New Solid Solution MAX Phases: \((Ti_{0.5}, V_{0.5})_3AlC_2\), \((Nb_{0.5}, V_{0.5})_2AlC\), \((Nb_{0.5}, V_{0.5})_4AlC_3\) and \((Nb_{0.5}, Zr_{0.2})_2AlC\)

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We synthesized the following previously unreported aluminum-containing solid solution M\(_{n+1}\)AX\(_n\) phases: \((Ti_{0.5}, V_{0.5})_3AlC_2\), \((Nb_{0.5}, V_{0.5})_2AlC\), \((Nb_{0.5}, V_{0.5})_4AlC_3\) and \((Nb_{0.5}, Zr_{0.2})_2AlC\). Rietveld analysis of powder X-ray diffraction patterns was used to calculate the lattice parameters and phase fractions. Heating Ti, V, Al and C elemental powders—in the molar ratio of 1.5:1.5:1.3:2—for 2 h in flowing argon, resulted in a predominantly phase pure sample of \((Ti_{0.5}, V_{0.5})_3AlC_2\). The other compositions were not as phase pure and further work on optimizing the processing parameters needs to be carried out if phase purity is desired.

**Keywords**: MAX Phase, Solid Solution, Rietveld Analysis, HRTEM, Lattice Parameter

1. Introduction

The world of ceramic materials has been enriched significantly over the last two decades by the discovery of the M\(_{n+1}\)AX\(_n\) (MAX) phases. The latter is a large, unique family \((70+\) phases) of layered hexagonal \((\text{space group } P6_3/mmc)\) compounds with a composition of \(M_{n+1}AX_n\), where \(M\) is an early transition metal (Sc, Ti, V, Cr, Nb, etc.), \(A\) is a group A element (mainly groups 13–16; Al, Si, Sn, In, etc.), \(X\) is carbon and/or nitrogen and \(n = 1, 2\) or \(3\).[1] The uniqueness of the MAX phases comes from their layered structure and metal-like nature of their bonding. They thus combine both metal and ceramic characteristics.[2] For example, similar to ceramics, some are quite stiff[3] and corrosion,[4] oxidation, and creep resistant. Similar to metals, they have high electrical and thermal conductivities, are not prone to thermal shock, and are most readily machinable.

Among the plentiful MAX phases, the Al-containing members have attracted the most attention, since some of them, such as Ti\(_2\)AlC and Ti\(_3\)AlC\(_2\), have exceptional oxidation resistance due to the formation of a thin alumina layer.[5,6] They also exhibit self-healing characteristics, wherein cracks that form are filled with alumina.[7,8]

Since each MAX phase has its own characteristic properties, combining different transition metals on the M-sites to form solid solutions is a further approach to tailoring properties. Table 1 lists all solid solution MAX phases known to date. The solid solutions are separated by the values of \(n\), as well by the elements that constitute the solid solution.

Note that some solid solutions allow for the formation of certain M atom containing MAX phases with \(n\) values that are not possible with the end members. For example, neither \(V_3AlC_2\) nor \(Cr_3AlC_2\) was reported experimentally, but \((V_{0.5}, Cr_{0.5})_3AlC_2\) was successfully synthesized.[26]

In terms of mechanical properties, the effects of solid solution are highly dependent on the system chosen. For example, substituting 20% of the Ti atoms with V in Ti\(_2\)AlC resulted in 45% increase in compressive strength.[9] Similarly, Meng et al. [9] found that a 15% substitution of V resulted in an increase in the Vicker hardness, \(H_v\), at 10 N, from 3.5 GPa for the end member, Ti\(_2\)AlC, to 4.5 GPa. Conversely, substitution of half the Ti with Nb in Ti\(_2\)AlC [37] did not lead to solid solution hardening, nor did the substitution of 50% Si with Ge in Ti\(_3\)SiC\(_2\).[32]

