

A New Diamond-Related Compound in the System $\text{Al}_2\text{O}_3\text{--Al}_4\text{C}_3\text{--AlN}$

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A new compound has been identified in the system $\text{Al}_2\text{O}_3\text{--Al}_4\text{C}_3\text{--AlN}$, which crystallizes in a diamond-related structure. This compound, for which the acronym "ALCON" is used, has the composition $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$. ALCON crystallizes in a rhombohedral space group ($R\bar{3}m$, no. 166): $a = 5.459(2)$ Å and $c = 14.952(6)$ Å (hexagonal description) or $a = 5.897(2)$ Å and $\alpha = 55.15(4)^\circ$ (rhombohedral description). ALCON is a compound with a very limited phase width with respect to the molar C/O ratio and the aluminium content. Electron diffraction results are in agreement with the structure as determined by X-ray powder diffraction. High-resolution transmission electron microscopy revealed the existence of twin defects in the (100) plane (hexagonal description). © 1995 Academic Press, Inc.

INTRODUCTION

Interest has recently focused on ceramics which combine a high thermal conductivity with a high electrical resistance at room temperature. Such materials can be used for heat sinks in microelectronic devices. As discussed by Slack (1), there are only a few materials which have a low electrical conductivity and a thermal conductivity higher than $100 \text{ W/m} \cdot \text{K}$ at room temperature. Most of them are compounds which crystallize in a diamond-like structure, e.g., BeO, SiC, and AlN. In addition to the binary compounds noted above, a number of ternary compounds also crystallize in a diamond-like structure. MgSiN_2 crystallizes in an orthorhombic structure, which is derived from the wurtzite structure (2, 3). Recently, we have reported on the preparation of fully dense MgSiN_2 ceramics (4–6). The thermal conductivity of these samples at room temperature has been estimated to be $20 \text{ W/m} \cdot \text{K}$.

Another ternary compound crystallizing in the diamond-related wurtzite structure is Al_2OC (7). Aluminum oxycarbides were been noticed by Foster *et al.* (8), who identified two ternary phases, Al_2OC and $\text{Al}_4\text{O}_4\text{C}$, in the phase system $\text{Al}_2\text{O}_3\text{--Al}_4\text{C}_3$. Al_2OC crystallizes in a wurtzite structure with a short range $\sqrt{3}a_w$, $2c_w$ superstruc-

ture (7). In addition to this short-range superstructure, a long-range ordering of Al in the tetrahedral sites occurs which results in a long-range superstructure. A first attempt to investigate the phase system $\text{Al}_2\text{O}_3\text{--AlN--Al}_4\text{C}_3$ has been reported by Henry *et al.* (9) but the results on quaternary compounds are limited to a number of unidentified phases. Cutler *et al.* (10) showed that a continuous solid solution between SiC or AlN and A_2OC can be formed. Furthermore, it has been observed that A_2OC is stabilized in the presence of other 2H compounds like AlN and SiC. Yohokawa *et al.* (11) observed two X-ray powder diffraction patterns for Al_2OC , prepared from reduction of Al_2O_3 by carbon in the presence of Si_3N_4 . The so-called high-temperature phase (α) exhibits the normal 2H wurtzite diffraction pattern while the low-temperature phase (α') is reported to show three additional major lines. The X-ray diffraction data of the α - and the α' -phase are presented in Refs. (12) and (13), respectively.

This paper describes a new compound in the phase system $\text{Al}_2\text{O}_3\text{--Al}_4\text{C}_3\text{--AlN}$ which crystallizes in a diamond-related crystal structure.

EXPERIMENTAL

Pertinent information on the starting powders used, Al_2O_3 , Al_4C_3 , and AlN, is given in Table 1. The powders were mixed in the appropriate ratios in an agate mortar. From the resultant powder mixture pellets were pressed using a PMMA (polymethyl meta-acrylate) die at 5 MPa. All experiments were done using a h-BN crucible. These pellets were heated in an Astro-C furnace (carbon element) in an Ar flow of $200 \text{ cm}^3/\text{min}$ at 1030 mbar. Prior to heating, the furnace was evacuated twice to about 30 mbar and subsequently filled with Ar up to 1030 mbar. $\text{B}_4\text{C--C}$ thermocouples were used which were calibrated using a C-type thermocouple. The heating rate was $20^\circ\text{C}/\text{min}$ to the set point temperature minus 100°C . A rate of $10^\circ\text{C}/\text{min}$ was used between the aforementioned point and the final temperature to avoid overshoot. The cooling rate was about $20^\circ\text{C}/\text{min}$ down to 1000°C . The weight loss of the pellets was determined by measuring the weight before and after heating.

