Inorg. Chem. **2007**, *46*, 1410–1418

Inorganic Chemistry
Article

Ta_3AlC_2 and Ta_4AlC_3 – Single-Crystal Investigations of Two New Ternary Carbides of Tantalum Synthesized by the Molten Metal Technique

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Received November 23, 2006

Single crystals of the new ternary carbides Ta_4AlC_3 and Ta_3AlC_2 were synthesized from molten aluminum and characterized XRD, EDX, and WDX measurements. Crystal structures were refined for the first time on the basis of single-crystal data. Both compounds crystallize in a hexagonal structure with space group $P6_3/mmc$ and $Z = 2$. The lattice constants are $a = 3.1131(3)$ Å and $c = 24.122(3)$ Å for Ta_4AlC_3 and $a = 3.0930(6)$ Å and $c = 19.159(4)$ Å for Ta_3AlC_2. The crystal structures can be explained with a building block system consisting of two types of partial structures. The intermetallic part with a composition TaAl is a two layer cutting of a hexagonal closest packing. The carbide partial structure is a fragment of the binary carbide TaC (NaCl type). It consists of three (Ta_4AlC_3) or two layers (Ta_3AlC_2) of CTa_6-octahedra linked via common corners and edges. Both compounds are members of the series $(TaC)_nTaAl$. The crystal quality of Ta_3AlC_2 is improved by using a Al/Sn melt for crystal growth leading to small quantities of Sn in the crystal: $Ta_3Al_{1-x}Sn_xC_2$, $x \approx 0.04$. On the basis of reliable data a detailed discussion of structural parameters is possible. According to the building principle structure models can be developed for the whole series $(MX)_nMM'$ including coordinates for all atoms.

Introduction

Recent investigations on Ti_3SiC_2,[1] Ti_3AlC_2,[2] Ti_4AlN_3,[3] and related compounds of the series $(MX)_n(MM')$ (M = "early" transition metal; M′ = main group metal; X = C, N; $n = 1, 2, 3,..$)[4] have shown up their excellent and unique material properties like damage and shock resistance or good thermal and electrical conductivity.[5] Recent investigations have shown that compounds of the systems $(MC)_nM'$ are excellent coating materials.[6] Therefore investigations on ternary systems transition metal(TM)/aluminum/carbon are of interest for basic research on the synthesis of new materials. In the special case of systems TM/Al/C with TM/C as a refractory compound knowledge on existence and stability of ternary (or multinary) compounds are of fundamental significance for the synthesis of technologically important hard metals ("cermets"). Furthermore formation and existence of multinary compounds play a key role on hardening Al-containing alloys ("superalloys": Ti/Al, Fe/Al, Ni/Al)[7] and in sintering processes.[8]

Up to now most of the synthetic investigations[9−12] were confined to conventional high-temperature syntheses. Pressed samples of stoichiometrically composed mixtures of the elements or binary compounds were heated in a high-temperature furnace or molten in an arc furnace, followed by an annealing process at much lower temperatures. A second way is the HIP-process (hot isostatic pressing)[4,13]

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10.1021/ic062231y CCC: $37.00

which is frequently used to obtain dense bodies of microcrystalline samples. Doing so it is tacitly assumed thermodynamic equilibrium conditions are reached and the detected phases represent all the stable phases. This assumption may not always be justified because there are problems to prove that equilibrium conditions had been reached. Especially if extremely high melting compounds are involved kinetic reasons as high activation energies or too long diffusion paths may prevent the formation of equilibrium phases. For that reason many ternary phase diagrams TM/Al/C (for example Ti/Al/C[14−16]) are incomplete despite very careful investigations.

Up to now 3 ternary compounds $Ta_xAl_yC_z$ are known. Ta_2AlC is a so-called H-phase[17] where two layers of Ta atoms and one layer of Al atoms are alternatingly packed in the way of a hexagonal closest sphere packing. All octahedral voids between the Ta layers are occupied by carbon atoms forming a layer of CTa_6 octahedra connected via common edges. Ta_3Al_2C[9,10] is a filled variant of the cubic β-Mn type with C in Ta_6 octahedra. $Ta_5Al_3C_{1-x}$[11] is a partially filled variant of the hexagonal Mn_5Si_3 structure. Here there are partially filled CTa_6 octahedra which are connected via common faces to linear chains and separated by Al atoms.

In the past we have demonstrated for several examples that using molten metals as solvents ("auxiliary bath method")[18,19] new compounds can be yielded, which are not accessible by conventional high-temperature techniques, i.e., Cr_4AlB_6,[20] $Ni_{20}AlB_{14}$,[21] $Nb_xB_yC_z$ like $Nb_4B_3C_2$,[22] Al_3BC,[23] or Al_3BC_3.[24] Especially for the synthesis of ternary compounds molten metals show several advantages. First the temperatures of synthesis can be lowered significantly because the mobility of the components is higher, and the reaction is accelerated or even enabled by the liquid phase. Second it can be achieved the formation of compounds with limited thermal stability, i.e., incongruent melting point or peritectic decomposition into two different solid phases ("subsolidus" regime). Third the growth of single crystals enabling a reliable characterization by X-ray structure analyses (mixed crystals, nonstoichiometry, super structures) and analytical methods (analyses by EDX and WDX on single crystals) is much easier because the molten metal can serve as a solvent. Finally it is possible to get "sizable" amounts of those phases which are formed under normal conditions only on the surface of the material (hardening, degradation, sintering) or between the components in a composite material.

The combination of different metals for the melt gives a wide field for the variation of the molten metal technique. Although the knowledge about the processes in the melt is quite vague because of the lack of powerful analytical methods the auxiliary bath technique complements the usual high-temperature methods a unique way.

For the system Ta/Al/C we were able to demonstrate that the use of aluminum and tin as auxiliary metals enables synthesis and crystal growth of the new compounds Ta_4AlC_3 and Ta_3AlC_2. On the basis of single-crystal data a detailed discussion of structural parameters is possible including the prediction of the crystal structures of further members $(MC)_nMM'$ with $n > 3$. To our knowledge single-crystal studies on "MAX-phases" with $X = C$ and N by means of X-rays are reported only for Cr_2AlC[17] and Ti_3SiC_2.[25] The lack of reliable single-crystal data for X-ray diffraction and elemental analysis as well can cause confusion as the system Ti/Al/N ($Ti_3Al_2N_2$, Ti_4AlN_3, Ti_3AlN_2[26]) illustrates.

