Ordered (Cr,V) Layers in Nanolamellar (Cr$_{0.5}$V$_{0.5}$)$_{n+1}$AlC$_n$ Compounds

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Nanolamellar MAX phase compounds (Cr$_{0.5}$V$_{0.5}$)$_{n+1}$AlC$_n$ are formed with $n = 1$, 2 and 3, and their 300 K structure is studied in detail by high-resolution neutron diffraction. While the $n = 1$ compound is found to have complete disordering of vanadium and chromium in the metallic layers, the $n = 2$ and 3 compounds show strong tendency for these elements' ordering, with the layer in the 2a(0,0,0) site of (Cr$_{0.5}$V$_{0.5}$)$_2$AlC$_2$ fully occupied by vanadium. The thermal expansion dependency of temperature is also studied by neutron diffraction for 2 < T < 550 K, revealing a negligible thermal expansion below 100 K for all of the compounds.

Keywords: Layered Ceramics, Neutron Diffraction, Thermal Expansion, MAX Phases

Introduction In the field of nanolaminated compounds, M$_{n+1}$AX$_n$ phases ($n = 1$, 2 or 3) have attracted much interest in the last 15 years. These hexagonal ternary carbides or nitrides, also called MAX phases, for which M is an early transition metal, A is an A-group element and X is carbon and/or nitrogen,[1] have an inherent nanolayered structure, M$_{n+1}$X$_n$ layers. These layers are characterized by strong covalent M–X bonds, being interleaved with A layers through weaker M–A bonds. This nanolamellar structure gives a unique combination of metal-like and ceramic-like properties with several potential applications.[2] Up to now, more than 60 MAX phases have been synthesized by using three different elements M, A and X, and new compounds, as the recently discovered Nb$_2$GeC[3] or Mn$_2$GaC,[4] will certainly be proposed in the future. Yet, probably the most promising way to fine-tune or optimize desired properties, as well as opening new routes for developing new characteristics in the MAX phases, such as magnetism, can be found by exploring solid solutions.

Isostuctural solid solutions can be obtained in the M, A or X sites, thus forming either quaternary carbides or nitrides, such as (M, A, X)$_{n+1}$ and M$_{n+1}$A$^{(\prime,\prime)}$X$_n$, or carbonitrides in the case of X-site solid solution. Recently, their potential use in tailoring desired property was demonstrated in the fine-tuning of thermal expansion coefficient (TEC) in the Cr$_2$(Al,Ge)$_{1-x}$C system.[5] Furthermore, solid solutions allow one to obtain new MAX phases. For example, it is possible to synthesize (Cr,Mn$_{1-x}$)$_2$AlC[6] or (Cr,Mn$_{1-x}$)$_2$GeC[7] compounds even when Mn$_2$AlC and Mn$_2$GeC are yet to be experimentally realized. Similarly, the formation of (Cr$_{0.5}$V$_{0.5}$)$_2$AlC$_3$ and (Cr$_{0.5}$V$_{0.5}$)$_2$AlC$_2$ was evidenced albeit neither bulk V$_3$AlC$_2$ nor Cr$_3$AIc$_2$ and Cr$_4$AlC$_3$ exist.[8]

The possibility to synthesize nanolamellar metallic-based materials, especially with desired electronic and magnetic properties such as Mn-containing MAX phases, is of interest not only for basic research but also for applications. The latter may be realized through the MAX phase’s 2D derivatives, the MXenes (M$_n$X$_{n+1}$),[9] already recognized as a promising new 2D family of compounds, there is large motivation for new MXene (M’$^\prime$,M’$^\prime$)$_n$X$_m$ compounds, preferably formed as ordered metallic layers with high n value. Order is sought for to help achieving enhanced magnetic properties such...
Experimental Details  

