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Effects of a low amount of C on the phase transformations in the AlN–Al_2O_3 pseudo-binary system

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Abstract

The effects of a low amount of C on the phase transformations in the AlN–Al_2O_3 pseudo-binary system are reported in samples having an AlN content in mol% ranging between 44 and about 0. Various complementary experimental techniques were used to determine the nature of the phase equilibria. Carbon is embedded in the components of three eutectics as a function of the average chemical composition of the sample in AlN. In two of them, a component belonging to the quaternary system Al–O–N–C and having a wide composition range was found. Its X-ray and neutron diffraction spectra are well refined with a hexagonal crystalline structure.

Keywords: AlN–Al_2O_3; Carbon; Phase equilibria; Phase transformations

1. Introduction

The Alons, compounds of Al, N and O in the AlN–Al_2O_3 pseudo-binary section are used as abrasive materials. We performed, recently, the crystalline structures of the ϕ' and δ phases by X-ray and neutron diffractions[1,2] and high resolution transmission electron microscopy.[3] The nature of the phase equilibria, temperature and composition range and coherence degree of the different phases submitted to different thermal treatments were also determined, in order to understand their transformations[4], and a thermodynamic assessment of the system was made.[5]

The Alons elaborated by the Péchiney-Electrométallurgie Society contain three main impurities: intentional carbon, and unintentional silicon and iron.

Silicon and iron are introduced during the different steps of the elaboration (grinding, mixing and melting). With the elements Al, O, N, silicon forms quaternary phases named sialons. In fact, the polytype phases of the ternary system Al–O–N have an extension in the quaternary system Al–O–N–Si. We have determined that the two elements Si and Fe are present in general in the final products as metallic precipitates such as: Si, Fe or belonging to the metallic binary systems Fe–Si, Fe–Al, Al–Si or ternary system Al–Fe–Si. They are not involved in the melting process of the Alons.

Carbon is introduced during the melting process of the elaboration in the arc furnace. In fact, in the bottom of the furnace, pieces of carbon are put in, in order to facilitate the starting of the melting. In addition, the tip of the carbon electrodes corrode during the melting and carbon pieces fall into the melting bath. The total weight amount of carbon is about 0.5 wt.% (that is about 100 g by melting of a pancake of 20 kg) and varies moderately from one melting to another one.

2. Experimental

The chemical composition of the samples studied are listed in the Table 1.

The samples were studied by several characterization techniques: X-ray (Cu $K_{\alpha 1}$ radiation), neutron ($\lambda =$ 2.466 Å) diffractions and optical (OM), scanning electron (SEM) microscopies and electron microprobe analysis. By SEM, the two types of contrast (chemical and topological) are the best by using back-scattered electrons. In the case of the chemical contrast, the grey level

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is inversely proportional to $\bar{Z}_{vol}$ (average volume number) equal to:

$$\bar{Z}_{vol} = \frac{\rho}{\bar{M}_{at}} \bar{Z}_{at} \quad (1)$$

with $\bar{Z}_{at}$, and $\bar{M}_{at}$, respectively the average atomic number and mass of the phase and ρ, its volume mass (g cm^{-3}). Theoretically, two phases having $\Delta\bar{Z}_{vol} \sim 1\%$ can be separated. We calculated $\bar{Z}_{at}(Al_2O_3) = \bar{Z}_{at}(AlN) = \bar{Z}_{at}(Al_4C_3) = 10$ e$^-$ and $\bar{M}_{at}(Al_2O_3) \sim \bar{M}_{at}(AlN) \sim \bar{M}_{at}(Al_4C_3) \sim 20.5$ g. Therefore $\bar{Z}_{at}$ and $\bar{M}_{at}$ are practically constant along the pseudo-ternary section Al_2O_3–AlN–Al_4C_3 and $\bar{Z}_{vol}$ is directly related to the volume mass of the phases: lower are these data, darker appears the phase by using the SEM. So the contrast of the phase becomes lighter from Al_4O_4C ($\rho = 2.72$), Al_4C_3 or Al_2OC ($\rho = 3$), "AlONC" ($\rho = 3.15$), AlN ($\rho = 3.26$), γ-AlON ($\rho = 3.68$), ϕ′-AlON, δ-AlON to α-Al_2O_3 ($\rho = 3.97$). The main phases observed in the different samples after slow or fast cooling are indicated in the Table 2, as well as their volume fraction (in %).

