3C2T, and TiC, which were loaded into the XPS system together on the same sample holder, and before the measurement of Al-1050. The peak position for the two Ag 3d3/2 spectra could be determined within ±0.01 eV. The binding energy for the Ag 3d3/2 was 368.33 ± 0.02 eV at both measurements, i.e., the binding energy scale between \( E_F \) and \( E_F \) was controlled by comparison with the \( E_F \) of each sample. Hence, differences in the obtained binding

---

**Table 1. Energy Resolution in the XPS Study of Ti3AlC2, Ti3C2T, TiC, and Commercial Pure Al Metal**

| compound   | resolution [eV] |
|------------|----------------|
| Ti3AlC2    | 0.28 ± 0.04    |
| Ti3C2T     | 0.22 ± 0.02    |
| TiC        | 0.26 ± 0.02    |
| Al         | 0.26 ± 0.08    |
| Al high resolution | 0.17 ± 0.03   |

All spectra were obtained using \( E_{pass} = 20 \) eV, except for the Al high-resolution spectrum, which was obtained using \( E_{pass} = 10 \) eV. The Al 2p3/2 and 2p1/2 spin–orbit split of 0.4 eV is resolved with this resolution.

---

**2.4. XPS Spectrum Curve Fitting.** The background contributions are represented by functions, which were subtracted from the XPS spectra before curve fitting. The curve fitting of the O 1s, Ti 2p, C 1s, and Al 2p XPS spectra for Ti3AlC2, Ti3C2T, TiC, and Al-1050 was performed using asymmetric Gaussian–Lorentzian curves. All four samples possess metallic conductivity, i.e., they all have delocalized electrons. These free-moving electrons can flow toward the created photoelectron core holes with the purpose to screen them and will, thus, interact with the escaping photoelectrons, i.e., reducing the kinetic energy of the photoelectrons, which will appear as tails on the high binding energy side of the photoelectron main intensity peaks. The Ti–C components in the Ti 2p and C 1s spectra and the Al components in the Al 2p spectra were therefore represented by asymmetric Gaussian–Lorentzian curves with tails toward higher binding energies. The TiO2 and the Al2O3 components, which are isolators and therefore do not have free-moving electrons, were best fitted by Gaussian–Lorentzian curves with small tails; oxidized Ti and Al are not only present on the surface but also embedded in the Ti3AlC2 and TiC samples, e.g., in grain boundaries, and some of the Ti 2p and Al 2p photoelectrons from TiO2 and Al2O3 impurities must then penetrate and interact with the conductive Ti–C materials before they escape the sample. The carbon-based and oxygen-based contamination at the surfaces, i.e., the noncarbide components C–C, CHx, C–OH, and COO in the C 1s spectra and a hydroxide (OH) component in the O 1s spectra, were fitted by symmetric Gaussian–Lorentzian curves.

The 2p feature of a component consists of two peaks, which is because of the atomic spin–orbit interaction that splits the 2p XPS features into two peaks, 2p3/2 and 2p1/2. Two examples of 2p3/2 and 2p1/2 spin–orbit split are shown in the Ti 2p and Al 2p XPS spectra of Ti metal and Al metal, respectively, presented in Figure 2. The intensity ratio between the 2p3/2 and 2p1/2 XPS peaks is 2:1, and it is therefore important to include a restriction in the curve fitting procedure that keeps the XPS intensity ratio equal to 2:1 for the two p-orbital components. It was therefore included in the curve fitting procedure that the integrated intensity for the curve that corresponds to the Ti 2p3/2 component must be twice as large as the corresponding integrated curve intensity for the Ti 2p1/2 component. The curve fitting parameters of the 2p3/2 and 2p1/2 XPS peaks, obtained for the Ti 2p and Al 2p spectra shown in Figure 2, are presented in Table 2.
energies for the corresponding core-level XPS spectra can therefore be related to charge redistribution in the studied compounds.33

3.1. Ti 2p XPS. Figure 3 presents the Ti 2p XPS spectra of Ti3AlC2, Ti3C2Tz, and TiC. The three spectra are fitted with two asymmetric Gaussian–Lorentzian curves representing the 2p3/2 and 2p1/2 spin–orbit split Ti–C components. The Ti3AlC2 and TiC spectra are also fitted with two asymmetric Gaussian–Lorentzian curves representing features identified as TiO2 components, 34–36 which is absent in the Ti3C2Tz spectrum. Instead, the Ti3C2Tz spectrum has additional two pairs of asymmetric Gaussian–Lorentzian curves representing Ti–C components where the binding energy position depends on the local bonding to the termination species fluorine (F) and oxygen (O). The results obtained from temperature-programmed XPS (TP-XPS), presented in a recent work,28 were combined with atomically resolved images of single 2D Ti3C2Tz sheets attained from an in situ scanning transmission electron microscope (STEM). The conclusions were that the Ti3C2 surfaces are terminated by F and O, exclusively, and that both elements prefer the face-centered cubic (fcc) site, which is the hollow site formed by three surface Ti atoms in a triangular formation where the center of the triangle is above a Ti atom in the second (middle) Ti-monolayer of the 2D Ti3C2 sheet.28 Adsorbed O also accepts a second site, which was not identified. However, while heating the Ti3C2Tz sample up to 750 °C F desorbs and O migrates from the second site to occupy the vacated fcc-sites. These processes were monitored

Figure 2. (a) Ti 2p XPS spectrum of commercially pure titanium. (b) Al 2p XPS spectrum of commercially pure Al-1050. The Ti 2p was obtained using Epass = 20 eV, while the Al 2p was obtained using Epass = 10 eV. The curve fitting is performed according to Section 2. The black and the red dashed lines are the Shirley background and the accumulated intensity of all fitted components, respectively.