(Cr0.5V0.5)n+1AlCn (n = 1, 2 and 3) solid-solution MAX phases were already experimentally evidenced.[8] One of the main interest of this Cr,V,Al,C system consists in the possibility of studying the evolution of the structural parameters and physical properties as a function of n since it is the only other example known to date, together with Ta2n+1AlCn.[16] of a system in which phases with n = 1, 2 and 3 can be obtained. Moreover, recently an Invar-like behavior of Cr2AlC was claimed to be observed below 80 K.[17] A search for similar TEC behavior in higher order MAX phases is of interest. Finally, (Cr0.3V0.5)nAlC2 is one of only two solid-solution MXene reported to exist.[9] and its detailed study is important. Naturally, most probable solid solutions can be achieved by mixing neighboring elements in the periodic table, due to similar atom size and electronic structure. Therefore, the study of possible structural ordering of such solid solution is greatly hindered by the inability of X-ray diffraction to distinguish neighboring elements. In contrast, neutron scattering from the nuclei can usually distinguish extremely well between neighboring atoms, and even between isotopes.[18] This is especially true for the (Cr,V) system, where vanadium has negligible neutron coherent scattering compared to that of chromium (∼100 times smaller).[18] This is the last, but not least, reason for our current concentration on the detailed temperature-dependent study of the (Cr,V)n+1AlCn system using neutron diffraction (ND).

Experimental Details  

(Cr0.5V0.5)n+1AlCn compounds were synthesized using conventional powder metallurgy techniques. Chromium (−200 mesh, 99.95%, Alfa Aesar GmbH & Co. KG, Karlsruhe, Germany), vanadium (−325 mesh, 99.8%, Alfa Aesar GmbH & Co. KG, Karlsruhe, Germany), aluminum (40–325 mesh, 99.8%, Alfa Aesar GmbH & Co. KG, Karlsruhe, Germany) and carbon graphite (< 40 μm, Chemwatch) powders were weighted to obtain the nominal compositions: 0.5(n + 1)Cr:0.5(n + 1)V:1.1Al:nC. An excess of 10% Al was chosen for aluminum loss compensation by evaporation during the sintering process. Following 3 h of mixing (Turbula™ shaker), cylindrical compacts, 12 mm in diameter and 3 or 4 g in weight, were obtained using a uniaxial pressure of 250 MPa. Pressure-less reactive sintering of samples was achieved in a furnace (Nabertherm™) under Ar flow. Annealing temperature and holding time were optimized to minimize possible impurity formation (1,400°C for 1 h, 1,500°C for 1 h and 1,400°C for 3 h for n = 1, 2 and 3, respectively). Four or five cylindrical samples of each compound were synthesized in the same batch. The obtained samples have a large open porosity and poor mechanical strength so that they were easily mechanically polished to remove possible secondary phases which exist close to the surface (mainly oxides) and to adjust their diameter to the vanadium containers used for the ND experiments (8 mm in diameter).

ND measurements were conducted on both G4.1 [17] and 3T2 [19] neutron diffractometers at the Orphée research reactor in the Laboratoire Léon Brillouin, Saclay, France. G4.1 is a two-axis powder diffractometer, equipped with a vertical focusing graphite monochromator (wavelength: λ = 2.426(1) Å), and linear BF3 multidetector. In this study, we used an angular step of Δ2θ = 0.1° and an angular coverage of 4–83.9° (momentum-transfer coverage of Q ≈ 0.18–3.46 Å⁻¹). 3T2 is a high-resolution two-axis powder diffractometer, equipped with a vertical focusing Ge monochromator (λ = 1.225193(1) Å), and a banana-type ³He multidetector. In this study, we used an angular step of Δ2θ = 0.05° and an angular coverage of 4.5–118.4° (Q ≈ 0.4–8.6 Å⁻¹). Due to its higher resolution, and significantly larger Q-range coverage, 3T2 was used for detailed structural studies, including cell parameters, atomic positions, atomic occupancies and anisotropic atomic displacement parameters (ADPs). Due to its higher flux, G4.1 was used for a detailed study of the TEC. Four or five cylindrical samples (~5 g in total) were put in a vanadium container, inside a helium cryofurnace. On G4.1, measurements were performed for 23–31 different temperature points in the range 1.5–340 K, whereas 5–7 different temperature points were studied on 3T2 in the range 2–500 K. Neutron counting time ranged from 20 min (for n = 1, 2) to 45 min (3) on G4.1, and between 6 and 14 h on 3T2. Results were analyzed by the Rietveld refinement method using FULLPROF (see Supplementary Material).[20]