R_c noted slow and fast was respectively equal to 15 and 500–1000 K min^{-1}. In the case of the fast cooling of the liquid on a metallic sheet, the C composition of the liquid is lower, see Table 6.

The phase transformations were followed by scanning differential thermal analysis in a device type SETARAM-TAG 24. The heating and cooling rates were equal to 10 K min^{-1}. The atmosphere used was argon at ~1 atm. Pure corundum was used as a standard for the melting temperatures (2327 K).

The neutron diffraction spectra were treated with the profile refinement method of Rietveld[6] with the help of the FullProf software of Rodriguez.[7]

3. Results and discussion

In the samples, the carbon is present under two forms:

(i) either as graphite which does not react during the melting;
(ii) or embedded in precipitates belonging to the quaternary system Al–O–N–C. As for the ternary system Al–O–N, the four elements Al–O–N–C can only exist in the solid state as combination of the neutral simple elements such as: Al_2O_3, AlN and Al_4C_3, so in a pseudo-ternary system. In this system, the phases containing carbon are listed in the Table 3.

The phase diagram Al_2O_3–Al_4C_3 plotted in the Fig. 1 has been studied by Foster et al.[8] The presence of an eutectic Al_2O_3–Al_4O_4C at the composition 90 Al_2O_3–10 Al_4C_3 (in mol%), that is 4.2 wt.% of Al_4C_3 has been found. Thermodynamics of the Al–C–O system, recently assessed by Lihrmann et al.[13] shows that Al_2OC decomposes below 1710°C in good agreement with the experimental data (1715°C) of Lihrmann et al.[14]

In the presence of AlN, this temperature becomes much lower. In fact, in the AlN–Al_2OC system, studied by Kuo et al.,[15] stable Al_2OC-rich precipitates were observed in a 61% AlN–39%Al_2OC solid solution

Table 1
Composition of the samples considered in the present work

Sample no.	Chemical composition (wt.%)						Composition (mol% AlN)
	Al	O	N	C	Fe	Si	Mean value
1	56.1	38	8–8.95	0.26–0.43	0.3	0.27	43.3±2.2
2			6.38				36.3±1.8
3	55	40	4.6–5.23	0.14	0.4	0.25	29.6±1.5
4	55.2	41	4.5–4.88	0.72	0.38	0.24	28.2±1.4
5	54.4	43	3.4	0.57	0.21	0.23	21.3±1.1
6	53.7–54.3	46–44	1.6–1.5	0.35–0.15	0.14	0.1	10.55±0.5
7	53.4	45	0.5	0.94			3.5±0.2

Table 2
Main phases in the samples studied

Sample no.	Cooling rate: (R_c)	AlN/polytypes (mol%)	γ (mol%)	φ′ (mol%)	δ (mol%)	α-Al_2O_3 (mol%)
1	Slow	7.8 AlN + 4.2 21R	88	Traces		
4	Slow	Traces	85	10		
5	Slow		56.7	42.1		1.1
6	Slow		3.5	85.9	4.4	5.9
7	Fast and slow				84.5	15.4

Table 3
Crystalline data of phases containing carbon

Chemical formula	M/X	System	a (Å)	b (Å)	c (Å)	Space group	Ref.	ASTM
Al_4O_4C		orth.	9.23	8.64	5.77		(8)	14–630
Al_2OC		hex.	3.170		5.078	$P6_3/mmc(194)$	(9)	36–148
Al_2OC		hex.	3.153		4.987	$P6_3/mmc(194)$	(9)	36–149
Al_4C_3		hex.	3.339		25.00	$R\bar{3}m(166)$	(10)	35–799
Al_5C_3N	5/4	hex.	3.281		21.67	$P6_3mc$ (186)	(11)	
$Al_6C_3N_2$	6/5	hex.	3.248		40.03	$R\bar{3}m$ (166)	(11)	
$Al_7C_3N_3$	7/6	hex.	3.226		31.70	$P6_3mc$ (186)	(11)	
$Al_8C_3N_4$	8/7	hex.	3.211		55.08	$R\bar{3}m$ (166)	(11)	
$(Al_2OC)_{(1-x)}(AlN)_x$ Wurtzite structure	1	hex.	3.123		4.994		(12)	26–9

exposed at 1600°C for 500 h. In addition, continuous Al_2OC–AlN (2H) solid solutions were found at 1880°C in the 0–44 mol% Al_2OC range[15] and at 1980°C in the 0–40 mol% range.[14]