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TABLE 1
Specification of the Starting Powders

Material (supplier)	Particle size (μm)	Impurities
Al_4C_3 (Cerac, WI)	2.7	99.9% pure ^a , 0.08% Si, %C: 24.93 (theo. 25.03)
Al_2O_3 (CR-6, Baikowski, France)	1	99.99% pure
AlN (F-grade, Tokuyoma Soda, Japan)	0.9	1.25%O, 0.21%C, 90 ppm Si, 250 ppm Ca

^a Analytical results on Al_4C_3 yielded to 24(1) wt.% C, 1.8(1) wt.% O, and 0.2(0.1) wt.% N.

Phase identification was carried out using X-ray diffraction (XRD) (Philips PW1800 diffractometer) using monochromatized $\text{CuK}\alpha$ radiation. The aluminium content was analyzed using inductively coupled plasma emission spectroscopy (ICP-OES) after dissolving the powder in diluted HCl. The oxygen content was measured using a Leco TC 436 O_2/N_2 analyzer and the carbon content was determined using a Strohline Coulomath 702 C/S analyzer. Nitrogen was determined as ammonium by ion chromatography after dissolving the powder in diluted HCl. An ICP analysis on B, Mg, Ca, and Si has been performed to investigate whether these elements are present as contaminants.

High-resolution transmission electron microscopy (HRTEM) was performed with a Philips CM30 Supertwin electron microscope operating at 300 kV. The sample was thoroughly powdered using an agate mortar in hexane. After being dried, liquid nitrogen was poured into the agate mortar. As a result of the thermoshock, the powder is crushed into smaller fragments. After being suspended in hexane, the sample was mounted on a Cu grid with a thin carbon-coated holey film.

RESULTS AND DISCUSSION

In our study on the Al_2OC -AlN system it was noticed that the XRD patterns of some samples showed some additional reflections at low 2θ (high d values) in addition to the normal wurtzite diffraction pattern (of AlN or Al_2OC). These reflections were observed in samples with a relatively high oxygen content. Furthermore, small shifts of the peak positions were observed relative to Al_2OC . To investigate whether these differences were caused by the formation of a superstructure of Al_2OC or by the formation of a new compound which contains more oxygen, a series of experiments were performed in which the molar C/O ratio was varied. In this series samples were prepared by heating mixtures with varying mo-

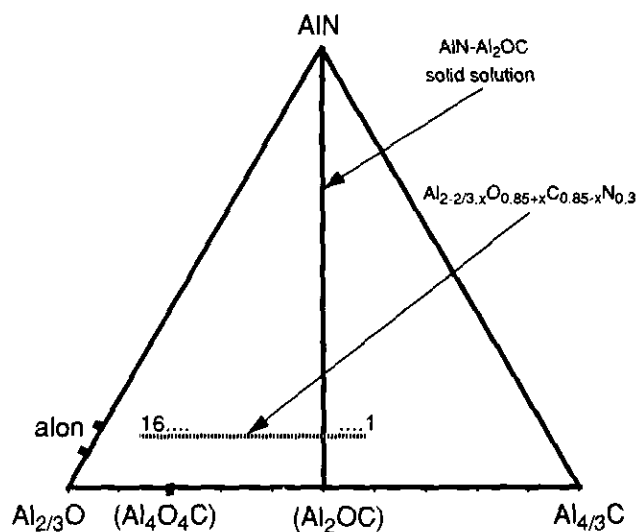


FIG. 1. The phase diagram Al_2O_3 - Al_4C_3 -AlN as known up to now. The compositions of the samples prepared are indicated.

lar C/O content at 1830°C in Argon for 30 min. The composition of these samples is $\text{Al}_{2-2/3x}\text{O}_{0.85+x}\text{C}_{0.85-x}\text{N}_{0.3}$, as indicated in the phase diagram of Fig. 1. For simplicity the diagram is constructed in such a way that the total amount of anions (cq. C, N, O) equals unity. After heating, the samples were analyzed using XRD. At molar C/O close to unity nearly single-phase Al_2OC : 15 mol% AlN is observed. At molar C/O ratios exceeding unity, Al_4C_3 and Al_2OC are found. A decreasing amount of Al_2OC in the samples is observed when the molar C/O decreases. At the same time an increasing amount of a new phase is observed. The relative amounts of Al_2OC and the new phase in the heated samples as estimated using the intensity of the (002) reflection of the simple