Table 2. Parameters Obtained for the Ti 2p and Al 2p Gaussian–Lorentzian Curve Fitting of the Commercially Pure Titanium and Aluminum XPS Spectrum

| compound | component | 2p3/2 [eV] | 2p1/2 [eV] | fwhm [eV] | ΔBE [eV] |
|----------|-----------|------------|------------|-----------|----------|
| Ti       | Ti        | 453.76 ± 0.03 | 459.94 ± 0.03 | 0.66; 1.21 | 6.18     |
| Al       | Al        | 72.78 ± 0.03  | 73.18 ± 0.03  | 0.28; 0.31 | 0.40     |

“The Ti 2p was obtained using Epass = 20 eV, while the Al 2p was obtained using Epass = 10 eV. Full width at half-maximum (fwhm) for the 2p1/2 and 2p3/2 curves. Binding energy difference (ΔBE) between the 2p1/2 and 2p3/2 components.”

Figure 3. Ti 2p XPS spectra of (a) Ti3AlC2 MAX-phase, (b) Ti3C2Tz MXene, and (c) cubic TiC. The peaks at ∼455 and ∼461 eV are the Ti–C components, while the peaks at ∼459 and ∼465 eV in (a) and (c) are from TiO2 impurities. The curve fitting is performed according to Section 2. The black and the red dashed lines are the Shirley background and the accumulated intensity of all fitted components, respectively.
The obtained curve fitting parameters of the Ti–C components of Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_x$, and TiC, obtained for the Ti 2p spectra shown in Figure 3, are presented in Table 3. The main 2p$_{3/2}$ Ti–C components are located at 454.75 ± 0.03, 455.06 ± 0.03, and 454.85 ± 0.03 eV for Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_x$, and TiC, respectively, which are about 1 eV higher than that for Ti metal; the obtained binding energies for Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ of Ti metal are 453.76 ± 0.03 and 459.94 ± 0.03 eV, respectively (see Figure 2). The Ti 2p$_{3/2}$ binding energy positions for the three Ti–C features indicate different degrees of charge depletion at the Ti sites compared to Ti metal. It is interesting to note, however, that the chemical shift of the Ti$_3$AlC$_2$ and TiC is very similar, while it is significantly larger for the Ti$_3$C$_2$T$_x$ features.

### 3.2. C 1s XPS

Figure 4 presents the C 1s XPS spectra of Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_x$, and TiC. The spectra are fitted with asymmetric Gaussian–Lorentzian curves representing the Ti–C component and symmetric Gaussian–Lorentzian curves representing the noncarbide components C–C and C–OH and COO. The obtained curve fitting parameters are presented in Table 4.

The C impurities and contamination are mainly graphite-like carbon formed at the growth of the Ti$_3$AlC$_2$ and TiC thin films and hydrocarbons (CH$_x$) from the laboratory atmosphere. The different binding energies obtained for the C–C components are because of different ratios between the sp$^2$ and sp$^3$ bonding, which are located at 284.3 and 285.2 eV, respectively, and different amounts of CH$_y$ component around 285.5 eV, which are not resolved. There is also some intensity around 286.5 and 289.8 eV, which are alcohol and carboxyl compounds from the laboratory atmosphere.

### 3.3. Al 2p XPS

Figure 5 presents the Al 2p XPS spectra of Ti$_3$AlC$_2$ and commercially pure Al-1050. Both the metallic Al and the Al$_2$O$_3$ compounds are curve-fitted with two asymmetric Gaussian–Lorentzian curves representing the 2p$_{3/2}$ and 2p$_{1/2}$ spin–orbit split, as described in Section 2. The obtained curve fitting parameters of the Al components are presented in Table 5. The binding energy of the metallic Al for both Ti$_3$AlC$_2$ and commercially pure Al-1050 are confirmed through high-resolution measurements (overall energy resolution of 0.17 eV), where the spin–orbit splits through TP-XPS, and it was clear that a Ti 2p$_{3/2}$ peak at 455.1 eV originates from Ti–C–T$_O$ where T$_O$ is the O terminating the Ti$_3$C$_2$ surface occupying the fcc-sites with a local coverage equal to one O per surface Ti. The other Ti 2p features are related to Ti atoms that are affected by the F occupying fcc-sites. Each surface Ti is surrounded by three fcc-sites, and different combinations of F and O can occupy the three neighboring fcc-sites denoted Ti–C–T$_{p}$, Ti–C–T$_{F,O}$, and Ti–C–T$_{O}$. Hence, Ti atoms can be immediately affected by only O, only F, or both F and O. More combinations are possible if vacant fcc-sites or influences from O atoms on the second site are included. However, details of the T$_F$ adsorption sites and structures are beyond the scope of this work and the F-related Ti 2p$_{3/2}$ feature around 456.1 eV is therefore curve-fitted with only two peaks representing Ti–C–T$_{F,O}$ and Ti–C–T$_p$, respectively, although the number of Ti–C–T$_{F,O}$ and Ti–C–T$_p$ peaks could very well be three or more.

The combined TP-XPS and high-resolution STEM study showed that Ti$_3$C$_2$T$_x$ with O occupying the fcc-sites, after that F has desorbed from the Ti$_3$C$_2$ surface, is well defined and the Ti 2p$_{3/2}$ Peak at 455.1 eV is, thus, the most suitable for the comparison with the obtained Ti–C peaks for Ti$_3$AlC$_2$ and TiC.