The ternary system Al_2O_3–AlN–Al_4C_3 has been studied by Henry et al.[16] Zambétakis[17] and Lihrmann et al.[18] The two first authors found the existence of the solid solution $Al_2OC_{(1-x)}AlN_x$ for AlN content equal respectively to 60 and 50 mol%.

The polytypes of the pseudo-binary system Al_4C_3-AlN having the formula $Al_nC_3N_{n-4}$ belong to the $R\bar{3}m$ space group (as well as Al_4C_3) if n is odd and $P6_3mc$ (as well as AlN-2H) if n is even. Their formula always verifies $M/X = n/(n-1)$, with $M = n_{Al}$ and $X = n_C + n_N$.

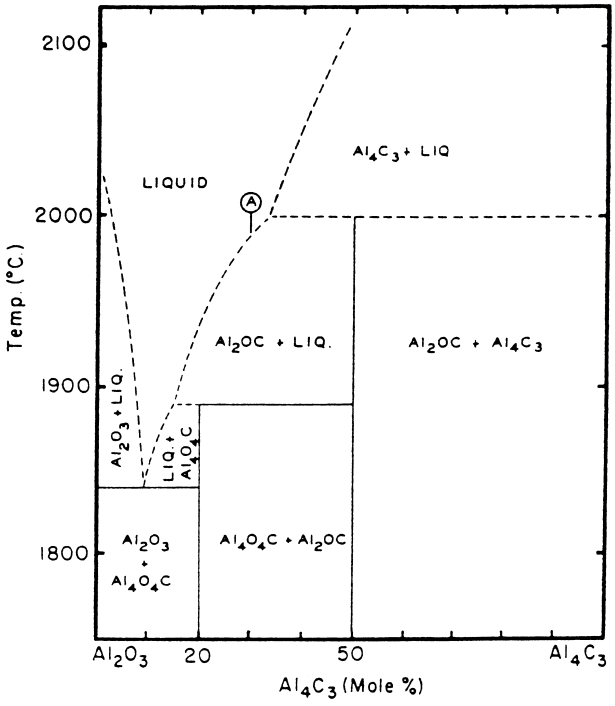

Fig. 1. Al_2O_3–Al_4C_4 pseudo-binary section from Foster et al.[8]

3.1. Optical and scanning electron microscopy analysis

As a function of the composition in AlN (mol%) of the sample, the nature of the matrix is different as shown in the Table 4. The phases containing carbon are observed at the grain boundaries of this matrix with an eutectic morphology which is more or less well resolved. Three different eutectics are revealed as a function of this composition in AlN: eutectic No. 1 in the Sample 5 and eutectics No. 2 and 3 in the Sample 6, as listed in the Table 4. With the help of the OM, they appear lighter than the phases of the Al_2O_3–AlN system while by using the back-scattered electrons in SEM they appear darker. These facts indicate that their density is weaker than the ones of the phases of the AlN–Al_2O_3 system as shown in the Eq. (1). Furthermore, they appear recessed from the matrix because their hardness is probably lower.

The "AlONC" phase belongs to the Al_2O_3–AlN–Al_4C_3 pseudo-ternary system.

The mol fraction of each component of the eutectics numbered 1 and 3 has been calculated by considering ρ("AlONC") $\sim$ 3.15 g cm^{-3}.

The eutectic numbered 1 (Fig. 2a) is generally resolved except in some rare cases when only nodules of "AlONC" are observed. Its temperature of melting is higher than 1950°C.