Another point of interest with solid solutions is their effect on thermal expansion. Barsoum et al. [38] found that the solid solution \((Ti_{0.5}, Nb_{0.5})_2AlC\) has
slightly greater thermal expansion coefficient (TEC) than its end members, 8.9 × 10^{-6} K^{-1} compared with 8.7 × 10^{-6} K^{-1}. A similar result, but of a greater difference, was found by Finkel et al. [39] with Ti3(Ge0.43, C0.56)C2 in the 323–1,473 K range. The TEC of the end members, Ti3SiC2 and Ti3GeC2, are 8.9 × 10^{-6} and 7.8 × 10^{-6} K^{-1}, respectively. The x = 0.5 solid solution has a TEC of 9.3 × 10^{-6} K^{-1}, suggesting a destabilization in the solid solution structure at a higher temperature. It must be noted, however, that more recently, Lane et al. [40] yielded a TEC value of 8.5 × 10^{-6} K^{-1} for Ti3GeC2, placing it more in line with the other results. The TECs of the end members and solid solution compositions in the Cr2(Al0.43, Ge0.56)xC system were more recently measured by Cabioch et al. [19] in the 298–1,073 K range. The results show that, with an increase in the AI content, the TEC along the [010] remains fairly constant at 14(1) × 10^{-6} K^{-1}, while the TEC in the [001] direction decreases from 17(1) × 10^{-6} K^{-1} to about 12(1) × 10^{-6} K^{-1}. More importantly, they found that for Cr2(Al0.43, Ge0.56)xC composition, the TECs along the two directions are equal, thus showing the possibility of TEC tailoring by the use of solid solution compounds. Probably the most significant effect of solid solutions is their effect on magnetic properties. For example, while Cr2AlC is a paramagnetic material, doping it with small amounts of Mn renders it magnetic with a Curie temperature that is a function of Mn content.[41–43] In general, the effects of solid solutions on mechanical, thermal, and especially magnetic properties is still a wide-open field of study. This is especially true since many solid solutions are yet to be discovered. Herein, we report on the following new solid solution, AI-containing, MAX phases: (Ti0.6, V0.4)x1.8AlC2, (Nb0.6, V0.4)x2AlC2, (Nb0.6, V0.4)x4AlC3, and (Nb0.6, Zr0.4)x2AlC. It is important to note that Reifenstein et al. [44] synthesized a (Nb0.6, Zr0.4)x2AlC phase, with a and c-lattice parameters (LPs) of 3.19 and 14.3 Å, respectively.

2. Experimental Details Powders, the characteristics of which are given in Table 2, were mixed in the atomic ratios listed in Table 3 using zirconia balls in

Table 1. List of the 68 solid solutions known to date.

| 211 (n = 1) | M element | Ti5(Al0.5, V0.5)x1.8AlC2 (x = 0.25, 0.75) [9–11] |
| 212 (n = 2) | A element | Ti3(Al0.43, Ge0.56)x1.8AlC2 (x = 0.5) [25] |
| 312 (n = 3) | X element | Ti3AlC, Ni1−xC (x = 0.5) [35] |

*aThis work.*

### Table 2. Source and characteristics of powders used.

| Powder     | Purity (wt%) | Particle size | Source                  |
|------------|--------------|---------------|-------------------------|
| Titanium   | 99.5         | −325 mesh     | Alfa Aesar, Ward Hill, MA, USA |
| Vanadium   | 99.0         | −325 mesh     | Alfa Aesar, Ward Hill, MA, USA |
| Niobium    | 99.8         | −325 mesh     | Alfa Aesar, Ward Hill, MA, USA |
| Zirconium  | 99.5         | 50 mesh       | Atlantic Equipment Engineers, Upper Saddle River, NJ, USA |
| Aluminum   | 99.5         | −325 mesh     | Alfa Aesar, Ward Hill, MA, USA |
| Graphite   | 99.0         | −300 mesh     | Alfa Aesar, Ward Hill, MA, USA |
plastic jars for 18 h. The initial concentration of the Al was set to be slightly higher than the stoichiometry, to minimize the formation of the transition metal binary carbides. After mixing, the powders were placed in alumina crucibles and heated at a rate of 5°C/min under argon, Ar, flow in a tube furnace to the soaking temperatures and times listed in Table 3. After furnace cooling, the resulting lightly sintered porous compacts were machined into a fine powder using a TiN-coated milling bit.

