The Crystal Structure and Chemical Properties of $\text{U}_2\text{Al}_3\text{C}_4$ and Structure Refinement of Al_4C_3

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A well crystallized sample of $\text{U}_2\text{Al}_3\text{C}_4$ was obtained by melting the elemental components in a carbon crucible in a high frequency furnace. The crystal structure of this compound was determined from single-crystal diffractometer data of a twinned crystal: $\text{P6}_3\text{mc}$, $a = 342.2(1)$ pm, $c = 2323.0(3)$ pm, $Z = 2$, $R = 0.030$ for 537 structure factors and 18 variable parameters. The structure can also be described in the higher symmetry space group $\text{P6}_3/\text{mmc}$ with one split aluminum position. It consists of close packed layers of uranium and aluminum atoms with carbon atoms at interstitial sites. The structure is closely related to that of Al_4C_3 , which was refined from single-crystal X-ray data to a residual of $R = 0.033$ for 135 F-values and 11 variables. The hydrolysis of $\text{U}_2\text{Al}_3\text{C}_4$ with diluted hydrochloric acid resulted in about 74 (wt-%) methane, 8% ethane and ethylene, and 18% saturated and unsaturated higher hydrocarbons.

Introduction

Cirilli and Brisi have investigated the ternary system uranium-aluminum-carbon [1] and found two ternary carbides to which they ascribed the tentative compositions “ $\text{U}_2\text{Al}_3\text{C}_3$ ” and “ UAl_5C_4 ”. We have recently determined the crystal structure of the latter compound, which turned out to have the composition UAl_3C_3 [2]. Here we report on the other ternary carbide for which we found the composition $\text{U}_2\text{Al}_3\text{C}_4$. Its structure is closely related to that of Al_4C_3 . Since the structural properties of that well known carbide [3] were determined only by film data [4, 5] we have also refined this structure from single-crystal diffractometer data. Preliminary results of this work were reported at a conference [6].

Sample Preparation and Lattice Constants

Starting materials were uranium in the form of small platelets (Merck, “nuklearrein”), aluminum foil (Alpha, 99.9%) and graphite flakes (Alpha, 99.5%). The uranium platelets were cleaned with concentrated nitric acid to remove oxide impurities. The samples were prepared from mixtures of

stoichiometric quantities of the elemental components in carbon crucibles, which were heated in a high frequency furnace at about 1500 °C for two hours.

Lattice constants were determined by least-squares fits of the Guinier powder data using $\text{CuK}\alpha_1$ radiation, α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard, and an optical densitometer to measure the positions of the diffraction lines. To prevent the reaction of the samples with the humidity of the air, the powders were covered by dried paraffin oil. The hexagonal lattice constants of $\text{U}_2\text{Al}_3\text{C}_4$ obtained this way ($a = 342.2(1)$ pm, $c = 2323.0(3)$ pm) are slightly larger than those from the four-circle diffractometer ($a = 341.79(3)$ pm, $c = 2320.9(2)$ pm), because of the usual systematic errors of the single-crystal data caused by absorption, which are difficult to correct. The lattice constants of Al_4C_3 determined from our powder data ($a = 333.5(1)$ pm, $c = 2496.7(3)$ pm) are in good agreement with those found by Stackelberg and Schnorrenberg [4] after conversion from the old Å units to the presently accepted values (factor 100.2): $a = 333.2$ pm, $c = 2499$ pm. The values given by Jeffrey and Wu [5] are also in good agreement: $a = 333.0$ pm, $c = 2489$ pm.

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Properties

$\text{U}_2\text{Al}_3\text{C}_4$ crystallizes in the form of thin, black platelets with metallic luster. The powdered samples deteriorate in air within a few hours, and thus the Guinier powder data were recorded under a protective film of paraffin oil. Using 2N hydrochloric acid the hydrolysis is much faster. The gaseous products of this reaction were investigated with a mass spectrometer (Varian MAT, CH5). Besides a nonaccounted amount of hydrogen about 74 (wt-)% methane, 8% ethane and ethylene and 18% saturated and unsaturated C_3 , C_4 , and C_5 hydrocarbons were obtained. This is somewhat surprising since the compound contains only isolated carbon atoms. Apparently the uranium atoms catalyse the formation of the higher hydrocarbons since Al_4C_3 produces only methane, as is well known, and as also confirmed by us [7].