Experimental Section

Synthesis and Characterization. Ta_4AlC_3. Ta_4AlC_3 is synthesized by reacting the elements with an excess of aluminum (molar ratios Ta:Al:C = 1:5:0.8 to 1:10:0.8). Commercially available powders of the elements Ta (Alfa Aesar, 99.9%), C (Chempur, 99.9+%), and Al (Riedel-de Haen, 99.9%) were intimately mixed and pressed into pellets (total mass: ca. 400 mg). The pellets were put into corundum crucibles and quickly (200 K/h) heated up to 1500 °C under an argon atmosphere. The samples were held for 50 h at 1500 °C and then cooled to 1000 °C with a cooling rate of 5 K/h and with 30 K/h to RT. The excess metal of the melt was removed by dissolving the regulus in diluted aqueous HCl. The residue was washed and dried. The XRD pattern (Figure 1) was indexed with a hexagonal unit cell with $a = 3.1131(3)$ Å and $c = 24.122(3)$ Å. Additional lines were assigned to $TaAl_3$.[27] Ta_4AlC_3 forms thin black hexagonal platelets with metallic luster and diameters up to 0.1 mm (Figure 2).

Because the formation of mixed crystals is well-known for MAX phases[28−30] the composition of Ta_4AlC_3 was checked by additional means. EDX measurements showed Ta and Al as the only elements with $Z > 11$ in a ratio of 82:18. WDX investigations confirmed the presence of carbon as the only light element with $12 > Z > 4$. The detection limit of N as the most likely contamination[29] is about 5% in relation to C.

Ta_3AlC_2 and $Ta_3Al_{1-x}Sn_xC_2$ ($x \approx 0.04$). Ta_3AlC_2 and $Ta_3Al_{1-x}Sn_xC_2$ ($x \approx 0.04$) were yielded in a similar way by reacting the

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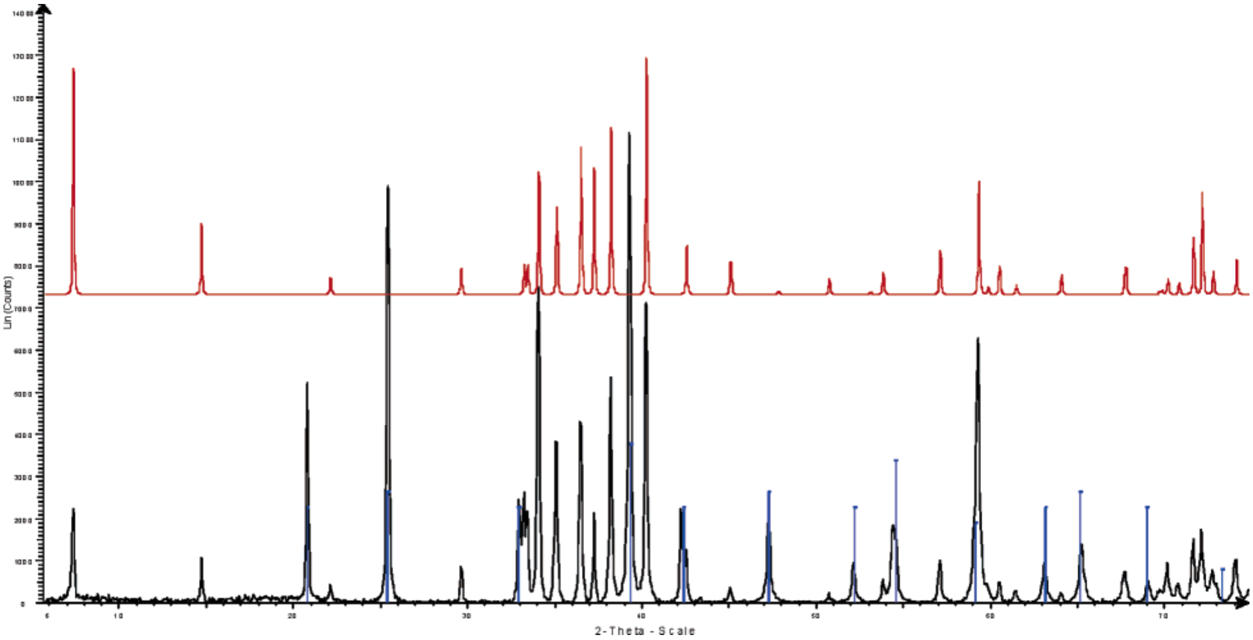

Figure 1. Calculated (top) and observed (bottom) X-ray powder pattern of Ta_4AlC_3, additional lines are from $TaAl_3$.

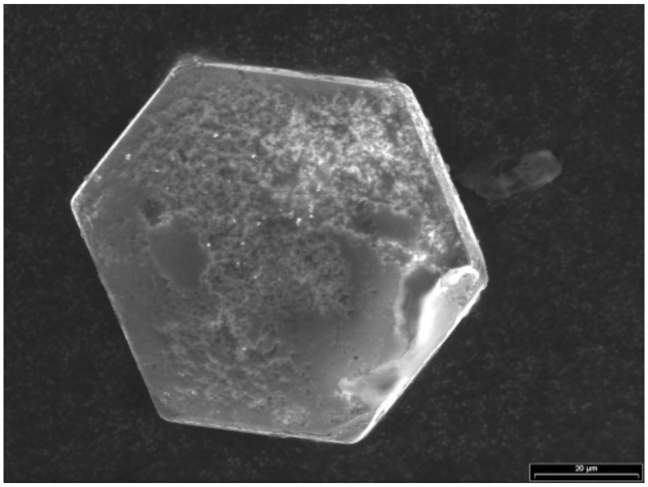

Figure 2. SEM picture of Ta_4AlC_3.

elements with a large excess of aluminum (molar ratios Ta:Al:C about 1:25:1). The addition of Sn (Merck, 99.9%); Al:Sn = 10:1) reduces the amount of byproducts (TaC, $TaAl_3$) and leads to better crystal qualities, but small amounts of it are incorporated in the crystals (see below). Pellets of the mixed and pressed elements were put into corundum crucibles, heated up to 1400 °C, held for 50 h at 1400 °C, and cooled with 5 K/h to 1000 °C and with 30 K/h to RT. The excess metal of the melt was removed by dissolving the regulus in diluted aqueous HCl. The residue was washed and dried. The XRD pattern (Figure 3) was indexed with a hexagonal unit cell with $a = 3.0930(6)$ Å and $c = 19.159(4)$ Å. Additional lines were assigned to $TaAl_3$[27] and to traces of TaC and Sn. Ta_3AlC_2 forms black hexagonal platelets and truncated hexagonal prisms with metallic luster and diameters up to 0.1 mm (Figure 4).

EDX investigations of Ta_3AlC_2 crystals synthesized without Sn revealed a Ta−Al ratio of 76:24. When using a Al/Sn melt the composition was 76:23:1. WDX measurements confirmed for both compounds the presence of carbon and the absence of N and O.