### Table 3. Parameters Obtained for the Ti 2p Gaussian–Lorentzian Curve Fitting of the Ti$_3$AlC$_2$ MAX-Phase, Ti$_3$C$_2$T$_x$ MXene, and Cubic TiC XPS Spectra

| compound     | component | 2p$_{3/2}$ [eV]         | 2p$_{1/2}$ [eV]         | fwhm$^c$ [eV] | ΔBE$^d$ [eV] |
|--------------|-----------|------------------------|------------------------|---------------|--------------|
| Ti$_3$AlC$_2$| Ti–C      | 454.75 ± 0.03          | 460.75 ± 0.03          | 0.88; 1.42    | 6.00         |
| TiO$_2$      | Ti–C      | 459.0                  | 464.8                  | 1.2; 1.6      | 5.8          |
| Ti$_3$C$_2$T$_x$| Ti–C–T$_O$| 455.06 ± 0.03          | 461.25 ± 0.03          | 0.71; 1.59    | 6.18         |
| Ti–C–T$_{F,O}$| Ti–C–T$_{F,O}$| 455.9            | 462.3                  | 1.2; 1.9      | 6.4          |
| Ti–C–T$_F$   | Ti–C–T$_F$| 456.9                  | 463.3                  | 1.2; 1.9      | 6.4          |
| TiC          | Ti–C      | 454.85 ± 0.03          | 460.88 ± 0.03          | 0.86; 1.15    | 6.03         |
| TiO$_2$      | Ti–C      | 458.8                  | 464.6                  | 1.2; 2.1      | 5.8          |

$^a$The Ti–C components are well-resolved features and can be determined with a high precision. $^b$The TiO$_2$, Ti–C–F$_p$, and Ti–C–T$_{F,O}$ components are determined within ±0.1 eV. $^c$Full width at half-maximum (fwhm) for the 2p$_{3/2}$ and 2p$_{1/2}$ curves. $^d$Binding energy difference (ΔBE) between the 2p$_{1/2}$ and 2p$_{1/2}$ components.
Table 4. Parameters Obtained for the C 1s Gaussian–Lorentzian Curve Fitting of the Ti3AlC2 MAX-Phase, Ti3C2T, MXene, and Cubic TiC XPS Spectra

| compound | component<sup>a,b</sup> | C 1s [eV]       | fwhm<sup>c</sup> [eV] |
|----------|-------------------------|-----------------|-----------------|
| Ti3AlC2  | Ti–C                    | 281.88 ± 0.03   | 0.57            |
|          | C–C + CH<sub>4</sub>    | 285.2           | 1.8             |
|          | C–OH                    | 286.5           | 1.2             |
|          | COO                     | 289.8           | 1.6             |
| Ti3C2T   | Ti–C                    | 281.97 ± 0.03   | 0.65            |
|          | C–C + CH<sub>4</sub>    | 284.3           | 1.5             |
|          | C–OH                    | 286.5           | 1.2             |
|          | COO                     | 289.8           | 1.6             |
| TiC      | Ti–C                    | 282.13 ± 0.03   | 0.59            |
|          | C–C + CH<sub>4</sub>    | 284.9           | 1.6             |
|          | C–OH                    | 286.6           | 1.3             |
|          | COO                     | 289.5           | 1.6             |

<sup>a</sup>The Ti–C components are well-resolved features and can be determined with a high precision. <sup>b</sup>The C–C + CH<sub>4</sub>, C–OH, and COO components are determined within ±0.1 eV. <sup>c</sup>Full width at half-maximum (fwhm) for the C 1s curves.

4. DISCUSSION

The Ti 2p XPS spectra of TiC and Ti3AlC2 in Figure 3 show the importance of carefully prepared samples. Although a short exposure to the laboratory atmosphere, about 2 h, the TiC and Ti3AlC2 samples have oxidized and recognizable TiO<sub>2</sub> features are present in the Ti 2p XPS spectra. However, the amount is low and the TiO<sub>2</sub> intensity contribution to the Ti 2p XPS spectra is well separated from the Ti–C components and does not introduce difficulties in the XPS spectrum curve fitting procedures. The Ti 2p XPS spectrum of the Ti3C2T<sub>e</sub> shows, on the other hand, no intensity contribution from TiO<sub>2</sub>. Instead, the main features are broadened, which is because of the termination species T<sub>f</sub> and T<sub>FO</sub> as shown in a recent TP-XPS study. The Ti 2p XPS curve fitting of the carefully prepared samples required only a few curves, i.e., the essential contributions to the Ti 2p XPS spectra of Ti3AlC2, Ti3C2T<sub>st</sub>, and TiC.

The Ti 2p XPS spectra of TiC and Ti3AlC2 are very similar. The small Ti 2p<sub>3/2</sub> binding energy difference between the Ti–C components in TiC and Ti3AlC2<sub>st</sub> which is only −0.10 eV,
Table 5. Parameters Obtained for the Al 2p Gaussian–Lorentzian Curve Fitting of the Ti3AlC2 and the Commercially Pure Al-1050 XPS Spectraa

| compound | component | 2p1/2 [eV] | 2p3/2 [eV] | fwhm [eV] | ΔBE [eV] |
|----------|-----------|------------|------------|-----------|-----------|
| Ti3AlC2  | Al        | 72.13 ± 0.03 | 72.53 ± 0.03 | 0.45; 0.45 | 0.40      |
|          | Al2O3     | 74.4        | 74.8        | 1.5; 1.5  | 0.40      |
|          | Al        | 72.76 ± 0.03 | 73.16 ± 0.03 | 0.39; 0.39 | 0.40      |
|          | Al2O3     | 74.4        | 74.8        | 1.5; 1.5  | 0.40      |

“*The binding energy for the Al metal agrees well with previously reported values of freshly cleaned Al(111) (Al 2p1/2,3/2 = 72.8 eV).39 The Al component can be determined with a high precision and is confirmed through high-resolution measurements where the spin–orbit splits are well resolved. The Al2O3 components are determined within ±0.1 eV. Full width at half-maximum (fwhm) for the 2p1/2 and 2p3/2 curves. *Binding energy difference (ΔBE) between the 2p1/2 and 2p3/2 components.