Single-Crystal Diffractometry

Single crystals of $\text{U}_2\text{Al}_3\text{C}_4$ and Al_4C_3 were isolated from the crushed samples prepared in the high frequency furnace. They were sealed into evacuated, thin-walled silica tubes to prevent hydrolysis. Intensity data were recorded on a four-circle diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. Background counts were taken at both ends of each $\theta/2\theta$ scan. Empirical absorption corrections were made from psi scan data. Further details are listed in Table I.

Table I. Crystal data for $\text{U}_2\text{Al}_3\text{C}_4$ and Al_4C_3 . Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

	$\text{U}_2\text{Al}_3\text{C}_4$	Al_4C_3
Formula weight	605.05	143.96
Space group	$\text{P6}_3\text{mc}$ (No. 186)	$\text{R}\bar{3}\text{m}$ (No. 166)
a [pm]	342.2(1)	333.5(1)
c [pm]	2323.0(3)	2496.7(3)
V [nm ³]	0.2356	0.2405
Formula units/cell	$Z = 2$	$Z = 3$
Calculated density [g/cm ³]	8.53	2.98
Crystal size [μm^3]	25×25×50	225×200×25
$\theta/2\theta$ scan up to	$2\theta = 80^\circ$	$2\theta = 105^\circ$
Ranges in hkl	$\pm 6 \pm 6 \pm 35$	$\pm 7 \pm 7 \pm 59$
Highest/lowest transmission	4.2	1.1
Total no. of reflections	5769	4579
Unique reflections	653	484
Reflections with $F_o > 4\sigma(F)$	537	135
Number of variables	18	11
Conventional residual	$R = 0.030$	$R = 0.033$
Weighted residual	$R_w = 0.083$	$R_w = 0.045$

The positions of the uranium atoms of $\text{U}_2\text{Al}_3\text{C}_4$ were obtained by direct methods and those of the lighter atoms by subsequent difference Fourier syntheses. The atomic positions for Al_4C_3 were taken from the previous determinations [4, 5]. The structures were refined by full-matrix least-squares calculations with atomic scattering factors [8], corrected for anomalous dispersion [9]. The weighting schemes reflected the counting statistics. Parameters for isotropic secondary extinction corrections were refined and applied to the calculated structure factors.

The refinement of the $\text{U}_2\text{Al}_3\text{C}_4$ structure was first carried out in the space group $\text{P6}_3/\text{mmc}$. It resulted in a large thermal parameter U_{33} for the Al1 position (1/3, 2/3, 1/4), which is situated on a mirror plane perpendicular to the c axis. Since such a large thermal parameter was considered unrealistic we refined this atom with a split position off the mirror plane (1/3, 2/3, 0.2422(5)). This refinement resulted in a residual of $R = 0.028$ for 14 variable parameters and 237 structure factors. It is possible to describe this structure in the lower symmetry space group $\text{P6}_3\text{mc}$, where the Al atoms of the split position fully occupy the position 2b, assuming that the crystal consists of two twin domains. This was easily accomplished with the SHELXL-93 program [10]. It resulted in a twin domain ratio of 0.39(6)/0.61(6). This ratio is within two standard deviations the same as the ratio of 0.5/0.5 for a statistical distribution of the aluminum atoms in the position 1/3, 2/3, 0.2422(5) of the higher symmetry space group $\text{P6}_3/\text{mmc}$. However, it is well known – e.g. for binary carbides [11] – that the statistical distribution is at best a thermodynamically stable form of a solid state compound at high temperatures. At lower temperatures at least some short range order has to be assumed for such compounds, and for that reason we prefer the refinement in the space group $\text{P6}_3\text{mc}$ with full occupancy of all atomic sites. Because of the proximity of the whole structure to the higher symmetry space group, we constrained the thermal parameters of those atoms, which occupy one atomic site in $\text{P6}_3/\text{mmc}$ (U1 and U2, Al2 and Al3, as well as C1 and C2). As a check for the composition we refined occupancy parameters in one series of least-squares cycles together with the thermal parameters in the higher symmetry space group $\text{P6}_3/\text{mmc}$. They varied between

$U_2Al_3C_4$	$P6_3mc$	x	y	z	$B_{11}=B_{22}$	B_{33}	B_{12}	B
U1	2b	1/3	2/3	0.56246	0.348(6)	0.266(8)	$B_{11}/2$	0.322(5)
U2	2b	1/3	2/3	0.93793(3)	0.348(6)	0.266(8)	$B_{11}/2$	0.322(5)
Al1	2b	1/3	2/3	0.2430(2)	—	—	—	0.34(6)
Al2	2a	0	0	0.1629(5)	—	—	—	0.43(3)
Al3	2a	0	0	0.3361(6)	—	—	—	0.43(3)
C1	2b	1/3	2/3	0.132(1)	—	—	—	0.4(1)
C2	2b	1/3	2/3	0.362(1)	—	—	—	0.4(1)
C3	2a	0	0	0.000(5)	—	—	—	0.5(1)
C4	2a	0	0	0.249(2)	—	—	—	0.4(2)