Results and Discussion  

The positions of observed (hkil) reflections in the ND diffractograms of all three samples in all measured temperatures were consistent
The reflection intensities in the ND diffractograms of the n = 2 and 3 samples for all measured temperatures in both diffractometers were inconsistent with a complete disorder of the atoms in the two (Cr,V) sites of each structure (Figure 1(b) and 1(c)). The best fit to the data was achieved when large preferred occupancy was allowed in the (Cr,V) layers (Table 1). For the n = 2 sample, refinement resulted in 100% and 27(1)% occupancy of vanadium in the 2a(0,0,0) and 4f(1/3,2/3,0.1290(1)) layers, respectively. For n = 3, it resulted in with 32(2)% and 84(1)% occupancy of vanadium in the 4e(0,0,zM′ = 0.1539(3)) and 4f(1/3,2/3,zM′ = 0.054(1)) layers, respectively. In both cases, significant carbon vacancies were also found. Rietveld refined parameters of the ordered compounds, obtained using the 300 K 3T2 data, are summarized in Table 1. The resulted crystallographic structure is given in Figure 2.

Due to the large difference between the thermal neutron scattering from Cr and V,[18] large discrepancies between observed and calculated intensities were obtained when a complete disorder on the (Cr,V) sites was fixed in the model, especially on the {0002}, {0004} and {1011} reflections. For n = 2, when 50% occupancy of Cr was forced into the model in both metallic sites, especially large goodness-of-fit, χ² > 10 [20], was resulted in the refinement, compared to χ² = 2.82 for the ordered model. In addition, some of the anisotropic ADPs diverged into non-physically large values. For n = 3, the random occupancy model resulted in with zM′ = 0.080(6), a slightly larger χ² = 2.78 and 35(2)% carbon vacancies, compared to zM′ = 0.055(6), χ² = 2.67 and 19(2)% carbon vacancies in the ordered model. Moreover, non-physically high values of anisotropic ADPs are obtained. A value of zM′ = 0.080(6) is ~45% higher than the commonly found value for this parameter in n = 3 samples,[2,16,21] and extremely unlikely to be correct. Therefore, we conclude that a strong preferred occupation in the (Cr,V) layers occur for the n = 2 and 3 samples (Table 1 and Figure 2).

It is important to note here that ordering of the (Cr,V) atoms within a layer was also considered. However, any such ordering will result in with superlattice reflections. No such superlattice reflections were observed in any of the samples’ ND data.

The temperature-dependent lattice parameters for all samples are shown in detail in Figure S1(a)–(c) in the supplementary material. The resulted thermal expansions relative to 2 K are given in Figure 3, and in more detail in Figure S1(d)–(f). TECs for each direction (Table 2) are calculated for 150 < T < 340 K using data collected on G4.1 and the average linear TEC method.[22] In this method, the local (in temperature)

with the hexagonal structure (space group P6₃/mmc) generally used for these compounds and with lattice parameters similar to those previously found (Table 1).[8] In all samples, the intended MAX phase was the major phase. The Rietveld analysis of the 3T2 data at 300 K (Figure 1) revealed 1.7(1) wt% of Cr₂Al and 2.2(2) wt% Al₂O₃ as impurity phases in the n = 1 sample; 2.0(1) wt% Cr₂Al, 0.4(1) wt% (Cr⁰.₅V⁰.₅)C and 2.6(3) wt% (Cr⁰.₅V⁰.₅)₂AlC in n = 2; 5(1) wt% (Cr₃V₀.₇)₂Al, 1.1(2) wt% Al₂O₃, 6.7(3) wt% (Cr₃V₀.₇)C, 3.1(2) wt% Cr₂AlC and 2.9(2) wt% (Cr₆₆V₀.₃₃)₂AlC in n = 3.