Table 6. Parameters Obtained for the O 1s Gaussian–Lorentzian Curve Fitting of the Ti3AlC2 MAX-Phase, Ti3C2T_x MXene, and Cubic TiC XPS Spectra

| compound | component | O 1s [eV] | fwhm [eV] |
|----------|-----------|-----------|-----------|
| Ti3AlC2  | TiO2      | 530.55 ± 0.05 | 1.4      |
|          | OH–TiO2   | 531.9      | 1.6    |
|          | Al2O3     | 532.8      | 1.6    |
| Ti3C2T_x | O_x       | 529.87 ± 0.05 | 0.91  |
|          | O_m       | 531.8      | 2.0    |
|          | Al2O3     | 532.8      | 1.8    |
| TiC      | TiO2      | 530.38 ± 0.05 | 1.2      |
|          | OH–TiO2   | 531.9      | 1.2    |
|          | Al2O3     | 533.0      | 1.5    |

“*The TiO2 and O_x components are well-resolved features and can be determined with a good precision. The OH–TiO2, O_m, and Al2O3 components are determined within ±0.1 eV. Full width at half-maximum (fwhm) for the O 1s curves.

Also, the metallic Al contribution in the Al 2p of Ti3AlC2 shows a negative shift in comparison to Al metal. The Al 2p binding energy shift is significantly larger compared to the Ti 2p and C 1s binding energy shifts between Ti3AlC2 and TiC, which suggests that the Al in Ti3AlC2 has gained charge compared to Al metal. The shift is −0.63 eV and is on the same order as the Al 2p binding energy shift of TiAl alloy;41 the Al 2p3/2 binding energy of TiAl is 72.3 eV, i.e., a shift of −0.5 eV compared to commercial pure Al metal (Al-1050).

The size of the Al 2p shift is too small to represent an asymmetric distribution of electrons between the Ti and Al atoms that are characteristic for a covalent bond, e.g., between the TiC layer and the Al-layer, because Al 2p3/2 core-level shifts between pure Al metal and Al-containing compounds are normally larger than ±1 eV, whereas Al-containing alloys normally show Al 2p3/2 core-level shifts less than ±1 eV.42 Instead, the sizes of the Ti 2p, C 1s, and Al 2p core-level shifts and that all shifts are in negative direction suggest a redistribution of the delocalized electrons from the TiC2 layers to the Al-layers,33 similar to the observed charge redistribution from Ti atoms toward the Al atoms in the TiAl alloy.11 This redistribution of delocalized electrons in the TiC2 layers resembles the response obtained when an ideal stoichiometric cubic MX compound is introduced with the appropriate amount and distribution of vacancies at the X sites, i.e., the net flow of delocalized electrons toward the created vacancies results in a more dense electron cloud around the defect to screen it.33,43,44 Hence, the redistribution of the delocalized electrons will cause a modification of the occupied valence orbital configurations in the MX compound, which in turn leads to a strengthening of the covalent Ti–C bonds.33,43,44 Similar to the case with vacancies in cubic MX

indicates that the charge states of the Ti in both materials are similar. In addition, the C 1s peaks of the Ti–C component and C contamination are also well separated for both TiC and Ti3AlC2, and the C 1s binding energy difference between TiC and Ti3AlC2 shows a small negative shift of −0.25 eV. The fact that both Ti 2p3/2 and C 1s show negative binding energy shifts for Ti3AlC2, in comparison to TiC suggests that the occupied Ti and C valence orbital configurations are slightly different and, thus, enhance the Ti 2p and C 1s core hole screening7 in the 2D Ti3C2-layers in Ti3AlC2 compared with the 3D TiC.

Figure 6. O 1s XPS spectra of (a) Ti3AlC2 MAX-phase, (b) Ti3C2T_x MXene, and (c) cubic TiC. The peaks at ~530.5 and 532.9 eV in (a) and (c) are the TiO2 and Al2O3 impurities, respectively, while the peaks at ~531.8 eV are from OH adsorbed on TiO2. The peaks at 529.9 and 531.8 eV in (b) are O chemisorbed on a not yet identified site and on the fcc-site, respectively. The curve fitting is performed according to Section 2. The black and the red dashed lines are the Shirley background and the accumulated intensity of all fitted components, respectively.
compounds, the inclusion of Al-monolayers between Ti$_3$C$_2$ layers will redistribute the delocalized electrons and thus enhance the core hole screening of the Ti 2p and the C 1s, as suggested by the negative core-level shifts,\textsuperscript{18} which successively leads to a strengthening of the covalent Ti–C bonds also in Ti$_3$AlC$_x$. The fact that the redistribution of the delocalized electrons, caused by the alternating stacking of Ti$_3$C$_2$-layers and Al-monolayers, will lead to a strengthening of the covalent Ti–C bonds is demonstrated when the Al-monolayer is alloyed with the more electronegative element silicon (Si); the electronegativity for Al and Si is 1.61 and 1.90, respectively, in the Pauling scale. As the amount of Si increases in Ti$_3$Al$_{1-x}$Si$_x$C$_2$, the mechanical strength, as obtained through Vickers hardness measurements, increases significantly,\textsuperscript{22} which indicates a strengthening of the covalent Ti–C bonds.\textsuperscript{45}

In addition, the redistribution of the delocalized electrons will provide bonding between the Ti$_3$C$_2$-layers and the Al-layers that are electrostatic between slightly positive Ti$_3$C$_2$-layers and slightly negative Al-layers.