To characterize the phases present in each sample, X-ray diffraction (XRD) of the powders, filling a groove of 20 × 20 × 1 mm³ dimensions in a glass holder, was carried out using a diffractometer (Rigaku, SmartLab, Tokyo, Japan) with Cu-Kα radiation (step scan 0.02° 2θ, 6–7 s per step). The incident slit size was 10 mm. Silicon (Si) powder (10 wt%) was added to every sample to act as an internal standard to calibrate the diffraction angles and instrumental peak broadening.

Rietveld refinements of the XRD patterns were conducted using FullProf [45]. Refined parameters were: six background parameters, LPs of all phases, scale factors from which relative phase fractions are evaluated, X profile parameters for peak width, atomic positions and global isotropic thermal displacement parameter for the major phases. Because of the predominantly pure phase (Ti0.5,V0.5)3AlC2, anisotropic thermal displacement parameter for the major phase was refined.

High-resolution transmission electron microscope (HRTEM) micrographs and selected area electron diffraction (SAED) of cross-sectional samples of (Ti0.5,V0.5)3AlC2 and (Nb0.5,V0.5)3AlC were obtained using FEI Tecnai G2 TF20 UT equipped with a field emission gun at a voltage of 200 kV and 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.

3. Results and Discussion
The XRD pattern obtained when the initial elemental ratios were those corresponding to (Ti0.5,V0.5)3AlC2 is shown in Figure 1(a) (black symbols) together with the calculated pattern obtained

| Starting composition (atomic ratio) | Soaking parameters | Resulted phases, wt% from Rietveld refinement of XRD |
|-----------------------------------|-------------------|-----------------------------------------------------|
| Ti:V:Al:C 1.5:1.5:1:3:2:0 | 1,450, 2 | 90.60(3)% (Ti0.5,V0.5)3AlC2, 9.40(8)% TiC |
| V:Nb:Al:C 1.0:1.0:1.3:1:0 | 1,550, 2 | 71.83(2)% (Nb0.5,V0.5)2AlC, 16.39(2)% (Nb0.5,V0.5)4AlC, 11.78(2)% Al3Nb |
| Nb:Zr:Al:C 1.5:0.5:1.1:1 | 1,600, 4 | 90.31(2)% (Nb0.8,Zr0.2)2AlC, 1.1(2)% Zr5Al3, 8.59(4)% ZrC |

Figure 1. Powder XRD patterns of sample with (Ti0.5,V0.5)3AlC2 starting composition: (a) observed pattern (black crosses), Rietveld generated pattern (red lines) and difference between the two (blue lines). The black and blue ticks below the pattern represent the peak positions of the 312 phase and TiC phase, respectively; (b) shown in center. The two other patterns were generated by Materials Studio assuming LPs listed in Table 4 for Ti3AlC2 [46] and V3AlC2 [47].
Table 4. Summary of the LPs and z-coordinates of the solid solutions obtained herein by Rietveld analysis of the XRD data, and those previously reported for their end members.