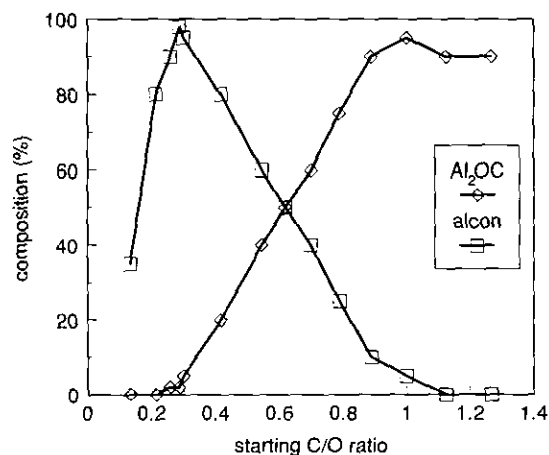


FIG. 2. Phase composition, Al_2OC or ALCON, of the samples with starting stoichiometry $\text{Al}_{2-2/3x}\text{O}_{0.85+x}\text{C}_{0.85-x}\text{N}_{0.3}$ as a function of the molar C/O ratio in the starting material.

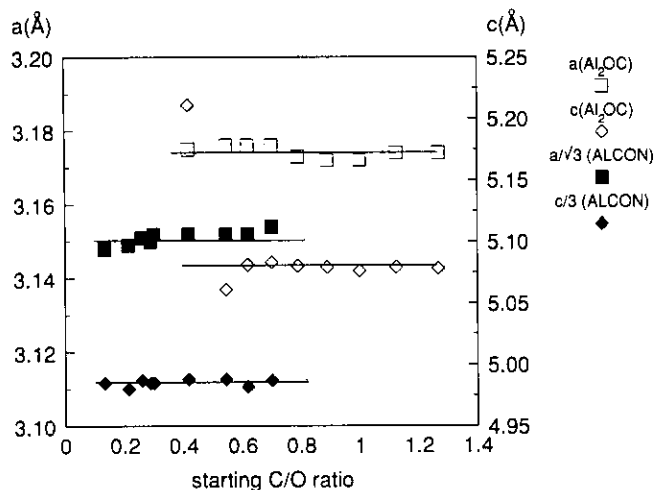


FIG. 3. Unit cell parameters calculated from XRD data for the Al_2OC and ALCON phases present in the reacted mixtures as a function of the molar C/O ratio.

wurtzite structure are presented in Fig. 2. The new phase, which will be called ALCON hereafter, is formed at a molar C/O ratio of 0.30. Below the ratio, in addition to ALCON and the spinel ALON (14), another unknown compound is found. For all samples the weight loss after heating of the mixture seems to be independent of the starting composition and is approximately 5%.

The unit cell parameters calculated from the XRD data for the Al_2OC and ALCON phase in samples with molar C/O ratio 0.1–1.2 are presented in Fig. 3. In the case of ALCON the cell parameters are plotted using $a/\sqrt{3}$ and $c/3$. The identification of the unit cell will be discussed below. Figure 3 clearly shows that the unit cell parameters for both the Al_2OC and the ALCON phase are independent of the molar C/O ratio. This indicates that no solid solution between both phases exists and that they must have a fixed molar C/O ratio.

The experiments described above show that nearly single-phase ALCON can be prepared using a starting molar C/O ratio of 0.30. However, 5% weight loss was still observed. Therefore a series of experiments were performed at lower temperatures in order to reduce evaporation. Furthermore these experiments may give information on the minimum temperature necessary for the formation of ALCON. The experiments were performed using the stoichiometry described above with molar C/O ratios of 0.417, 0.307, 0.288, and 0.259. The samples were fired at 1550 and 1600°C for 4 hr. A large amount of ALCON was obtained in XRD but some reflections are broad, indicating that the samples are not well crystallized. At 1650°C nearly single-phase ALCON was prepared with a weight loss of approximately 3%. The best results are obtained for molar C/O ratios of 0.417 and 0.307. However, always a few percent of Al_2O_3 , ALON,