Based on the arguments above, one would expect that the Ti 2p core level would shift back slightly toward higher binding energies when the Ti$_3$AlC$_x$ has the Al-layers removed, e.g., through HF(aq) etching, to form the 2D Ti$_3$C$_2$T$_x$. However, because of termination species (T$_x$), in the form of chemisorbed O,\textsuperscript{28} the Ti 2p core-level shift is 0.32 ± 0.06 eV as a consequence of a partial charge transfer from the Ti atoms in the Ti$_3$C$_2$-layer to the chemisorbed O. When the termination species also includes the chemisorbed F, which is more electronegative compared to O, the core-level shift is even larger (see Table 3). While the Ti$_3$AlC$_2$ shows a Ti 2p core-level shift of −0.10 ± 0.06 eV$,^1$ compared to TiC, the Ti 2p core-level shift between the Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$ is three times larger. Hence, in contrast to the electrostatic interaction between the Ti$_3$C$_2$-layer and the Al-layer in the Ti$_3$AlC$_2$, the bonding interaction between the Ti$_3$C$_2$-layer and the chemisorbed species in Ti$_3$C$_2$T$_x$ is significantly stronger. This difference in bonding strength might be the driving force when MAX-phases are converted to MXene through an etching process.

The information presented in this work suggests that it should be possible to tune the electrostatic interaction between the A-layer and the M$_m$X$_n$X$_n$-layer through A-layer alloying, which could be beneficial for sought-after properties such as improved corrosive resistance, electric and thermal conductivity, mechanical properties, and thermal expansion.

Direct and practical information can also be gained through the A element core-level shift between a MAX-phase material and the pure A element in the Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$. It is therefore crucial that the handling and storage of MAX-phase samples properly. Ar$^+$ sputtering prior to XPS investigation because features from impurities, such as TiO$_2$, Al$_2$O$_3$, and graphite-like carbon and contaminations, such as hydrocarbon, alcohol, and carboxyl compounds, which are well separated from the Ti–C components in the Ti 2p, C 1s, and Al 2p spectra but only a few hundredth of an eV (less than −0.04 eV shift for the corresponding comparison with the atomic laminate material Mo$_2$Ga$_2$C.\textsuperscript{25}

This implies a significantly reduced electrostatic interaction between the Mo$_2$C-layers and the Ga$_2$-layers in Mo$_2$Ga$_2$C compared to the Ga-layers in Mo$_2$GaC. Based on the significantly smaller Ga 3p core-level shift for the Ga$_2$-layer in the Mo$_2$Ga$_2$C, compared to pure Ga metal, it can be predicted that it is more feasible to synthesize Mo$_2$CT$_x$ MXene from Mo$_2$Ga$_2$C instead of Mo$_2$GaC, which in fact is consistent with the reported synthesis.\textsuperscript{36}

Confident in the method of predicting practically feasible MXene compounds, it should be equally challenging to remove Al from (Cr,Mn)$_2$AlC as it is from Ti$_3$AlC$_2$ because the core-level shift between (Cr$_x$Mn)$_2$AlC (spectra not shown) and pure Al metal is −0.47 ± 0.12 eV. The process to form the not yet synthesized (Cr$_x$Mn)$_2$CT$_x$ MXene compound can, however, be more dependent on other parameters, such as stability of the (Cr$_x$Mn)$_2$C-layers against selected etchant. If that would be the case, then the challenge is to find a new suitable etchant rather than to only facilitate removal of the Al-layers.

To summarize, the curve fitting of pure Ti$_3$AlC$_2$ requires only, in total, five curves representing Ti 2p$_{3/2}$, Ti 2p$_{1/2}$, C 1s, Al 2p$_{2/3}$, and Al 2p$_{1/2}$. All additional curves correspond to impurities, such as TiO$_2$, Al$_2$O$_3$, and graphite-like carbon and contaminations, such as hydrocarbon, alcohol, and carboxyl compounds, which are well separated from the Ti–C components in the Ti 2p, C 1s, and Al 2p spectra but only if the amounts of impurities and contaminations are kept to a minimum. It is therefore very important to handle and store MAX-phase samples properly. Ar$^+$ sputtering prior to XPS acquisition is not an option since preferential sputtering removes O from TiO$_2$ and Al$_2$O$_3$ forming metallic Ti and Al that will show metallic features superimposed on the Ti$_3$AlC$_2$ features in the Ti 2p and Al 2p spectra.

Curve fitting of pure Ti$_3$C$_2$T$_x$ requires additional curves that correspond to the termination species and the effect they have on the Ti 2p. It is therefore crucial that the handling and storage of MXene samples are carefully monitored before an XPS investigation because features from impurities, such as TiO$_2$, can overlap the features from the termination species. Another reason to reduce the amount of impurities to a minimum is that they can adsorb molecules from the atmosphere. Especially, TiO$_2$ is known to adsorb H$_2$O that dissociates into OH$^-$ and a significant amount of TiO$_2$ in a MAX-phase sample or a MXene sample will therefore show a significant amount of OH contribution in an XPS study or, actually, in any study where the selected technique is sensitive toward OH, e.g., nuclear magnetic resonance (NMR).\textsuperscript{36}

An early study of O adsorption on TiC showed that TiO$_2$ is formed after a large exposure to O$_2$ at room temperature,\textsuperscript{55} which is also observed in the present study through the well-resolved Ti 2p$_{3/2}$ and O 1s peaks at 548.8 and 530.4 eV.