Table 4
Characteristics of the phases observed in Samples 5 and 6

Eutectic no.	Matrix		Components of the eutectic			
	Phases	C_{min} (AlN%)	Phase 1	Vol.%	Mol%	Phase 2
1	γ, φ′	> 16	γ, φ′	40	44.5	"AlONC" (+s.s.Al_2OC-AlN)
2	φ′	13 à 16	φ′	45	56	Al_4O_4C
3	φ′, δ	< 13	$Al_2O_{3\alpha}$	65	70	"AlONC" (+s.s.Al_2OC-AlN)

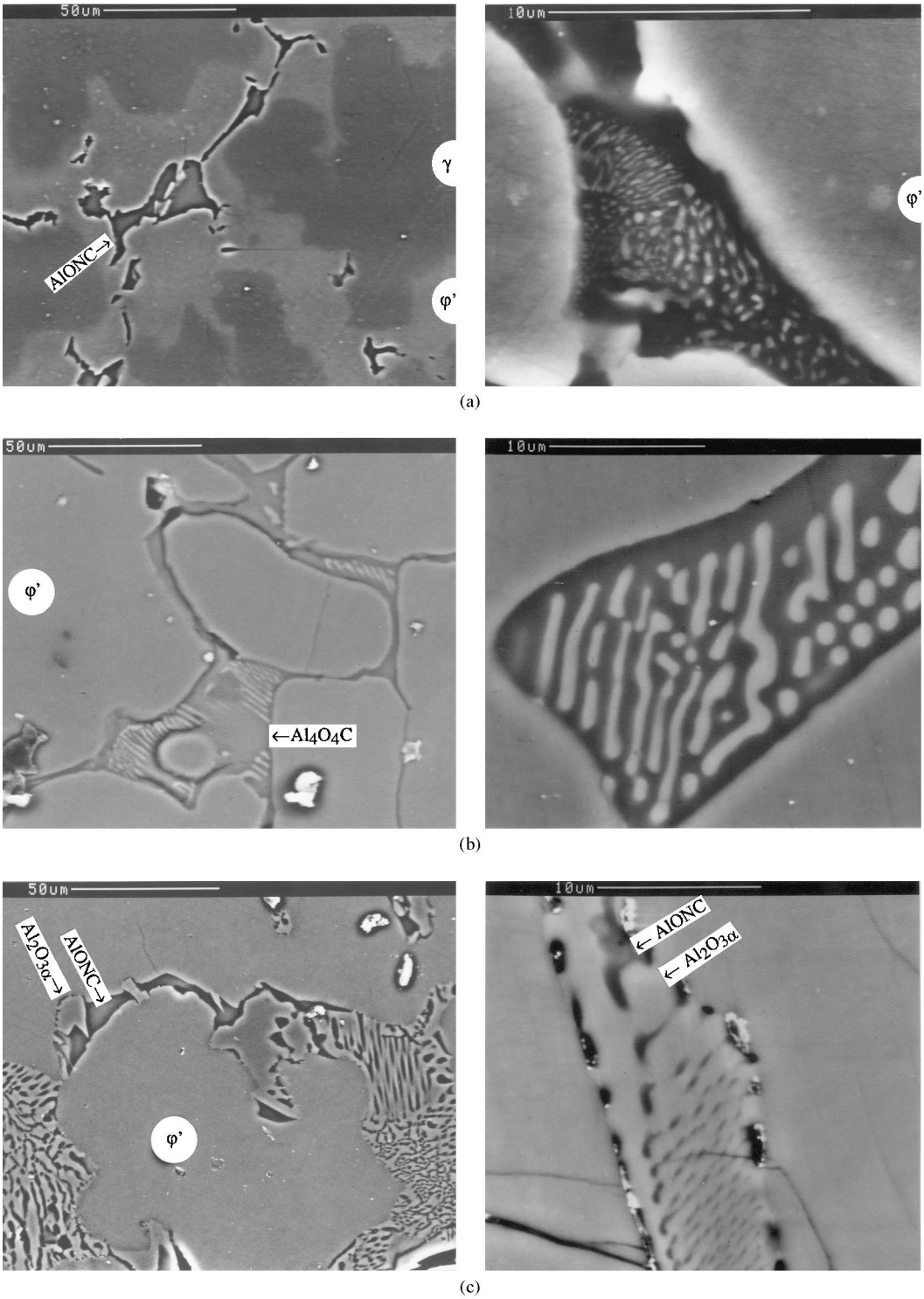

Fig. 2. Back-scattered electron micrographs of the eutectics. (a) Eutectic No. 1 (ϕ′-AlON + "AlONC") in the (ϕ′-AlON + γ-AlON) matrix of sample 5. (b) Eutectic No. 2 (ϕ′-AlON + Al_4O_4C) in the (ϕ′-AlON) matrix of Sample 6. (c) Eutectic No. 1 (Al_2O_3 + "AlONC") in the (ϕ′-AlON) matrix of Sample 5.

The eutectic numbered 2 presents sometimes lamella with a large size and some nodules with about a 1.5 μm interdistance, Fig. 2b.

The morphology of the eutectic numbered 3 is either lamellar with an interdistance varying from 0.45 to 1.5 μm, or with nodules of "AlONC" having a ~ 0.8 μm interdistance, Fig. 2c. The average composition of the eutectic 3 has been confirmed with the help of the electron microprobe. On some micrographs, corundum grains are clearly observed near this eutectic.

The average composition of the eutectics numbered 1, 2 and 3 is more and more depleted in nitrogen because they precipitate in equilibium with a matrix which is also more and more depleted in nitrogen.

3.2. Chemical, X-ray and neutron diffraction analysis

A low amount of the graphite-2H (space group $P6_3/mmc$) is detectable with the help of the neutron diffraction due to the high intensity of the (002) reflection of the graphite. The refined **c** parameter is equal to 6.728 Å against data found in the literature such as: (**a**,**c**) = (2.464 Å, 6.711 Å)[19] and (**a**,**c**) = (2.470 Å, 6.724 Å).[20] The different techniques of analysis allow to determine the weight fractions listed in the Table 5.

In the Sample 7, slowly cooled, noted with the symbol (*) in Table 5, the carbon is present both as a graphite and as precipitates contrary to the Sample 7 fastly cooled and noted by the symbol (**) in the same table. This difference is certainly due to the process of cooling on a metallic sheet. In fact, only the liquid phase situated in the upper part of the furnace and which contains a lower amount in carbon is then gathered.