Al_4C_3	$R\bar{3}m$	x	y	z	$B_{11}=B_{22}$	B_{33}	B_{12}	B
Al1	6c	0	0	0.29422(6)	0.55(3)	0.48(5)	$B_{11}/2$	0.52(4)
Al2	6c	0	0	0.12967(7)	0.40(4)	0.94(5)	$B_{11}/2$	0.58(4)
C1	3a	0	0	0	—	—	—	0.54(9)
C2	6c	0	0	0.2168(2)	—	—	—	0.23(6)

Table II. Atomic parameters of $U_2Al_3C_4$ and Al_4C_3 . The last column contains the isotropic thermal parameters and the equivalent isotropic thermal parameters B ($\times 100$, in units of nm^2), respectively. The values of B_{13} and B_{23} are zero because of the local symmetry of the occupied positions of both structures. The z parameter of the U1 atoms was held constant to define the origin of this polar structure.

the values of 0.79(5) for the carbon position 1/3, 2/3, z and 1.02(2) for the aluminum position 0,0, z . Since all occupancy values were within five standard deviations at the ideal values, we assumed the ideal values also for the refinements in $P6_3mc$.

Occupancy parameters were also refined for the Al_4C_3 structure and here the occupancy of the C2 position was found to be rather high with 112.4% and a standard deviation of 1.3% (9.5σ off the ideal value). It seemed possible that any nitrogen or oxygen impurities are accommodated on that site. Refining this site with mixed carbon/nitrogen occupancy resulted in a 44(6)/56(6)% distribution. This seemed to be a rather high nitrogen content

and it would have meant that about one third of the carbon atoms of our Al_4C_3 sample were substituted by nitrogen atoms. We ruled out the possibility of such a high nitrogen content for two reasons. One is, that already Al_5C_3N has a different crystal structure [5]. The other reason is, that with one third of the carbon atoms substituted by nitrogen atoms the compound would need to accommodate one electron per formula unit in the conduction band, and thus the compound should be black. However, our crystal of Al_4C_3 had a pale yellow color. We therefore assumed the ideal occupancy parameters again in the final least-squares cycles. The positional parameters in the standardized form [12] and the interatomic distances are given in the Tables II–IV. The structure factor tables are available from the authors.

Discussion

While the positional parameters of Al_4C_3 are confirmed by the present refinement (albeit with more than 10 times smaller standard deviations),

Table III. Interatomic distances of $U_2Al_3C_4$. All distances shorter than 420 pm (U–U, U–C), and 337 pm (U–Al, Al–Al, Al–C), and 328 pm (C–C) are listed.

U1:	3C3	245(7)	Al3:	1C4	201(6)
	3C1	255(1)		3C2	206.8(8)
	3Al2	305.8(9)		3Al1	293(1)
	6U1	342.2(1)		3U2	308(1)
	3U2	350.3(1)	C1:	3Al2	210.5(9)
U2:	3C3	245(7)		3U1	255(1)
	3C2	264(2)		1Al1	259(2)
	3Al3	308(1)	C2:	3Al3	206.8(8)
	6U2	342.2(1)		3U2	264(2)
	3U1	350.3(1)		1Al1	277(2)
Al1:	3C4	198.1(4)	C3:	3U1	245(7)
	1C1	259(2)		3U2	245(7)
	3Al2	271.3(9)	C4:	3Al1	198.1(4)
	1C2	277(2)		1Al2	201(6)
	3Al3	293(1)		1Al3	201(6)
Al2:	1C4	201(6)			
	3C1	210.5(9)			
	3Al1	271.3(9)			
	3U1	305.8(9)			

Table IV. Interatomic distances of Al_4C_3 . All distances shorter than 316 pm (Al–C) and 333 pm (Al–Al, C–C) are listed.