The reflection intensities in the ND diffractograms of the n = 1 sample for all measured temperatures were consistent with a complete disorder of the atoms in the (Cr,V) site (Figure 1(a)). The Rietveld refinement of the Cr,V occupancy ratio resulted in with the 1:1 ratio with negligible refinement uncertainty. No additional reflections corresponding to ordered superlattice or long-range magnetic ordering were observed. Rietveld refined parameters obtained using the 300 K 3T2 data are summarized in Table 1. The resulted crystallographic structure is given in Figure 2.

Figure 1. Rietveld refinement of the structural models described in (solid red lines) to the 300 K ND data collected on the 3T2 diffractometer at λ = 1.225193(1) Å (open black circles), for the (Cr⁰.₅V⁰.₅)ₙAlCₙ samples with (a) n = 1, (b) n = 2 and (c) n = 3. The difference between model and experiment is presented by the dashed green line at the bottom of each diffractogram. The blue tags represent the reflections’ positions of the phases used in the model, with the first line of tags belonging to the major MAX phase.
Table 1. Refined crystallographic parameters of \((\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n\) with \(n = 1, 2\) or 3, at 300 K, as determined by the Rietveld analysis of neutron diffraction data.

|   | \(n = 1\) | \(n = 2\) | \(n = 3\) |
|---|---|---|---|
| \(a (\text{Å})\) | 2.89237(4) | 2.89502(4) | 2.91036(7) |
| \(c (\text{Å})\) | 12.9749(3) | 17.7529(3) | 22.4169(9) |
| \(V (\text{Å}^3)\) | 94.003(3) | 128.855(3) | 164.477(9) |
| \((\text{Cr}_{1-x}\text{V}_x)_{1}\) | \(x\) | 0.5 | 0.27(1) |
|   | \(z\) | 0.0837(3) | 0.1290(1) |
|   | \(U_{11} (\text{Å}^2)\) | 0.015(2) | 0.014(2) |
|   | \(U_{33} (\text{Å}^2)\) | 0.013(2) | 0.028(6) |
| \((\text{Cr}_{1-x}\text{V}_x)_{2}\) | \(x\) | - | 1 |
|   | \(z\) | - | - |
|   | \(U_{11} (\text{Å}^2)\) | - | 0.05(1) |
|   | \(U_{33} (\text{Å}^2)\) | - | 0.03(1) |
| \(\text{Al}\) | \(U_{11} (\text{Å}^2)\) | 0.015(2) | 0.013(2) |
|   | \(U_{33} (\text{Å}^2)\) | 0.012(1) | 0.055(6) |
| \(\text{C}_1\) | SOF | 1 | 0.95(1) |
|   | \(z\) | - | 0.06973(6) |
|   | \(U_{11} (\text{Å}^2)\) | 0.0110(8) | 0.0107(9) |
|   | \(U_{33} (\text{Å}^2)\) | 0.0136(3) | 0.033(4) |
| \(\text{C}_2\) | SOF | - | - |
|   | \(z\) | - | - |
|   | \(U_{11} (\text{Å}^2)\) | - | 0.1073(1) |
|   | \(U_{33} (\text{Å}^2)\) | - | 0.011(2) |

| \(R_{wp} (%)\) | 5.58 | 5.40 | 3.296 |
| \(R_{exp} (%)\) | 3.23 | 3.22 | 1.99 |