Predicting possible conversion of MAX-phases to MXene compounds through estimation of the XPS core-level shift between the A element in a MAX-phase and a pure A element phase is not limited to A equal to Al. It can, for example, also be applied when the A element is Ga, although Ga 3p is less sensitive to the local environment compared to Al 2p. One example is the promising candidate for a high-performance thermoelectric material, the 2D-layered molybdenum carbide (Mo$_2$CT$_x$) MXene.\textsuperscript{36,47} A Ga 3p XPS investigation showed a core-level shift of −0.14 ± 0.06 eV between a pure Ga metal spectrum and a Mo$_2$GaC spectrum, but only a few hundredth of an eV (less than −0.04 eV shift) for the corresponding comparison with the atomic laminate material Mo$_2$Ga$_2$C.\textsuperscript{25}

This implies a significantly reduced electrostatic interaction between the Mo$_2$C-layers and the Ga$_2$-layers in Mo$_2$Ga$_2$C compared to the Ga-layers in Mo$_2$GaC. Based on the significantly smaller Ga 3p core-level shift for the Ga$_2$-layer in the Mo$_2$Ga$_2$C, compared to pure Ga metal, it can be predicted that it is more feasible to synthesize Mo$_2$CT$_x$ MXene from Mo$_2$Ga$_2$C instead of Mo$_2$GaC, which in fact is consistent with the reported synthesis.\textsuperscript{36}

Several studies of O adsorption on TiC showed that TiO$_2$ is formed after a large exposure to O$_2$ at room temperature,\textsuperscript{55} which is also observed in the present study through the well-resolved Ti 2p$_{3/2}$ and O 1s peaks at 548.8 and 530.4 eV.

The Journal of Physical Chemistry C publ.acs.org/JPCC

Published: September 24, 2020 - 27732–27742

https://dx.doi.org/10.1021/acs.jpcc.0c07413

J. Phys. Chem. C 2020, 124, 27732–27742

27739
respectively, as shown in Figures 3c and 6c. Further, the O₂ exposure experiment showed that only a single feature around 530.4 eV is generated.⁵⁵ Yet Figure 6c shows a distinct feature at 531.8 eV, which then must originate from another O-containing species, such as adsorbed OH or H₂O. However, the Ti 2p spectrum in Figure 3c or the C 1s spectrum in Figure 4c does not show any features indicating OH or H₂O adsorption on the TiC surface. A feature at 531.8 eV is, on the other hand, observed when OH is adsorbed on TiO₂.⁴⁰ and it is therefore reasonable to conclude that both the TiC and Ti₃AlC₂ samples contain TiO₂ impurities that are covered with OH. The Ti₃C₂T₄ spectra in Figures 3b and 6b show, on the other hand, no indication of TiO₂ or OH, which suggests that the Ti₃C₂T₄ sample, to some extent, is protected from TiO₂ formation by the termination species O and F, although probably only for a limited exposure time.⁵⁶ The Al₂O₃ components in the Ti₃AlC₂ spectra shown in Figures 5a and 6a are also because of the exposure to the atmosphere prior to the XPS investigation. In addition, the TiC sample shows some small Al₂O₃ contribution, which is because of the sapphire substrate that was used when the Ti₃AlC₂ and TiC samples were produced. The magnetron sputtering technique removes some Al atoms from the substrate that are back-scattered onto the sample surface. (There might also be other sources of Al in the system after previous depositions using Al targets.) The insignificant amount of Al₂O₃ in the Ti₃C₂T₄ sample is, on the other hand, a residuum from the etching process of Ti₃AlC₂.

The comparison between XPS data of TiC, Ti₃AlC₂, Ti₃C₂T₄, and commercially pure Al metal provides evidence of electrostatic interaction between the Al-layers and the 2D Ti₃C₂T₄ layers in the laminated MAX-phase material. The redistribution of the delocalized electrons from the 2D Ti₃C₂T₄ layers to the Al-monolayers will cause changes in the Ti and C valence orbital configurations that will strengthen the covalent Ti–C bonds. The driving force to form the 2D MXene material Ti₃C₂T₄ from the MAX-phase Ti₃AlC₂ is that the termination species can promote more efficient bonding configuration in the Ti₃C₂T₄. The efficiency of the A-layers to attract the delocalized electrons from the Mₙ+1Xₙ-layers determines the difficulty to remove the A-layers from the MAX-phase material. Determination of the binding energy shift between the A-layer core-level position and the corresponding core-level position of the pure A material is, thus, a comparatively easy method to predict new practically feasible MXene compounds.

5. CONCLUSIONS

Through comparison of Ti₃AlC₂ MAX-phase with Ti₃C₂T₄ MXene, cubic TiC, and commercially pure Al-1050, the presented XPS investigation shows a redistribution of the delocalized electrons from the Ti₃C₂T₄ layers to the Al-layers in Ti₃AlC₂. The size of the charge redistribution is comparable to the charge rearrangement between Ti atoms and Al atoms in TiAl alloy. Hence, the laminated layers in the Ti₃AlC₂ are held together through electrostatic interaction between the slightly positively charged Ti₃C₂T₄-layers and the slightly negatively charged Al-layers. This may be one of the properties facilitating MXene synthesis through selective etching of the MAX-phase A-layers. For comparison, the XPS investigation shows that the interaction between the Ti₃C₂T₄-layer and the chemisorbed termination species F and O in 2D Ti₃C₂T₄ is significantly larger. The study further shows that through the determination of the Al 2p and Ga 3d core-level shifts, compared to pure Al and Ga metals, it is possible to predict practically feasible MXene compounds and estimate the challenge to remove the A-layers.