| MAX phase | a-LP (Å) | c-LP (Å) | Atom (Wyckoff) | z-Coordinate | Ref. |
|-----------|---------|---------|----------------|------------|------|
| (Ti0.5, V0.5)3AlC2 | 2.99941(6) | 18.1494(7) | Ti/V (4f) | 0.1294(2) | 0.0701(7) | This work |
| Ti3AlC2 | 3.075 | 18.578 | Ti (4f) | 0.128 | [46] |
| V3AlC2 | 2.908a | 17.778a | V (4f) | 0.1298 | [47] |
| (Nb0.5, V0.5)2Al2C | 3.0098(1) | 13.488(1) | Nb/V (4f) | 0.0903(2) | [48] |
| (Nb0.5, V0.5)2AlC | 3.04 | 13.5 | Nb/V (4f) | 0.0554(3) | [49] |
| V2AlC | 3.106 | 13.888 | Nb/V (4f) | 0.1585(3) | [50] |
| (Nb0.5, V0.5)4AlC3 | 3.0961(2) | 23.821(2) | Nb/V (4f) | 0.0554(3) | [51] |
| Nb4AlC3 | 3.13 | 24.121 | Nb (4e) | 0.1574 | [52] |
| V4AlC3 | 2.931 | 22.719 | V (4e) | 0.1548 | [53] |
| (Nb0.8, Zr0.2)2Al2C | 3.13468(8) | 14.0003(7) | Nb/Zr (4f) | 0.0914(1) | This work |
| (Nb0.4, Zr0.4)2Al2C | 3.19 | 14.3 | Nb/Zr (4f) | 0.0554(3) | [44] |
| Nb2AlC | 3.106 | 13.888 | Nb/Zr (4f) | 0.1086 | [37] |
| Zr2AlC | 3.255a | 14.570a | Nb/Zr (4f) | 0.1086 | [44] |

Note: When reported, numbers in parentheses represent one standard deviation of the last significant digit.
aEstimated from theoretical calculations, not experimental.

from the Rietveld analysis (red lines); the difference between the two is shown in blue. The \( \chi^2 \) value was 3.918. The sample was found to be a predominately pure solid solution, at 72(1) wt%, with 7.4(6) wt% TiC, along with the Si that was added as an internal standard, 21.1(5) wt%. The \( a \)-LP and \( c \)-LP were calculated from the refinement to be 2.99941(6) and 18.1494(7) Å, respectively. Henceforth, 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 LP of the internal Si standard, we evaluate the systematic uncertainty to be < 0.04%. This value is similar for all refinements reported here. The solid solution’s \( a \) and \( c \) LP values are situated approximately halfway between the \( a \) and \( c \) LP of the end members (Table 4).

This is best seen in Figure 1(b) where the observed XRD patterns are compared with those calculated using Materials Studio [52] for the end members, assuming the LPs listed in Table 4. The \( z \)-coordinates of the Ti/V atoms, as well as the C atoms, obtained from refinements were 0.1294(2) and 0.0701(7), respectively.

HRTEM images of the sample along the [11\( \bar{2} \)0] zone axis with its SAED can be seen from Figure 2(a) and 2(b). From the transmission electron microscope (TEM) and SAED images, the \( a \)-LP and \( c \)-LP were measured to be 3.02 and 18.3 Å, respectively. For all samples, \( a \)-LP and \( c \)-LP were measured with an estimated uncertainty of <1%.

The difference between the \( a \)-LP obtained from XRD and TEM is about 0.9%; that of the \( c \)-LP is 0.8%, less than the estimated uncertainty of the LPs determined by TEM. The results obtained through Rietveld refinement confirm these values.

The XRD pattern obtained when the starting molar stoichiometric ratios of Nb, V, Al and C were all equal is shown in Figure 3(a) (black symbols) together with the calculated pattern obtained from the Rietveld analysis (red lines); the difference between the two is shown in blue. The \( \chi^2 \) value was 1.677. In this case three phases were detected: (Nb0.5, V0.5)2Al2C, (Nb0.5, V0.5)4AlC3 and Al1Nb. Their respective weight percents were 64.0(7), 14.6(3) and 10.5(2) wt%. The Si added as an internal standard accounts for the remaining 10.9(5) wt%. The \( a \)-LP and \( c \)-LP for the (Nb0.5, V0.5)2Al2C phase solid solution were calculated to be 3.0098(1) and 13.488(1) Å, respectively. Not surprisingly, these values, again, fall between the values of the end members (Figure 3(b) and Table 4). The refinement calculated a \( z \)-coordinate value of 0.0903(2) for the V/Nb atoms found in the \( n = 1 \) phase. For the \( n = 3 \) phase, the \( z \)-coordinate for the V/Nb atoms at the \( x,y \)-coordinates (0,0) was 0.1585(3) and at the \( x,y \)-coordinates of (1/3,2/3) was 0.0544(3).
As for the C atoms, a \( z \) coordinate value of 0.110(2) was determined.