Refinement was done using the \(P6_3/mmc\) space group with the following atomic positions: for \(n = 1\) (\(\text{Cr}_{1-x}\text{V}_x\)) at \(4f(2/3,1/3,z)\), \(\text{Al}\) at \(2d(1/3,2/3,1/4)\); for \(n = 2\) (\(\text{Cr}_{1-x}\text{V}_x\)) at \(4f(1/3,2/3,z)\), (\(\text{Cr}_{1-x}\text{V}_x\)) at \(2a(0,0,0)\), \(\text{Al}\) at \(2b(0,0,1/4)\) and \(\text{C}_1\) at \(4f(2/3,1/3,0)\); for \(n = 3\) (\(\text{Cr}_{1-x}\text{V}_x\)) at \(4e(0,0,0)\), (\(\text{Cr}_{1-x}\text{V}_x\)) at \(2c(1/3,2/3,1/4)\), \(\text{C}_1\) at \(2a(0,0,0)\) and \(\text{C}_2\) at \(4f(2/3,1/3,0)\). \(x\) is the vanadium occupancy. \(U_{11}\) (perpendicular to) the basal plane. SOF is the site occupation factor. Numbers in parentheses represent standard deviation of the last significant digits as obtained in the refinement. When standard deviation is not specified, the reported value was fixed in the refinement. The weighted profile \((R_{wp})\) and expected \((R_{exp})\) agreement factors are also given.

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linear thermal expansions are calculated using discrete derivatives of the measured data. The resulting values are then averaged to give the average linear TEC. In this case, the standard uncertainty of the mean value is the reported uncertainty. For the \(3T_2\) data at \(150 < T < 550\) K, TECs were determined by simple linear-fits, due to the lack of enough temperature points (Table 2). The uncertainty of the linear-fit method is underestimated, as it ignores the variations in the local linear thermal expansion with temperature (cf. Figure 3).\[22\]

The central finding of this work is one of the first observed bulk \((\text{M}_1\text{M}_2)_n\text{AX}_n\) phases with strong tendency for ordering of the \((\text{M}_1,\text{M}_2)\) layers, and the first observed for the \((\text{Cr},\text{V})\) solid solutions. It is also the first reported \(n = 3\) phase with this tendency. ND results clearly show full ordering of the \(\text{V}\) layer between two 75%-rich \(\text{Cr}\) layers in \(n = 2\), and two 80%-rich \(\text{V}\) layers between two 70%-rich \(\text{Cr}\) layers in \(n = 3\) (Figure 2). In both cases, the \(\text{Cr}\)-rich layers neighbor the \(\text{Al}\) layers. The possible ordering of the \(\text{M}\) layers in the \(\text{MAX}\) phase system was already previously considered for the \((\text{Cr},\text{Mn})_2\text{GeC}\) and \((\text{Cr},\text{Mn})_2\text{AlC}\) solid solutions.\[6,7,23\]

Calculations have shown that formation enthalpy favors ordering, when positive (negative) enthalpy was calculated for random (ordered) structure. Yet, configurational entropy destabilizes the structure at elevated temperatures. Our finding for the \(n = 1\) phase studied here supports this idea. However, calculations have also shown that both \(\text{Cr}_3\text{AlC}_2\) and \(\text{Cr}_4\text{AlC}_3\) are unstable, and that the stability of their \(\text{V}\) counterparts is relatively weak, as \(\text{V}_4\text{AlC}_3\) stabilizes only with a significant amount of \(\text{C}\) vacancies.\[24\] These calculations are supported
Figure 2. Crystal structure of the \( (\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n \) compounds with \( n = 1 \) (left), \( n = 2 \) (middle) and \( n = 3 \) (right), visualized as a result of the Rietveld analysis of the 300 K ND data taken on 3T2. Refined layers’ distances are also given. For \( n = 2 \) and \( n = 3 \), a strong preferred occupation on the two \((\text{Cr, V})\) sites is observed. Reported \((\text{Cr, V})\) occupancies match the occupancies determined from the Rietveld analysis of the ND data (see also Table 1).

Figure 3. Thermal expansions of \( a \) (left) and \( c \) (right) lattice parameters in \( (\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n \) as determined by the Rietveld analysis of temperature-dependent ND data, measured on G4.1 (open symbols) and 3T2 (filled symbols). When not being observed, uncertainties are smaller than symbols’ size.