X-ray powder diagrams of the residues showed the presence of $TaAl_3$ as a byproduct. For Ta_3AlC_2 additionally small amounts of TaC were observed, but in both cases only one ternary compound was found. At higher temperatures (1500−1600 °C) the formation of $TaAl_3$ and TaC was enforced. From this a peritectic formation of Ta_4AlC_3 and Ta_3AlC_2 can be concluded. The remarkable fact that Ta_2AlC as the ternary phase $(TaC)_nTaAl$ with the highest content of Al was never observed shows the special reactivity in molten metals. Because of the better quality of the crystal (and therefore the quality of the data obtained) and the higher reliability of the refinement we used the data of $Ta_3Al_{1-x}Sn_xC_2$ for discussion (see below).

XRD patterns were recorded with a Siemens D5000 (Cu-Kα1-radiation, Ge-monochromator, gas-filled PSD, Debye−Scherrer geometry, transmission). REM pictures and EDX measurements were done using a Jeol SM 6400 (Ge detector). For WDX investigations a Cameca SX 50 (analyzer crystal PC2, diamond and c-BN as standards) was used.

Structure Analyses. Ta_4AlC_3. A hexagonal platelet (edge length 0.04 mm, thickness 0.005 mm) was selected under a microscope. Reflection intensities were measured using a conventional four circle diffractometer (Siemens P4, Mo-Kα). The indexing routine of the four circle diffractometer led to a hexagonal unit cell. Lattice constants were refined from the coordinates of 25 high angle reflections to $a = 3.1123(5)$ Å and $c = 24.111(5)$ Å. Measurement of 1318 reflections up to $2\theta = 70°$ and merging in Laue class $6/mmm$ resulted in a data set of 209 unique reflections (166 with $I > 2\sigma(I)$). The reflection conditions $00l$ with $l = 2n$ and hhl with $l = 2n$ were found. Unit cell dimensions and reflection conditions suggested isotypism to $Ti_4Al_{1-x}Sn_xC_{3-y}N_y$.[29] These parameters were used as a starting model for the refinement. Finally R-values of $R_1(F) = 0.0341$ and $wR_2(F^2) = 0.0578$ were received. The refinement of the site occupation factors revealed no significant deviations from a stoichiometric composition. Further details are listed in Tables 1−3.

Ta_3AlC_2. A small hexagonal platelet ($0.02 \times 0.02 \times 0.005$ mm^3) of Ta_3AlC_2 was used for the structure analysis (STOE IPDS I, Mo-Kα). The indexing routine led to a hexagonal unit cell with lattice constants $a = 3.1004(4)$ Å and $c = 19.200(4)$ Å. 1735 intensities were merged in the Laue-class $6/mmm$ to a data set of 149 independent reflections. The reflection conditions $00l$ with $l = 2n$ and hhl with $l = 2n$ were fulfilled. These results led to the

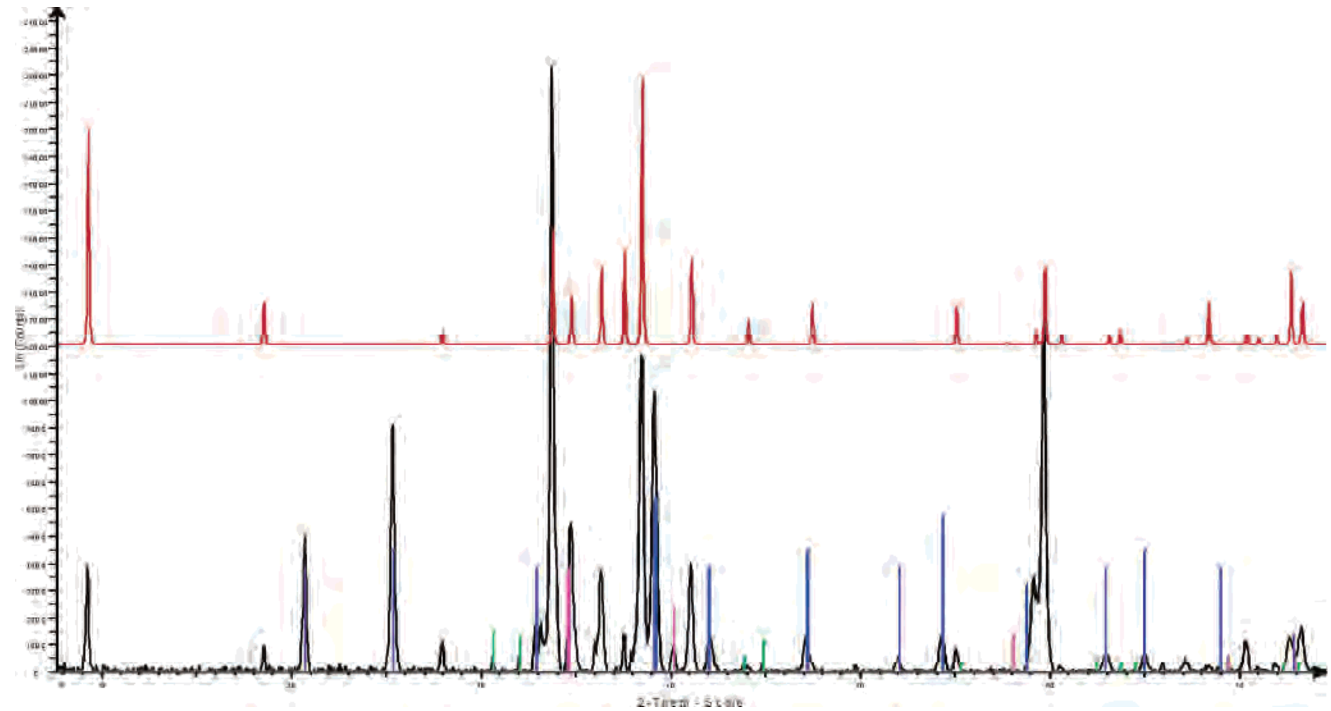

Figure 3. Calculated (top) and observed (bottom) X-ray powder pattern of Ta_3AlC_2, additional lines are from $TaAl_3$.