Al1:	1C2	194.2(4)	C1:	6Al1	216.0(1)
	3C1	216.0(1)	C2:	1Al1	194.2(4)
	3Al1	274.9(1)		3Al2	195.2(1)
	3Al2	297.6(2)		1Al2	218.5(4)
Al2:	3C2	195.2(1)			
	1C2	218.5(4)			
	3Al1	267.4(2)			
	3Al2	297.6(2)			

the crystal structure of $\text{U}_2\text{Al}_3\text{C}_4$ represents a new structure type, where the metal atoms form a close packed arrangement (Fig. 1). Three close packed layers of aluminum atoms are followed by two close packed layers of uranium atoms in such a way, that ten layers are needed to form one translation period along the c axis of the hexagonal cell. Starting with the uranium atom at $z = 0.06$ the stacking sequence for the layers UAlAlAlUUAAlAlAlU is BACABCABAC in the ABC notation or cchccccchcc . The latter is the same as $(\text{hcccc})_2$ using the Jagodzinski-Wyckoff notation or $(5)_2$ in the Zhdanov notation. In accordance with the close packed arrangement of the metal atoms, each metal atom should have 12 metal neighbors. However, some of the corresponding distances (e.g. the Al–Al distances corresponding to the a axis of 342.2 pm) are rather large and cannot be considered as bonding interactions. This is also the case for the closely related structures of UAl_3C_3 [2] and Al_4C_3 (Fig. 1).

Fig. 1. The crystal structures of $\text{U}_2\text{Al}_3\text{C}_4$, UAl_3C_3 [2] and Al_4C_3 . The stacking sequence of the closed packed layers in $\text{U}_2\text{Al}_3\text{C}_4$ are indicated in the ABC and the hc notations.

The carbon atoms occupy interstitial sites formed by the metal atoms. The C3 atoms of $\text{U}_2\text{Al}_3\text{C}_4$ are octahedrally surrounded by uranium atoms (Fig. 2). This is also the environment of the carbon atoms in UC with NaCl type structure. In

Fig. 2. Near-neighbor coordinations in the structure of $\text{U}_2\text{Al}_3\text{C}_4$. The site symmetries of the central atoms are indicated. All coordination polyhedra have their three-fold axis arranged vertically.

a first approximation the C1 and C2 atoms may also be considered to have octahedral coordination with three uranium and three aluminum atoms in facial arrangement. However, this coordination is augmented by a fourth aluminum atom, somewhat further away, outside the triangular faces formed by aluminum atoms of the octahedron. Finally, the C4 atoms have a trigonal bipyramidal aluminum environment, which is similar to the environment of the C2 atoms of Al_4C_3 . However, in the Al_4C_3 structure these carbon atoms are situated not exactly in the center of trigonal bipyramids. Their environment might also be described as primarily tetrahedral with three aluminum neighbors (Al2) at 195.2 pm and one at 194.2 pm. The fifth aluminum atom is at 218.5 pm outside the trigonal face formed by the three Al2 neighbors. The average C–Al distance of 199.7 pm for the five Al neighbors of the C2 atoms in Al_4C_3 , however, is very similar to the average of the five C–Al distances of 199.3 pm for the C4 atoms in $\text{U}_2\text{Al}_3\text{C}_4$. The C2 atoms of the closely related UAl_3C_3 structure (Fig. 1) also have trigonal bipyramidal aluminum coordination with C–Al dis-

tances of 196.3 pm (3×) and 200.7 pm (2×), and an average of 198.1 pm.

The Al1 atoms of $U_2Al_3C_4$ have three carbon neighbors at 198.1(4) pm. Two additional carbon atoms complete this coordination to a trigonal bipyramidal one, however, the corresponding Al1–C distances of 259(2) and 277(2) pm are rather large. These distances would be equal (268 pm) if the structure were refined in the higher symmetry space group $P6_3/mmc$, as was discussed already above. The other two aluminum positions of $U_2Al_3C_4$ are coordinated tetrahedrally by carbon atoms with average Al–C distances of 208.1 and 205.4 pm.

Both uranium atoms of $U_2Al_3C_4$ (they occupy only one position in a refinement in $P6_3/mmc$) have octahedral carbon coordination with average U–C distances of 250 and 254 pm, which are slightly greater than the U–C distances of 248 pm in UC with NaCl type structure [13, 14]. The U–U distances of 342.2 pm are rather large considering that the average U–U distance in the α -modification of elemental uranium is 314 pm [15]. Similarly, if we take half of this distance (157 pm) as

the metallic radius of uranium and add the metallic radius of aluminum (143 pm [15]) we obtain 300 pm for a bonding U–Al interaction, and this distance is shorter than the U–Al distances of 306 and 308 pm in $U_2Al_3C_4$.

Thus, the stability of this compound is essentially determined by the metal-carbon interactions. Since the carbon atoms are isolated from each other, they obtain the oxidation number –4 and accordingly the compound may be written with the formula $(U^{+3.5})_2(Al^{+3})_3(C^{-4})_4$, suggesting a mixed or intermediate valency for the uranium atoms.

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