Assuming similar qualitative behavior for the formation enthalpy in the \( n = 1, 2 \) and 3 solid solutions, we may presume that disordered solid solutions with \( n = 2, 3 \) will, too, be unstable, and ordering of the metallic layers is needed for the stabilization of the compounds, as we observe experimentally here. More calculations on solid solutions of \( n > 1 \) MAX phases are needed to shed light on our presumption.

The above-mentioned presumption is supported experimentally.[21] Assuming similar qualitative behavior for the formation enthalpy in the \( n = 1, 2 \) and 3 solid solutions, we may presume that disordered solid solutions with \( n = 2, 3 \) will, too, be unstable, and ordering of the metallic layers is needed for the stabilization of the compounds, as we observe experimentally here. More calculations on solid solutions of \( n > 1 \) MAX phases are needed to shed light on our presumption.

The above-mentioned presumption is supported experimentally by the recent finding of ordering in \( (\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2 \), again, a system containing chromium.[15] In this work, full ordering of Cr in the 4f(1/3, 2/3, \( z \)) site and Ti in the 2a(0,0,0) site was observed using ND. This ordering is in accordance with the 2:1 ratio of the nominal Cr:Ti content. In our work, where the nominal Cr:V ratio is 1:1 for all studied samples, such full ordering is not expected in the \( n = 2 \) phase. Interestingly, however, our analysis show that the layer at the 2a(0,0,0) site is 100% occupied with V, causing a mixed, yet Cr rich, layer in the 4f(1/3, 2/3, \( z \)) 2a(0,0,0) site (Figure 2). Moreover, one could presume that a 1:1 Cr:V ratio is more prone to fully order in the \( n = 3 \) phase, where the two possible sites for \((\text{Cr, V})\) have the same multiplicity in 4e(0,0,\( z \)) and 4f(1/3, 2/3, \( z \)). However, no such full occupancy is favorable in the analysis of the experimental data. Our attempts to force
Table 2. TEC, $\alpha$, in $10^{-6}$ K$^{-1}$ units, along $a$ and $c$ lattice directions in the $(\text{Cr}_0.5\text{V}_0.5)_{n+1}\text{AlC}_n$ system, as determined by temperature-dependent ND on the G4.1 [average (150–340 K)] and 3T2 [linear (150–550 K)] diffractometers at the LLB, France.

|     | 1                | 2                | 3                |
|-----|------------------|------------------|------------------|
| $\alpha_a$ | Average (150–340 K) | 7.0(4) | 7.3(5) | 5.9(9) |
|       | Linear (150–550 K) | 7.9(1) | 8.2(1) | 7.1(1) |
| $\alpha_c$ | Average (150–340 K) | 6.4(6) | 5.2(5) | 6(1) |
|       | Linear (150–550 K) | 8.1(1) | 6.4(1) | 7.0(2) |

Average denotes the determination of $\alpha$ by averaging overall local (in temperature) TEC in the reported range. Linear denotes the determination of $\alpha$ by linear fit of measured points (3 for $n = 1$ and 2; 4 for $n = 3$). Numbers in parentheses are one standard deviation of the last significant digits.

Conclusions In conclusion, we report here on the formation of $(\text{Cr}_0.5\text{V}_0.5)_{n+1}\text{AlC}_n$ compounds with $n = 1, 2, 3$. The $n = 2, 3$ compounds show strong tendency for ordering in the form of rich chromium and vanadium layers. It is shown that the general structural evolution as a function of $n$ of this system slightly deviates from that of the only other example of existing $n = 1, 2, 3$ (Ta$_{n+1}\text{AlC}_n$) in a way that supports the existence of ordering. In addition, the observed low-temperature TEC behavior of Cr$_2$AlC[17] is maintained throughout the studied system, albeit ordering. Finally, we suggest that the formation of metallic nanolaminates ordering, which may be especially desirable for magnetic elements, should be sought out in these high-level MAX phases rather than in $n = 1$. However, further calculations and experiment are needed to decide whether the present case is common or rare.

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