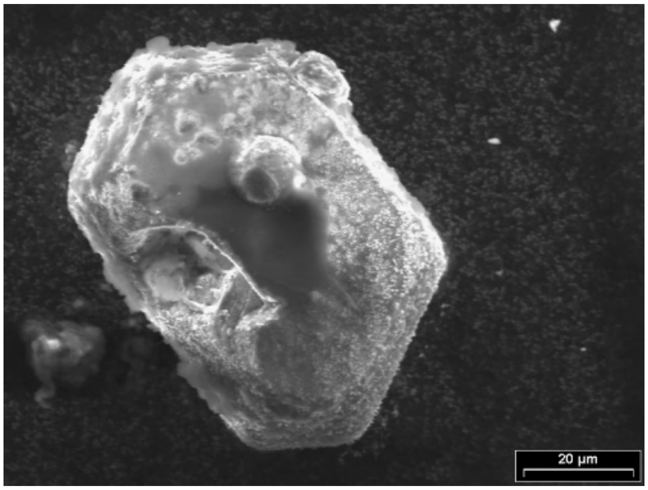

Figure 4. SEM picture of $Ta_3Al_{1-x}Sn_xC_2$ ($x = 0.04$).

assumption of isotypism to Ti_3SiC_2.[25] With space group $P6_3/mmc$ and the coordinates of Ti_3SiC_2 as a starting model the refinement converged quickly. Within the standard deviations the occupation factors of Ta and Al confirmed the proposed composition. The final R-values were $R_1(F) = 0.0338$ and $wR_2(F^2) = 0.0407$. Further details are summarized in ref 32.

$Ta_3Al_{1-x}Sn_xC_2$ ($x \approx 0.04$). The use of tin improved the crystal quality but was not necessary for the formation of single crystals. The refinement of several data sets of crystals grown from Al/Sn melts revealed a slightly higher electron density on the Al position, but the refinement of the site occupation factor was coupled to the thermal displacement parameters. Therefore a clear separation was not possible. Because Al/Sn substitution in crystals grown from a Al/Sn melt was already observed for other systems ($Ti_2Al_{1-x}Sn_xC$,[28] $Ti_4Al_{1-x}Sn_xC_{3-y}N_y$,[29] $Ti_3Al_{1-x}Sn_xC_{2-y}N_y$[29]) we assume mixed crystals according to the formula $Ta_3Al_{1-x}Sn_xC_2$.

The measurement with a four circle diffractometer (Siemens P4, Mo-Kα) revealed a hexagonal unit cell with $a = 3.0899(2)$ Å and $c = 19.135(3)$ Å. 1079 intensities were measured and merged to a data set of 229 independent reflections (187 with $I > 2\sigma(I)$). The refinement resulted in R-values of $R_1(F) = 0.0296$ and $wR_2(F^2) = 0.0565$. Further details are listed in Tables 1, 4, and 5. The high residual electron density is a result of the measurement at high diffraction angles ($2\theta = 80°$) and the electron number of Ta. It is reduced on limiting the θ-range without significant changes (+3.4/−2.3 $e^-/Å^3$ for $2\theta_{max} = 60°$). Because the data of the Al/Sn grown crystals were superior we use them for the structure discussion.

Further details on the structure refinement (complete list of distances and angles, F_o/F_c-list) may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49)724-808-666, e-mail: crysdata@fiz-karlsruhe.de) on quoting the registry number CSD-416854 (Ta_4AlC_3), CSD-416855 (Ta_3AlC_2), and CSD-416856 ($Ta_3Al_{1-x}Sn_xC_2$).

Structure Descriptions and Discussion

Ta_3AlC_2 and $Ta_3Al_{1-x}Sn_xC_2$ are isotypical to Ti_3SiC_2. The crystal structure can be described as the closest sphere packing of metal atoms with alternately three layers of Ta and one layer of Al. The stacking sequence is AB**A**BAC**A**C (according to the labeling of Jagodzinski (h**h**hc)$_2$[33] with Ta2 in the cubic sequence and Al in the middle hexagonal sequence (marked with bold letters). All octahedral voids between Ta atoms (i.e., 1/2 of all octahedral voids) are occupied by C atoms (Figure 5). Emphasizing the CTa_6-octahedra the crystal structure of Ta_3AlC_2 consists of double layers of edge sharing octahedral separated by layers of Al atoms (Figure 5). The surroundings of Ta, Al, and C (Figure 6) can be derived from the motif of the layer sequence. The anticuboctahedron of Al consists of 6 Al and 6 Ta1, the

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(32) Data for Ta_3AlC_2: Ta1: $z = 0.13423(6)$, $U_{equ} = 0.0095(3)$, Ta2: $U_{equ} = 0.0088(3)$, Al: $U_{equ} = 0.0143(22)$, C: $z = 0.0675(11)$, $U_{equ} = 0.008(3)$.

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Table 1. Structure Refinement of $Ta_3Al_{1-x}Sn_xC_2$ ($x \approx 0.04$) and Ta_4AlC_3

	$Ta_3Al_{1-x}Sn_xC_2$ ($x \approx 0.04$)	Ta_4AlC_3
crystal shape	hexagonal platelet	hexagonal platelet
crystal color	metallic lustrous	metallic lustrous
crystal size	$0.03 \times 0.03 \times 0.005$ mm^3	$0.04 \times 0.04 \times 0.005$ mm^3
formula weight	593.83 g/mol	786.81 g/mol
crystal system	hexagonal	hexagonal
space group	$P6_3/mmc$	$P6_3/mmc$
lattice constants	$a = 3.0899(2)$ Å $c = 19.135(2)$Å	$a = 3.1123(5)$ Å $c = 24.111(5)$ Å
cell volume	158.21 Å^3	202.26 Å^3
formula units	2	2
density, calculated	12.466 g/cm^3	12.919 g/cm^3
radiation	Mo $K_{\alpha1}$	Mo $K_{\alpha1}$
θ−range	$-1 \leq h \leq 5, -5 \leq k \leq 1, -1 \leq l \leq 34$	$-4 \leq h \leq 4, -4 \leq k \leq 4, -38 \leq l \leq 38$
temperature	23 °C	23 °C
$2\theta_{max}$	80°	70°
diffractometer	Siemens P4	Siemens P4
mode of measurement	$\Omega/2\theta$ −scan	$\Omega/2\theta$ −scan
reflections measured	1079	1318
independent reflections	229	209
reflections $I > 2\sigma(I)$	187	166
absorption correction	empirical; ψ−scan	empirical; ψ−scan
$R_{int.}$, R_{sigma}	0.0859, 0.0521	0.1242, 0.0590
absorption coefficent	102.47 mm^{-1}	107.85 mm^{-1}
extinction coefficent[31]	0.0226(15)	0.0024(5)
max./min. transmission	0.0287; 0.0083	0.0357; 0.0095
structure solution	known model[25]	known model[29]
refinement	SHELXL[31]	SHELXL[31]
residual electron e$^-$/Å^3 min, max, sigma	+7.87,[a] −4.25, 0.69	+3.95, −3.85, 0.79
weighting function[31]	0.0195; 0.0	0.0218; 2.35
number of parameters	12	15
R-factors	$R_1(F) = 0.0296$ $wR_2(F^2) = 0.0565$	$R_1(F) = 0.0341$ $wR_2(F^2) = 0.0578$

[a] 0.60 Å from Ta; reduced to +3.4/−2.3 e$^-$/Å^3 for $2\theta_{max} = 60°$.

