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Mo₂TiAlC₂: A New Ordered Layered Ternary Carbide

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Abstract

Herein we report on the synthesis of a new layered ternary carbide, viz. Mo₂TiAlC₂, that was synthesized by heating an elemental mixture at 1600 °C for 4 h under Ar flow. Its lattice parameters were calculated via Rietveld analysis of powder X-ray diffraction patterns to be 2.997 Å and 18.661 Å. High-resolution scanning transmission electron microscopy further showed that this phase is ordered, with the Ti layers sandwiched between two Mo layers in a M₃AX₂ type layered ternary carbide structure.

Keywords: Ordered MAX phases, Ternary carbides

The MAX phases are a large family of hexagonal, ternary, carbides and nitrides with a general formula $M_{n+1}AX_n$, (MAX) where $n = 1, 2, 3$ etc., M is an early transition metal (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and etc.), A is a group 13 to 16 element (Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As etc.) and X is carbon and/or nitrogen [1-3]. These phases combine some of the best attributes of metals and ceramics, which can be attributed to their thermodynamically nanolaminated layered structure and the metal-like nature of their bonding. Like metals, they are electrically and thermally conductive, most readily machinable [4, 5], not susceptible to thermal shock, plastic at high temperatures, and exceptionally damage tolerant [6]. Like ceramics, some of them are elastically rigid (Young's moduli > 300 GPa), lightweight (≈ 4 Mg/m³), maintain their strengths to high temperatures [1, 3] and some of them are creep and oxidation resistant [7-10].

Among the more than 70+ different MAX phases that have been synthesized to date, some of the Al-containing ones, notably Ti_2AlC , have attracted the most attention due to their exceptional oxidation resistance as a result of thin protective alumina layer that forms on its surface [7, 10, 11]. More recently, crack self-healing characteristics have also been reported during oxidation of Ti_2AlC and Ti_3AlC_2 [12, 13].

Based on all the studies carried out over the past 60 years, only certain M elements can be combined with certain A elements to form MAX phases. For instance, Al containing MAX phases can only have Ti, V, Cr, Nb and Ta as their M elements. Conversely, Mo, Hf, Zr, and others do not form Al-containing MAX phases. Furthermore, almost all solid solution MAX phases synthesized to date follow similar rules. There are few exceptions wherein a solid solution contains a M element, that does not generally bond to Al, such as Zr in $(Nb_{0.8},Zr_{0.2})_2AlC$ [14], and $(Nb_{0.6},Zr_{0.4})_2AlC$ [15],

and Mn in $(\text{Cr}_{0.7}, \text{Mn}_{0.3})_2\text{GaC}$ [16]. In both examples the mass fraction of the non-Al bonding M element is less than 0.5 of the total M-content.

Recently, Liu et al. reported on synthesizing of $\text{Cr}_2\text{TiAlC}_2$, from Cr_2AlC and TiC [17]. Based on their neutron diffraction data, they concluded that the Cr-layers sandwiched the Ti-layers in a M_3AX_2 MAX phase structure. Even more recently, Caspi et al. used high-resolution neutron diffraction to show that when $n = 2$, in the $(\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n$ system, the V and Cr atoms showed a strong tendency to ordering, with V only occupying the middle layer. Said otherwise, the 2a (000) sites were fully occupied by vanadium [18].

Of special interest to this work are Mo-containing MAX phases. To date the only known Mo-containing MAX phase was Mo_2GaC [19]. In this study, for the first time, we report on a new Mo-containing ordered MAX phase, $\text{Mo}_2\text{TiAlC}_2$. In this phase, which is isostructural with Ti_3SiC_2 [4, 20], the Ti atoms are sandwiched between two Mo-layers that in turn are adjacent to the Al planes resulting in a Mo-Ti-Mo-Al-Mo-Ti-Mo stacking order. The C-atoms are in between the Mo and Ti layers.

To synthesize this compounds elemental powders of Mo, Ti, Al and graphite (all from Alfa Aesar, Ward Hill, MA), with mesh sizes of -250, -325, -325 and -300, respectively, were mixed in the molar ratio of Mo:Ti:Al:C 2:1:1.1:2 with zirconia milling balls, in plastic jars, for 18 h. The powder mixture was then placed in a covered alumina crucible and heated at a rate of 5 °C/min to 1600 °C and held for 4 h under flowing argon (Ar). After furnace cooling, the slightly sintered porous compact was milled into a fine powder using a TiN-coated milling bit.

X-ray diffraction (XRD) was carried out on a diffractometer (Rikagu Smartlab, Tokyo, Japan), using step scans of 0.02° in the 3° – 120° 2θ range with a step time of 7 s with a $10 \times 10 \text{ mm}^2$ window slit. Scans were made with Cu-K α radiation (40 kV and 44 mA). Ten wt.% silicon powder was added to the sample powder for XRD as an internal standard to calibrate the diffraction angles and instrumental peak broadening.

The XRD diffractograms were analyzed by the Rietveld refinement method, using the FULLPROF code [21, 22]. Refined parameters were: five background parameters, scale factors from which relative phase fractions are evaluated, X and Y profile parameters for peak width, lattice parameters (LPs) and atomic positions for all phases. High resolution scanning electron microscopy (HRSTEM) and X-ray energy dispersive spectroscopy (EDX) were carried out with the a double corrected FEI Titan3 60–300 operated at 300 kV, equipped with the Super-X EDX system. Selected area electron diffraction (SAED) characterization was performed using a FEI Tecnai G2 TF20 UT instrument equipped with a field emission gun runs at a voltage of 200 kV and a point resolution of 0.19 nm.