or $\text{Al}_4\text{O}_4\text{C}$ is present in the fired mixture, indicating that the compound ALCON contains more nitrogen. Therefore a few mixtures were heated with molar C/O ratios between 0.3 and 0.4 and a higher AlN content. They were heated at 1650°C for 4 hr. At the composition $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$ single-phase ALCON was obtained. Finally, experiments were performed in an attempt to prepare ALCON with a minimum in weight loss using two heating steps. In the first heating cycle the powder was heated at 1600°C for 2 hr. The observed weight loss was 0.8%. Hereafter the powder was thoroughly mixed in an agate mortar and pelletized again. In the second heating cycle the pellet was heated for 4 hr at 1650°C. The weight loss in this case was 1.1%. The XRD patterns of these samples show that well-crystallized single-phase powder was synthesized using this procedure. To investigate the presence of contaminants an ICP analysis was performed. Very small amounts of B, Mg, Ca, and Si (Mg, Ca <0.001 wt.%, Si <0.04 wt.%, B <0.05 wt%) were found.

TABLE 2
List of d -Values and Normalized Intensities for ALCON

2θ	$d(\text{obs.})$	$d(\text{calc.})$	I/I_{100}	Hexagonal	Rhombohedral
				hkl	hkl
17.882	4.9562	4.9505	9	0 0 3	1 1 1
19.778	4.4854	4.4807	16	1 0 1	1 0 0
22.340	3.9763	3.9747	10	0 1 2	1 1 0
30.590	2.9201	2.9211	3	1 0 4	2 1 1
32.900	2.7202	2.7201	100	1 1 0	1 0 -1
36.125	2.4844	2.4842	61	0 0 6	2 2 2
37.645	2.3875	2.3870	94	1 1 3	2 1 0
38.638	2.3284	2.3282	<1	0 2 1	1 1 -1
40.083	2.2478	2.2477	1	2 0 2	2 0 0
45.455	1.9938	1.9932	3	0 2 4	2 2 0
49.605	1.8363	1.8365	37	1 1 6	3 2 1
51.572	1.7707	1.7708	6	2 1 1	2 0 -1
52.773	1.7333	1.7347	4	0 1 8	3 3 2
		1.7346		1 2 2	2 1 -1
55.350	1.6585	1.6583	3	0 0 9	3 3 3
57.203	1.6091	1.6094	2	2 1 4	3 1 0
58.638	1.5731	1.5733	57	3 0 0	1 1 -2
60.438	1.5305	1.5315	2	1 2 5	3 2 0
61.788	1.5003	1.5003	7	3 0 3	3 0 0
63.515	1.4635	1.4639	2	2 0 8	4 2 2
65.825	1.4177	1.4172	63	1 1 9	4 3 2
68.813	1.3632	1.3631	10	2 2 0	2 0 -2
70.757	1.3304	1.3303	45	3 0 6	4 1 1
71.702	1.3152	1.3148	21	2 2 3	3 1 -1
72.360	1.3049	1.3048	68	0 1 11	4 4 3
		1.3047		1 3 1	2 1 -2
73.330	1.2900	1.2901	4	1 2 8	4 3 1
		1.2901		3 1 2	3 0 -1
75.252	1.2617	1.2622	2	0 2 10	4 4 2
76.452	1.2449	1.2464	3	0 0 12	4 4 4

Note. Rhombohedral Structure ($R - 3m$, no. 166): $a = 5.459(2)$ Å and $c = 14.952(6)$ Å (Hexagonal Description) or $a = 5.897(2)$ Å and $\alpha = 55.15(4)^\circ$ (Using Rhombohedral Axes).