Table 2. Coordinates, Thermal Displacement Parameters (in Å^2), and Site Occupation Factors in Ta_4AlC_3[a]

atom	site	x	y	z	U_{eq}	sof[b]	U_{11}	U_{33}
Ta1	4e	0	0	0.15801(3)	0.0070(2)	1.004(6)	0.0068(3)	0.0074(3)
Ta2	4f	1/3	2/3	0.05820(3)	0.0074(2)	0.996(6)	0.0073(3)	0.0075(3)
Al	2c	1/3	2/3	1/4	0.009(2)	0.95(5)	0.010(3)	0.008(3)
C1	4f	2/3	1/3	0.1079(8)	0.007(3)	1.01(9)	0.007(5)	0.008(6)
C2	2a	0	0	0	0.012(6)	1.17(15)	0.017(9)	0.002(8)

[a] esd's in parentheses, $U_{11} = U_{22} = 2U_{12}$, $U_{23} = U_{13} = 0$. [b] In order to check for mixed occupations and/or vacancies site occupation factors were treated by turns as free variables at the end of the refinement,

Table 3. Selected Distances (in [Å]) and Angles in Ta_4AlC_3[a]

Ta1−C1	2.166(11) 3x	Ta2−C1	2.206(11) 3x
Ta1−Al	2.8545(8) 3x	Ta2−C2	2.2304(5) 3x
Ta1−Ta2	3.0693(11) 3x	Ta2−Ta1	3.0693(11) 3x
Ta1−Ta1	3.1123(5) 6x	Ta2−Ta2	3.1123(5) 6x
Ta1−Ta2	3.1961(11) 3x	Ta2−Ta1	3.1961(11) 3x
Al−Ta1	2.8545(8) 6x	Ta2−C1−Ta2	89.7(6)°
Al−Al	3.1123(5) 6x	Ta1−C1−Ta1	91.8(6)°
C1−Ta1	2.166(11) 3x	Ta1−C1−Ta2	89.19(3)°
C1−Ta2	2.206(11) 3x	Ta2−C2−Ta2	88.48(2)°
C2−Ta2	2.2304(5) 6x	Ta2−C2−Ta2	91.52(2)°

[a] esd's in parentheses.

anticuboctahedron of Ta1 is formed by 6 Ta2, 3 Ta1, and 3 Al atoms with 3 additional C atoms in the octahedral voids. The cuboctahedron of Ta2 is built up by 6 Ta2 and 6 Ta1 atoms with 6 additional C atoms in the octahedral voids. The Ta−C distances are 2.185 and 2.211 Å with the longer distance to the inner Ta layer (Ta2). In total the Ta−C distances are shorter than in TaC (2.228 Å = 1/2 a, NaCl type[34]). The metal−metal distances within the layers are given by the lattice constant a (3.090 Å). Between the Ta layers they are slightly longer (3.126 Å) but shorter than in TaC (3.151 Å). Because of the smaller atomic radius of Al the distances Ta−Al are shorter (2.854 Å). They are comparable to the values of 2.713 Å and 2.872 Å in $TaAl_3$,[27] a structure with a closest sphere packing, too.

The structure of Ta_4AlC_3 is isotypical to $Ti_4Al_{1-x}Sn_xC_{3-y}N_y$[29] and Ti_4AlN_3,[3] respectively, and shows a close relationship to Ta_3AlC_2. The difference is an additional layer of Ta atoms leading to a closest packing of metal atoms with a sequence AB**A**BACB**C**BC = (h**h**hcc)$_2$. Like in Ta_3AlC_2 carbon occupies all octahedral voids formed exclusively by Ta atoms, i.e., 60% of all voids. All in all there are tripel layers of CTa_6 octahedra with layers Al atoms between (Figure 7). Similar to Ta_3AlC_2 the surroundings of the atoms in Ta_4AlC_3 result from the layer sequences of the closest packing (Figure 8). The C atoms of central layer (*C*2) are exactly in the center of the Ta_6 octahedra by reasons of symmetry with 6 equal distances of 2.230 Å. This is very similar to the binary TaC. The "outer" carbon atoms (C1) are slightly

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(34) Fries, R. J.; Wahman, L. A. *J. Am. Ceram. Soc.* **1967**, *50*, 475.

Table 4. Coordinates, Thermal Displacement Parameters (in Å^2), and Site Occupation Factors in $Ta_3Al_{1-x}Sn_xC_2$ ($x \approx 0.04$)[a]

atom	site	x	y	z	U_{eq}	sof[b]	U_{11}	U_{33}
Ta1	4*f*	1/3	2/3	0.13418(3)	0.0084(2)	0.994(6)	0.0084(2)	0.0082(2)
Ta2	2*a*	0	0	1/2	0.0082(2)	0.993(7)	0.0080(2)	0.0084(3)
Al/Sn	2*b*	0	0	1/4	0.0143(22)	0.96(4)	0.0122(15)	0.011(2)
C	4*f*	2/3	1/3	0.0683(6)	0.010(3)	1.10(5)	0.010(3)	0.010(4)

[a] esd's in parentheses, $U_{11} = U_{22} = 2U_{12}$, $U_{23} = U_{13} = 0$. [b] In order to check for mixed occupations and/or vacancies site occupation factors were treated by turns as free variables at the end of the refinement

Table 5. Selected Distances (in [Å]) and Angles in $Ta_3Al_{1-x}Sn_xC_2$ ($x \approx 0.04$)[a]

Ta1−C	2.185(7) 3x	Al/Sn−Ta1	2.8540(4) 6x
Ta1−Al/Sn	2.8540(4) 3x	Al/Sn−Al/Sn	3.0899(4) 6x
Ta1−Ta1	3.0899(4) 6x	C−Ta1	2.185(7) 3x
Ta1−Ta2	3.1260(2) 3x	C−Ta2	2.211(7) 3x
Ta2−C	2.211(7) 6x	Ta1−C−Ta1 88.6(3)°	
Ta2−Ta2	3.0899(4) 6x	Ta1−C−Ta2 90.7(1)°	
Ta2−Ta1	3.1260(5) 6x	Ta2−C−Ta2 88.6(3)	

[a] esd's in parentheses.