The specimens were prepared by embedding the MAX powder in a Ti grid, reducing the Ti-grid thickness down to 50 μm via mechanical polishing and finally Ar $^+$ ion milling to reach electron transparency.

Figure 1a shows the XRD pattern obtained from the powder. Each peak is labeled on the pattern. Figure 1b compares the experimental XRD pattern (black) with the calculated pattern obtained from the Rietveld analysis (red) from $2\theta = 21$ to 120° . The difference between the two is shown in (blue). The χ^2 value was 2.44, which shows the good agreement between model and measured data. The sample was found to be a

predominately pure $\text{Mo}_2\text{TiAlC}_2$ phase. $\text{Mo}_2\text{TiAlC}_2$ a -LP and c -LP were calculated from the refinement to be 2.99703(4) and 18.6608(3) Å, respectively.

Small peaks of a M_2AX phase were also identified as the only impurity in the powder. A solid solution $(\text{MoTi})_2\text{AlC}$ showed a very good fit with it. The $(\text{MoTi})_2\text{AlC}$ a - and c -LPs were calculated from the refinement to be 3.021(5) and 11.756(4) Å, respectively. The reported uncertainties of all structural values determined from Rietveld refinement are the uncertainties of the refinement process and are mainly of statistical origin. From the refined LPs of the internal Si standard, we evaluate the systematic uncertainty to be < 0.01 %. In $\text{Mo}_2\text{TiAlC}_2$, the refinement calculated z -coordinate for Mo at the x, y coordinates of (2/3, 1/3) was 0.13327(6) and for C at x, y coordinates of (1/3, 2/3) was 0.0691(5). In $(\text{MoTi})_2\text{AlC}$ the z -coordinate for M (Mo and Ti) at the x, y coordinates of (1/3, 2/3) was 0.069(2).

Given the 2:1 ratio of Mo:Ti and based on the recent work showing ordering of the M-atoms in $\text{Cr}_2\text{TiAlC}_2$ [17], it was reasonable to assume that this phase was ordered as well. A schematic of such a unit cell is shown as an inset in Fig. 1. HRTEM images of a sample along the $[11\bar{2}0]$ zone axis with its SAED are shown in Figs. 2a and c, respectively. Figure 2d shows the SAED along the $[1\bar{1}00]$ zone axis. The a - and c -LP were measured from SAED images to be 2.93(3) and 18.9(7) Å, both values in good agreement with those measured from the XRD patterns.

Figure 2b is the overlap of Fig. 2a and the total EDX mapping, in which the Mo, Ti and Al atoms are shown in blue, green and red, respectively. Based on this map it is clear that every green, or Ti, layer is sandwiched between two blue, or Mo, layers. Figure 2e shows an EDX line scan along the $[11\bar{2}0]$ axis of the micrograph shown in Fig. 2f.

The Mo, Ti and Al lines have the same coloring as in Fig. 2b. In other words, the line scan confirms the ordering sequence.

Based on the totality of our results it is thus reasonable to conclude that Mo_2TiAlC , is highly ordered, with the Mo layers sandwiching the Ti- layers in a structure that is iso-structural with Ti_3SiC_2 [20]. In this compound the layer sequence – excluding C – is: Al-Mo-Ti-Mo-Al-Mo-Ti-Mo etc.

It is worth noting that $(\text{MoTi})_2\text{AlC}$ was the only other phase detected in the XRD patterns. This M_2AX phase is thus also a new solid solution in the MAX phase family that to date has not been reported. However, given its chemistry, it is unlikely that this MAX phase is ordered. This comment notwithstanding, more work should be dedicated to synthesizing and characterizing this new phase.

The importance of this work lies beyond the compounds made herein, since it opens up a new avenue to make MAX phases with bonds that had not been previously observed. For example, in this work the MAX phase created contains Mo-Al bonds. As noted in the introduction, before this work the only Mo-containing MAX phase was comprised of Mo-Ga-Mo layers. We note in passing that Mo_3AlC_2 does not exist and it follows that the Ti layer is crucial in stabilizing it and lowering its energy.

The fact that Mo is on the outer layers of M sites might lead to different properties for this new phase than a regular Ti-Al containing solid solution. The implications for totally new MXenes chemistries has also not escaped us and will be the subject of a separate forthcoming paper.

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Figure Captions

Figure 1. (a) Powder XRD patterns of $\text{Mo}_2\text{TiAlC}_2$, black rectangles show location of Si powder peaks, added as an internal standard; Inset shows schematic of $\text{Mo}_2\text{TiAlC}_2$ unit cell. (b) Powder XRD patterns of $\text{Mo}_2\text{TiAlC}_2$, observed pattern (black crosses), Rietveld generated pattern (red line) and difference between the two (blue line). The black and blue ticks below the pattern represent the peak positions of the $\text{Mo}_2\text{TiAlC}_2$ phase, and Si phase, respectively.

Figure 2. (a) HRSTEM of $\text{Mo}_2\text{TiAlC}_2$ along the $[11\bar{2}0]$ zone axis, (b) the overlap of EDX mapping on (a) showing the Mo atoms in blue, Ti atoms in green and Al atoms in red, (c) and (d) SEAD of $\text{Mo}_2\text{TiAlC}_2$ along the $[11\bar{2}0]$ and $[1\bar{1}00]$ zone axes, respectively, (e) EDX line scan profile of Mo (blue circles), Ti (green squares), and Al (red triangles), (f) STEM of the EDX line scanned region the results of which are shown in (e).

Fig. 1

Fig. 2