At 3.0961(2) and 23.821(2), the \( a \)-LP and \( c \)-LP values for the \((\text{Nb}_{0.5}, \text{V}_{0.5})_4\text{AlC}_3\) phase, respectively, were also between the values of the end members (Table 4). The HRTEM image in Figure 2(c) shows \((\text{Nb}_{0.5}, \text{V}_{0.5})_2\text{AlC}\) along the \([11\bar{2}0]\) zone axis with its SAED, Figure 2(d). From the TEM and SAED images, \( a \)-LP and \( c \)-LP were calculated to be 2.99 and 13.55 Å respectively. The difference between the \( a \)-LP obtained from XRD and TEM is about 0.6%; that of \( c \)-LP is 0.4%, less than the estimated uncertainty of the LPs determined by TEM. HRTEM images of the \( n = 3 \) phase along the \([11\bar{2}0]\) zone axis with its SAED are shown in Figure 2(e) and 2(f), respectively. The \( a \)-LP and \( c \)-LP were measured at 3.12 and 23.73 Å, respectively. The difference between the \( a \)-LP obtained
4. Conclusion

Herein, we reported on the synthesis of the previously unreported solid solution MAX phases, \((\text{Ti}_{0.5}, \text{V}_{0.5})_2\text{AlC}_2\), \((\text{Nb}_{0.5}, \text{V}_{0.5})_2\text{AlC}_3\), and \((\text{Nb}_{0.8}, \text{Zr}_{0.2})_2\text{AlC}\), as well as the \((\text{Nb}_{0.8}, \text{Zr}_{0.2})_2\text{AlC}\) phase. Using Rietveld analysis of XRD patterns, the LPs and phase fractions were calculated. In all cases, the LPs of the new solid solution phases were in between those of their end members. By heating a powder mixture, with Ti:V:Al:C from XRD and TEM is about 0.7%; that of c-LP is 0.4%. Again, these values are relatively close, confirming the overall methodology used in this work.

The XRD pattern obtained when the initial elemental ratios were those corresponding to \((\text{Nb}_{0.8}, \text{Zr}_{0.2})_2\text{AlC}\) is shown in Figure 4(a) (black symbols), together with the calculated pattern obtained from the Rietveld analysis (red lines); the difference between the two is shown in blue. The \(\chi^2\) value was 3.476. Here again three phases were detected: \((\text{Nb}_{0.8}, \text{Zr}_{0.2})_2\text{AlC}, \text{Zr}_5\text{Al}_3\) and \(\text{ZrC}\) phases. The respective wt\% were: 82.0(7), 1.0(2) and 7.8(3). At 9.2(3) wt\%, the Si accounts for the balance.

The \(a\)-LP and \(c\)-LP for the \((\text{Nb}_{0.8}, \text{Zr}_{0.2})_2\text{AlC}\) phase were calculated to be 3.13468(8) and 14.0003(7), respectively. As noted above, Reiffenstein et al. [44] were the first to report on a 211 phase in the Nb–Zr–Al–C system, namely \((\text{Nb}_{0.6}, \text{Zr}_{0.4})_2\text{AlC}\). The \(a\) and \(c\)-LPs of the latter were 3.19 and 14.3 Å. In the same paper, the \(a\) and \(c\) LPs of the fictitious \(\text{Zr}_2\text{AlC}\) phase were estimated to be 3.25 and 14.5 Å. These values were used to generate the XRD pattern for \(\text{Zr}_2\text{AlC}\) shown in Figure 4(b). The \(z\)-coordinate of the Nb/Zr atoms was determined by Rietveld refinement to be 0.0914(1).
molar ratios of 1.5:1.5:1.3:2.0, at 1, 450°C for 2 h resulted in a predominantly phase pure (Ti₀.₅, V₀.₅)₁₃AlC₂ sample. The other compositions were not as phase pure and further work on optimizing the processing parameters needs to be carried out if phase purity is desired.

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