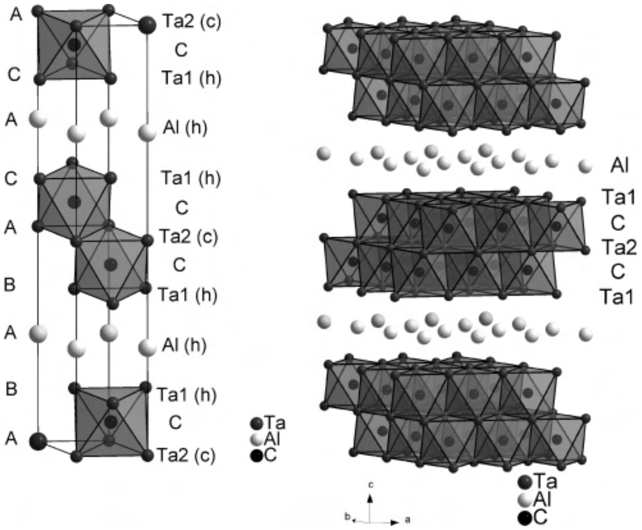

Figure 5. Crystal structure of Ta_3AlC_2; left: unit cell, right: layer structure.

shifted toward the Al layers (C1−Ta1: 2.166 Å; C1−Ta2: 2.206 Å) leading to a flattening of the C1 octahedron. This compression of the CTa_6 octahedra in direction [*001*] is also seen in the Ta−Ta distances between the layers. They amount to 3.074 Å in the outer layer (Ta1−Ta2) and 3.192 Å in the central layer (Ta2−Ta2). Within the layers all metal−metal distances correspond to the lattice constant *a* (3.112 Å). The Ta−Al distances of 2.855 Å are similar to Ta_3AlC_2.

It is easy to understand that the central Ta layers (Ta2) in Ta_4AlC_3 and Ta_3AlC_2 are located in cubic sequences of the closest sphere packing because the complete occupation of octahedral voids in a hexagonal sequence would lead to the electrostatically unfavorable formation of face sharing CTa_6 octahedra. This motif has never been observed in transition-metal carbides.[35,36] The transition Ta_2AlC − Ta_3AlC_2 − Ta_4AlC_3 corresponds to an enlargement of the cubic TaC layers as they were observed in the binary TaC with a NaCl type structure. This insertion of "additional" TaC layers does not change the space group type $P6_3/mmc$. The Al atoms are always on mirror planes at $z = 1/4$ and $z = 3/4$. For all compounds with the general composition $(TaC)_nTaAl$ following a structure principle as described below space group $P6_3/mmc$ will be expected if no further deviations from the idealized structure like distortions, partial occupations, ordering variants, or stacking faults are present.

The crystal structures of Ta_3AlC_2 and Ta_4AlC_3 are examples for the separation of different interactions in different parts of the structure as it is frequently observed for ternary transition-metal carbides. There is a separation in carbide partial structure with only Ta−C interactions and an intermetallic part with Al−Ta contacts. Direct contacts Al−C seem to be avoided by this structure principle. The

Table 6. Lattice Constants, Volumes, and Layer Sequences of Compounds $(TaC)_nTaAl$, $n = 1-5$[a]

compound	Ta_2AlC ($n = 1$)	Ta_3AlC_2 ($n = 2$)	Ta_4AlC_3 ($n = 3$)	Ta_5AlC_4 ($n = 4$)	Ta_6AlC_5 ($n = 5$)	TaC ($n \rightarrow \infty$)
a in [Å]	3.075	3.090	3.112	3.125	3.138	3.151
c in [Å]	13.83	19.135	24.111	29.1	34.0	7.718 (5.145)
volume in [Å^3]	113.3	158.2	202.3	246	290	44.24
space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$	R-3m
layer sequence	A**B**AB**A**B	AB**A**BAC**A**C	AB**A**BACB**C**BC	CAB**A**BACBA**B**AB	CAB**A**BACBAC**A**CAB	ABCABC
Jagodzinski symbol	$(h\mathbf{h}h)_\infty$	$(h\mathbf{h}hc)_2$	$(h\mathbf{h}hcc)_2$	$(h\mathbf{h}hccc)_2$	$(h\mathbf{h}hcccc)_2$	$(c)_\infty$

[a] Data for TaC are transformed from the NaCl type structure ($Fm\bar{3}m$) with $a = 4.456$ Å.[34]

Table 7. Sites and Idealized Coordinates of Compounds $(TaC)_nTaAl$, $n = 1-5$[a]

	Ta_2AlC				Ta_3AlC_2				Ta_4AlC_3				Ta_5AlC_4				Ta_6AlC_5			
		x	y	z		x	y	z		x	y	z		x	y	z		x	y	z
Al	2c	1/3	2/3	3/12	2b	0	0	4/16	2c	1/3	2/3	5/20	2c	1/3	2/3	6/24	2b	0	0	7/28
Ta1	4f	2/3	1/3	1/12	4f	1/3	2/3	2/16	4e	0	0	3/20	4f	2/3	1/3	4/24	4f	2/3	1/3	5/28
Ta2					2a	0	0	0	4f	1/3	2/3	1/20	4f	1/3	2/3	2/24	4e	0	0	3/28
Ta3													2a	0	0	0	4f	1/3	2/3	1/28
C1	2a	0	0	0	4f	2/3	1/3	1/16	4f	2/3	1/3	2/20	4e	0	0	3/24	4f	2/3	1/3	2/28
C2									2a	0	0	0	4f	2/3	1/3	1/24	4f	1/3	2/3	4/28
C3																	2a	0	0	0

[a] Sites 4e and 4f have a free variable for the *z*-value.

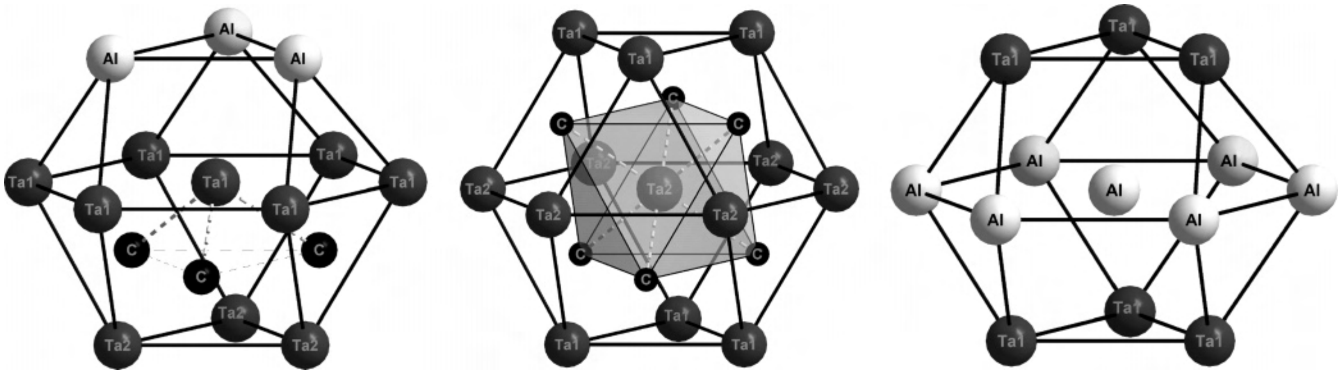

Figure 6. Coordination polyhedra in Ta_3AlC_2.