■ AUTHOR INFORMATION

Corresponding Author

Lars-Ake Näshund — Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden; orcid.org/0000-0001-8433-796X; Email: lars-ake.naslund@liu.se

Authors

Per O. Å. Persson — Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden; orcid.org/0000-0001-9140-6724

Johanna Rosen — Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden; orcid.org/0000-0002-5173-6726

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.0c07413

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Dr. Joseph Halim at Linköping University for preparing the Ti₃AlC₂, Ti₃C₂T₄, and TiC samples and providing the XRD diffractograms. The study has partly been accomplished through funding from the Swedish Foundation for Strategic Research (SSF) through program funding (EM16-0004), the Swedish Research Council (VR) grant no. 642-2013-8020, and the KAW Fellowship/Scholar program.

■ REFERENCES

(1) Barsoum, M. W. MAX Phases: Properties of Machinable Carbides and Nitrides; Wiley VCH GmbH & Co.: Weinheim, 2013.

(2) Sun, Z. M. Progress in research and development on MAX phases: a family of layered ternary compounds. Int. Mater. Rev. 2011, 56, 143–166.

(3) Barsoum, M. W. The MXₙ(AXₙ) Phases: A New Class of Solids; Thermodynamically Stable Nanolaminates. Prog. Solid State Chem. 2000, 28, 201–281.

(4) Sokol, M.; Natu, V.; Kota, S.; Barsoum, M. W. On the Chemical Diversity of the MAX Phases. Trends Chem. 2019, 1, 210–223.

(5) Alhabeb, M.; Maleski, K.; Anasori, B.; Lelyukh, P.; Clark, L.; Sin, S.; Gogotsi, Y. Guidelines for Synthesis and Processing of Two-Dimensional Titanium Carbide (Ti₃C₂T₄) MXene. Chem. Mater. 2017, 29, 7633–7644.

(6) Naguib, M.; Kurtoğlu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti₃AlC₂. Adv. Mater. 2011, 23, 4248–4253.

(7) Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Transition Metal Carbides. ACS Nano 2012, 6, 1322–1331.

(8) Xie, Y.; Dall’Agne, Y.; Naguib, M.; Gogotsi, Y.; Barsoum, M. W.; Zhuang, H. L.; Kent, P. R. Prediction and Characterization of MXene Nanosheet Anodes for Non-Lithium-Ion Batteries. ACS Nano 2014, 8, 9606–9615.

(9) Pang, J.; Mendes, R. G.; Bachmatiuk, A.; Zhao, L.; Ta, H. Q.; Gemming, T.; Liu, H.; Liu, Z.; Rummeli, M. H. Applications of 2D
MXenes in energy conversion and storage systems. *Chem. Soc. Rev.* 2019, *48*, 72–133.

(10) Wang, X. H.; Zhou, Y. C. Layered Machinable and Electrically Conductive Ti₃AlC₂ and Ti₄AlN₃ Ceramics: a Review. *J. Mater. Sci. Technol.* 2010, *26*, 385–416.

(11) Naguib, M.; Mohalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th Anniversary Article: MXenes: A New Family of Two-Dimensional Materials. *Adv. Mater.* 2014, *26*, 992–1005.

(12) Medvedeva, N. I.; Enyashin, A. N.; Ivanovskii, A. L. Modeling of the Electronic Structure, Chemical Bonding, and Properties of Ternary Silicon Carbide Ti₃SiC₂. *J. Struct. Chem.* 2011, *52*, 785–802.

(13) Zhou, Y. C.; Wang, X. H.; Sun, Z. M.; Chen, S. Q. Electronic and structural properties of the layered ternary carbide Ti₃AlC₂. *J. Mater. Chem. B* 2001, *1*, 2335–2339.

(14) Mashitlar, O.; Naguib, M.; Dyatkin, B.; Gogotsi, Y.; Barsoum, M. W. Kinetics of aluminum extraction from Ti₃AlC₂ in hydrofluoric acid. *Mater. Chem. Phys.* 2013, *139*, 147–152.

(15) Ivanovskii, A. L.; Medvedeva, N. I. Electronic structure of hexagonal Ti₃AlC₂ and Ti₃AlN₂. *Mendelev Commun.* 1999, *9*, 36–38.

(16) Myhra, S.; Crossley, J. A. A.; Barsoum, M. W. Crystal-chemistry of the Ti₃AlC₂ and Ti₃AlN₂ layered carbide/nitride phases – characterization by XPS. *J. Phys. Chem. Solids* 2001, *62*, 811–817.

(17) Barsoum, M. W.; Crossley, A.; Myhra, S. Crystal-chemistry from XPS analysis of carbide-derived Mn⁺¹AX₂ (n = 1) nano-laminate compounds. *J. Phys. Chem. Solids* 2002, *63*, 2063–2068.

(18) Sun, Z.; Music, D.; Ahuja, R.; Li, S.; Schneider, J. M. Bonding and classification of nanolaminated ternary carbides. *Phys. Rev. B* 2004, *70*, No. 092102.

(19) Magnuson, M.; Palmquist, J.-P.; Mattesini, M.; Li, S.; Ahuja, R.; Eriksson, O.; Emmerlich, J.; Wilhelmsson, O.; Ekldun, P.; Höberg, H.; Hultman, L.; et al. Electronic structure investigation of Ti₃AlC₂, Ti₃SiC₂, and Ti₃GeCₓ by soft x-ray emission spectroscopy. *Phys. Rev. B* 2005, *72*, No. 245101.