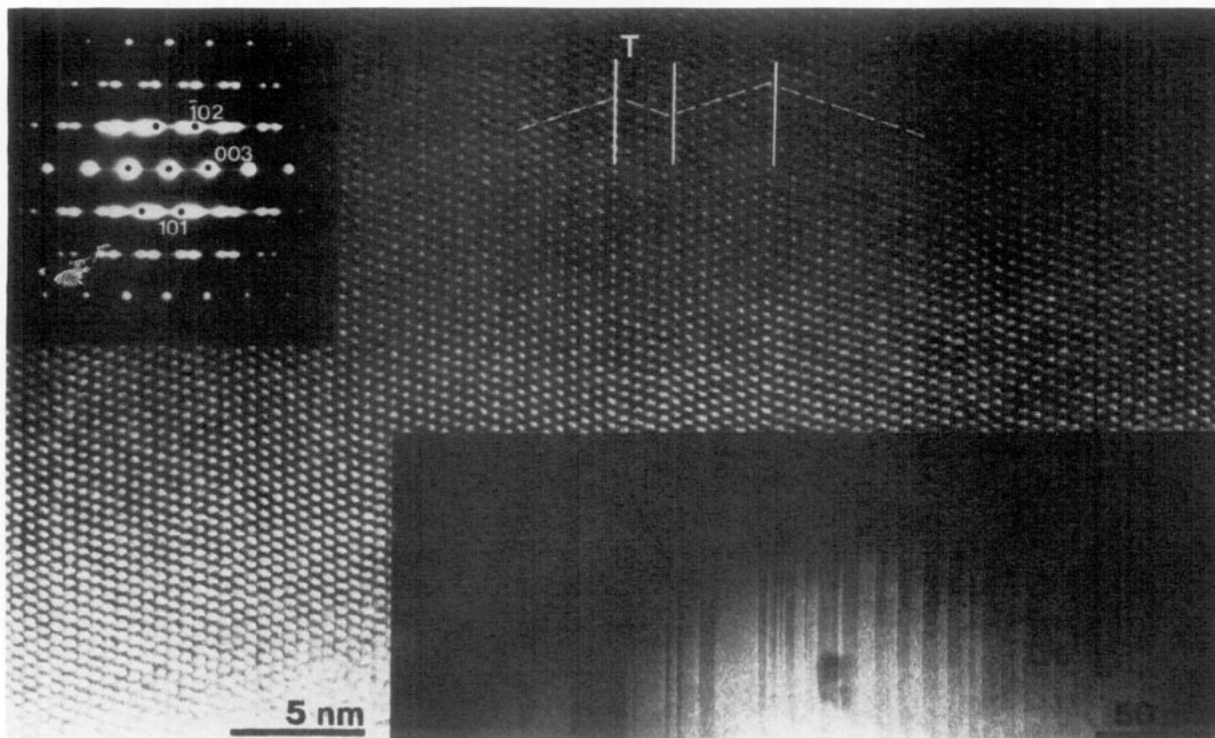


FIG. 4. HRTEM image taken along the $[1-20]$ zone-axis, showing the ABC stacking of the (003) planes and the occurrence of twins (T). The spacing between the subsequent twins is not periodic, which can be seen in the lower magnification TEM image of the inset (bottom right). The corresponding SAED pattern is shown in the inset (top left). The diffraction spots marked by a black dot have been indexed.

The XRD pattern can be indexed using rhombohedral symmetry. The symmetry found in rhombohedral structures can also be described using hexagonal axes. The systematic absences found were: $hkl: -h + k + l = 3n$ (using hexagonal axes) indicating spacegroup $R - 3m$ (no. 166). The unit cell parameters are $a = 5.459(2) \text{ \AA}$ and $c = 14.952(6) \text{ \AA}$ (hexagonal description) or $a = 5.897(2) \text{ \AA}$ and $\alpha = 55.15(4)^\circ$ (using rhombohedral axes). Indexed XRD data of ALCON are presented in Table 2. The structure is related to the wurtzite structure by multiplication of the a -axis by a factor $\sqrt{3}$ and the c -axis by a factor 3. The tripled c -axis is most probably due to the stacking sequence of hexagonal- and cubic-close packed layers. The nature of the multiplication of the a - (and b -) axis is not clear. The exact atomic parameters still have to be determined; this work will be done in the near future.

The powder grains have further been investigated by TEM. In Fig. 4, a TEM image is shown of the grain the $[1-20]$ zone-axis orientation. A large number of parallel but aperiodically spaced planar defects is observed. By means of HRTEM these defects can be identified as twin lamellae lying in the (001) twin plane. As a consequence, the corresponding selected area electron diffraction (SAED) pattern consists of reflections from both

twin variants, as well as streaks perpendicular to the (001) twin plane. The lattice spacings and angles between lattice planes, as derived from this and other zone-axis patterns, are in agreement with the structure as determined with X-ray powder diffraction.

CONCLUSION

A new phase has been identified in the phase diagram $\text{Al}_2\text{O}_3\text{-Al}_4\text{C}_3\text{-AlN}$ which crystallizes in a diamond-related structure. This phase, for which the acronym ALCON is used, has the composition $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$. ALCON crystallizes in a rhombohedral structure ($R - 3m$, no. 166): $a = 5.456 \text{ \AA}$ and $c = 14.956 \text{ \AA}$ (using hexagonal axes) or $a = 5.897 \text{ \AA}$ and $\alpha = 55.11^\circ$ (rhombohedral description).

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