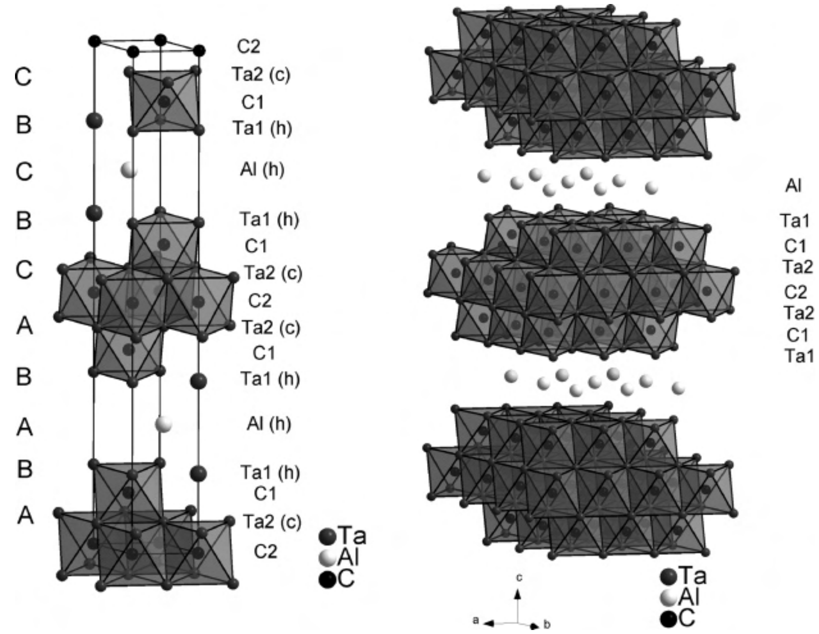

Figure 7. Crystal structure of Ta_4AlC_3; left: unit cell, right: layer structure.

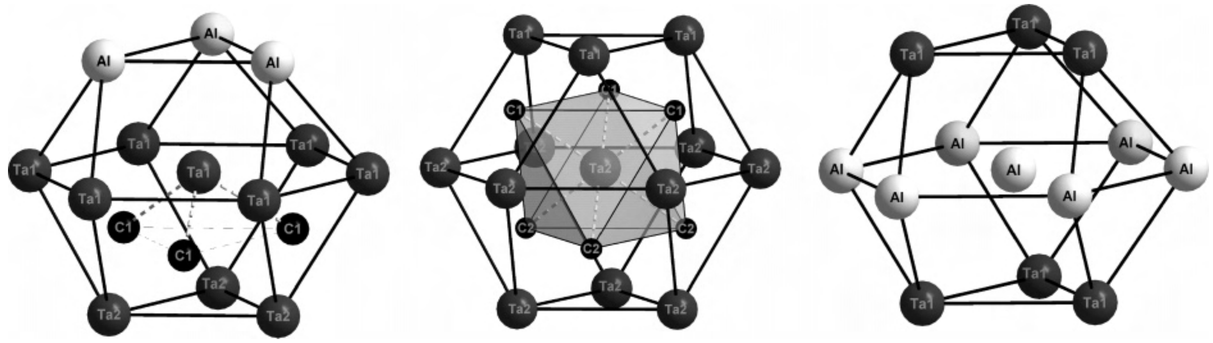

Figure 8. Coordination polyhedra in Ta_4AlC_3.

resulting layer structure is clearly seen in the SEM picture of Ta_4AlC_3 (Figure 9). It illustrates the description of the phases $(MX)_nMM'$ as "nanolaminates"[4] and explains the anisotropy of the physical properties.

Because Ta_4AlC_3 and Ta_3AlC_3 are the first examples for single-crystal investigations on a hole series $(TaC)_nTaAl$ with $n = 1$, 2, and 3 a detailed discussion of the structures is possible. Especially the carbon positions are not estimated from geometrical reasons, i.e., in the center of the M_6 octahedron, but determined as real parameters. Figure 10 shows the layer distances perpendicular to the *c*-direction for Ta_3AlC_2 and Ta_4AlC_3. While the central carbide layer is nearly undisturbed compared to the binary carbide TaC, the deviation, i.e., the compression in [00*1*]-direction, grows with coming closer to the Al layer. In TaC the distances between the layers are $D = 2.573$ Å (Ta−Ta) and $d = 1.286$ Å (Ta−

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(35) Toth, L. E. *Transition Metal Carbides and Nitrides*; Academic Press: New York, 1971.

(36) Villars, P. *Pearson's Handbook, Crystallographic Data for Intermetallic Phases*; ASM International: Materials Park, OH, 1997.

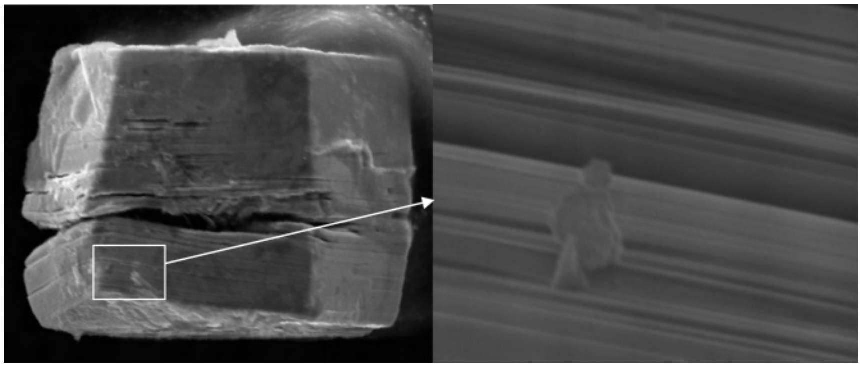

Figure 9. SEM picture of a Ta_4AlC_3 crystal showing the lamellar structure; the right picture is an enlarged cutting of the left picture.