(20) Magnuson, M.; Wilhelmsson, O.; Palmquist, J.-P.; Jansson, U.; Mattesini, M.; Li, S.; Ahuja, R.; Eriksson, O. Electronic structure and chemical bonding in Ti₃AlC₂ investigated by soft x-ray emission spectroscopy. *Phys. Rev. B* 2006, *74*, No. 195108.

(21) Mauchamp, V.; Bugnet, M.; Chartier, P.; Cabioc’h, T.; Jaouen, M.; Vinson, J.; Jorissen, K.; Rehr, J. J. Interplay between many-body effects and charge transfers in Cr₂C₃ bulk plasmon excitation. *Phys. Rev. B* 2012, *86*, No. 125109.

(22) Zhou, Y. C.; Chen, J. X.; Wang, J. W. Strengthening of Ti₃AlC₂ by incorporation of Si to form Ti₃Si₃Al₃C₂ solid solutions. *Acta Mater.* 2006, *54*, 1317–1322.

(23) Cabioc’h, T.; Ekldun, P.; Mauchamp, V.; Jaouen, M.; Barsoum, M. W. Tailoring of the thermal expansion of Cr₂(Al₇Ge₁₂₋ₓ)Cₓ phases. *J. Eur. Ceram. Soc.* 2013, *33*, 897–904.

(24) Hu, C.; Lai, C.-C.; Tao, Q.; Lu, J.; Halim, J.; Sun, L.; Zhang, J.; Yang, J.; Anaour, B.; Wang, J.; et al. Mo₄Ga₂C: a new ternary nanolaminated carbide. *Chem. Commun*. 2015, *51*, 6560–6563.

(25) Lai, C.-C.; Meshkian, R.; Dahlqvist, M.; Lu, J.; Näslund, L.-Å.; Rivin, O.; Caspi, E. N.; Ozeri, O.; Hultman, L.; Ekldun, P.; et al. Structural and chemical determination of the new nanolaminated carbide Mo₄Ga₂C from first principles and materials analysis. *Acta Mater.* 2015, *99*, 157–164.

(26) Meshkian, R.; Näslund, L.-Å.; Halim, J.; Lu, J.; Barsoum, M. W.; Rosen, J. Synthesis of two-dimensional molybdenum carbide, Mo₇C₂ from the gallium based atomic laminate Mo₄Ga₂C Cr₃. *Mater. Sci.* 2015, *108*, 147–150.

(27) Halim, J.; Cook, K. M.; Naguib, M.; Ekldun, P.; Gogotsi, Y.; Rosen, J.; Barsoum, M. W. X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes). *Appl. Surf. Sci.* 2016, *362*, 406–417.

(28) Persson, I.; Näslund, L.-Å.; Halim, J.; Barsoum, M. W.; Darakchieva, V.; Palaisitis, J.; Rosen, J.; Persson, P. O. Å. On the organization and thermal behavior of functional groups on Ti₃AlC₂ MXene surfaces in vacuum. *2D Mater.* 2018, *5*, No. 015002.

(29) Grechnyi, G.; Hultman, L. Compromising Science by Ignorant Instrument Calibration—Need to Revisit Half a Century of Published XPS Data. *Angew. Chem., Int. Ed.* 2020, *59*, 5002–5006.

(30) Grechnyi, G.; Hultman, L. X-ray photoelectron spectroscopy: Towards reliable binding energy referencing. *Prog. Mater. Sci.* 2020, *107*, No. 100591.
of Paired Hydroxyl Groups on Reduced TiO$_2$(110). *Phys. Rev. Lett.* 2006, 96, No. 066107.

(50) Lauritsen, J. V.; Foster, A. S.; Olesen, G. H.; Christensen, M. C.; Kühnle, A.; Helveg, S.; Rostrup-Nielsen, J. R.; Clausen, B. S.; Reichling, M.; Besenbacher, F. Chemical identification of point defects and adsorbates on a metal oxide surface by atomic force microscopy. *Nanotechnology* 2006, 17, 3436–3441.

(51) Bikondoa, O.; Pang, C. L.; Ithnin, R.; Muryn, C. A.; Onishi, H.; Thornton, G. Direct visualization of defect-mediated dissociation of water on TiO$_2$(110). *Nat. Mater.* 2006, 5, 189–192.

(52) Pang, C. L.; Sasahara, A.; Onishi, H.; Chen, Q.; Thornton, G. Noncontact atomic force microscopy imaging of water dissociation products on TiO$_2$(110). *Phys. Rev. B* 2006, 74, No. 073411.

(53) Zhang, Z.; Bondarchuk, O.; Kay, B. D.; White, J. M.; Dohnálek, Z. Imaging Water Dissociation on TiO$_2$(110): Evidence for Inequivalent Geminate OH Groups. *J. Phys. Chem. B* 2006, 110, 21840–21845.

(54) Hope, M. A.; Forse, A. C.; Griffith, K. J.; Lukatskaya, M. R.; Ghidiu, M.; Grey, C. P. NMR reveals the surface functionalisation of Ti$_3$C$_2$ MXene. *Phys. Chem. Chem. Phys.* 2016, 18, 5099–5102.

(55) Frantz, P.; Didziulis, S. V. Detailed spectroscopic studies of oxygen on metal carbide surfaces. *Surf. Sci.* 1998, 412/413, 384–396.

(56) Magnuson, M.; Halim, J.; Nåslund, L.-Å. Chemical bonding in carbide MXene nanosheets. *J. Electron Spectrosc. Relat. Phenom.* 2018, 224, 27–32.