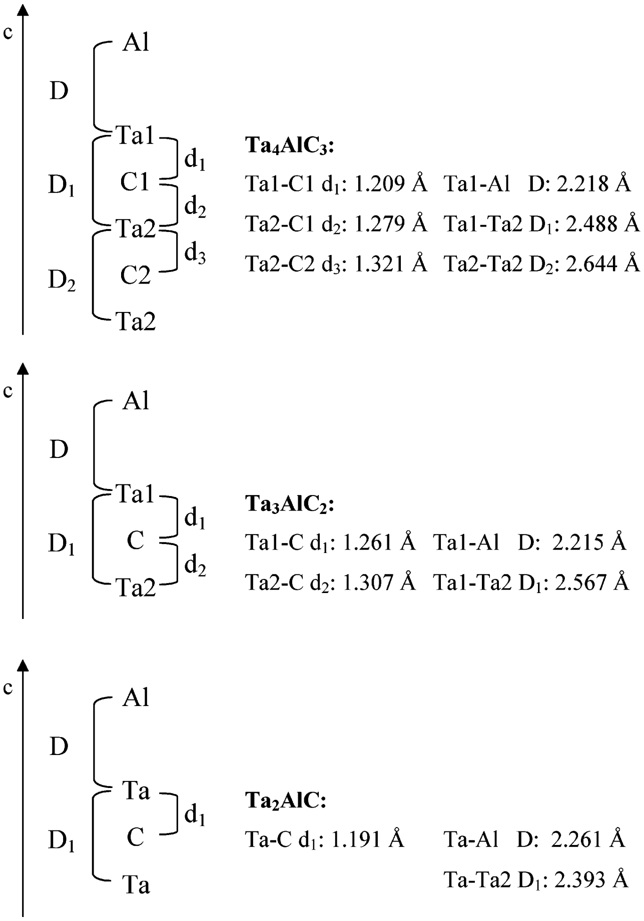

Figure 10. Interlayer distances in Ta_4AlC_3, Ta_3AlC_2, and Ta_2AlC; values for Ta_2AlC are calculated with $z_{Ta} = 0.0865$.

C), respectively. Especially in the case of Ta_4AlC_3 the description of the structure as a "quasi"binary compound (TaAl) and $(TaC)_n$ is clearly seen. Combined to the generalized modular building principle (see below) the deviations of the "idealized" structures can be used to derive real coordinates for all phases $(MX)_nMM'$.

Generalized Modular Building Principle for Phases $(MX)_nMM'$

The crystal structures of Ta_2AlC, Ta_3AlC_2, and Ta_4AlC_3 can easily be generalized by a modular building principle. All structures are characterized by alternating layers of intermetallic and carbidic partial structures. The intermetallic part is always a fragment of a closest sphere packing with layer of Al atoms and two neighboring Ta layers in a hexagonal sequence. The second next Ta layers are in hexagonal sequence, too, so there is always a block with the sequence (h**h**h) with Al in the middle. Subsequent layers of Ta are always in a cubic sequence. According to the value of n the number of additional Ta layers in a cubic sequence c is $(n - 1)$. The total number of metal atom layers in direction $[00l]$ is $2n + 4$.

Two cases can be separated. If n is an even number (Ta_3AlC_2, Ta_5AlC_4,...) the site 2a (0, 0, 0) is occupied by Ta. The following $n/2$ Ta positions are on sites 4f (1/3, 2/3, z) and (2/3, 1/3, z) or 4e (0, 0, z), respectively. The value of z is given by $m/(2n + 4)$ with m as an even number $m \leq n$. The carbon atoms are also on 4f sites with z-values $m/(2n + 4)$, but now m is an odd number with $m < n$. Al is always located on the mirror plane at $z = 1/4$ and $z = 3/4$ (site 2b (0, 0, 1/4) or 2c (1/3, 2/3, 1/4)). If n is an odd number (Ta_2AlC, Ta_4AlC_3, Ta_6AlC_5,...) the relative positions of Ta and C are inverted. n Ta atoms are still on sites 4f and 4e with $z = m/(2n + 4)$, but now m is an odd number with $m \leq n$. One C-atom is on site 2a and $(n - 1)/2$ carbon atoms are on sites 4f and 4e with $z = m/(2n + 2)$, m as an even number and $m < n$. The Al positions are the same in all cases.

The lattice constants can be estimated. The insert of additional TaC-layers results in a slight enlargement of the a-axis. With $a = 3.075$ Å for Ta_2AlC and $a = 3.151$ Å for TaC the values for the end members of the row are given. From this missing values can be derived by "interpolation". Lattice constant c is enlarged by ≈ 5 Å for each TaC-layer. It can be calculated more reliable from the additional volume of 44 Å^3 per additional TaC-layer if the value for a is known.

This procedure can be applied for other unknown MAX-phases $(MX)_nMM'$ if the lattice constants for MX and one of the ternary compounds are known. Furthermore in case of distinct deviations it can give a hint to mixed occupations for the metal positions and/or a C/N substitution.[29,30]

According to the variation of the stoichiometry and following a proposal of Nowotny and Jeitschko[17,25] the new compounds Ta/Al/C can be assigned as "312-phase" (Ta_3AlC_2) and "413-phase" (Ta_4AlC_3), respectively. In the course of our investigations we had hints for the existence of a "514-phase" and additional stacking variants, but the poor quality of the crystals disabled a satisfying characterization. But further variation of the experimental conditions (temperature program, auxiliary metals) will give an access to these higher carbides, too.

Conclusions

The application of the auxiliary bath technique enabled the synthesis of the new MAX-phases Ta_3AlC_2 and Ta_4AlC_3 of the system Ta/Al/C. Analyses by EDX and WDX confirmed the compositions and the absence of N and O. Investigations by means of XRD on single crystals revealed an ordered structure without mixed occupation Ta/Al and C vacancies. On the basis of the well resolved crystal structures a systematic description of the structural parameters of MAX-phases is possible. This enables to estimate the distances in compounds where the structures were not yet refined. The generalized modular building principle for phases $(MX)_nMM'$ is developed which can serve a useful tool to predict lattice constants and crystal structures of unknown phases with $n > 3$.

Note in Addition. During the preparation of this manuscript a contribution on the high-pressure behavior of Ta_4AlC_3 was published.[37] XRD investigations on powder samples confirm the existence of Ta_4AlC_3 and its classification as a "413-phase" with a hexagonal structure ($P6_3/mmc$, $Z = 2$, $a = 3.087(5)$ Å, $c = 23.70(4)$ Å). In comparison to our results the deviations of the lattice constants are considerable.

Acknowledgment. Thanks are due to Bayerisches Geo-Institut (BGI, Universität Bayreuth) for the access to WDX measurements and to Detlev Krausse for his support.

Supporting Information Available: CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC062231Y

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(37) Manoun, B.; Saxena, S. K. El-Raghi, T.; Barsoum, M. W. *Appl. Phys. Lett.* **2006**, *88*, 201902.