The difference between the wt.% C determined by chemical analysis and measured by neutron diffraction gives the wt.% C dissolved in the liquid phase. This dissolution is complete in Sample 5, partial in Sample 6 and practically equal to zero in Sample 1. This can be explained by the transformation more or less fast in the liquid state when the melting starts. The average total weight fraction of carbon (~0.5 wt.%) in the samples corresponds in the ternary system Al_2O_3–AlN–Al_4C_3 to 1.25 mol% of Al_4C_3. As an example, it can be noted that 0.5 wt.% of dissolved C corresponds to 6.5 vol.% of "AlONC" and 0.1 wt.% of C to 1.5 vol.% of Al_4O_4C.

3.3. Study of "AlONC"

3.3.1. Composition (microprobe)

As the samples analysed with the help of the microprobe are in general covered with a thin sheet of carbon, the weight fraction of carbon is determined as the following difference: wt.% C = 100- (wt.% Al + wt.% O + wt.% N). This equation was first used without correction. As the charge balance showed a shift corresponding to an excess of carbon, the coefficients of Al, O and N have been verified. It seems that the real curling on these phases is slightly lower than the one on the matrix, maybe due to the recessed morphology of the precipitates. By using a sum of the weight fractions equal to 98.5 instead of 100, a charge balance equal to zero was found.

The mol composition of the "AlONC" phase linearly varies between P_1 [25% Al_2O_3– 75% AlN] and P_2 [60% Al_2O_3– 20% AlN–20% Al_4C_3], Fig. 3. The intersection point of this straight line with the Al_2O_3–Al_4C_3 section would be at 26.5 mol% Al_4C_3, which does not correspond to a compound cited in the literature: in fact, Al_4O_4C is found at 20 mol% Al_4C_3 and Al_2OC at 50 mol% Al_4C_3. Three domains can be distinguished in the mole% AlN composition range:

The general formula of the polytypes in the AlN–Al_2O_3 pseudo-binary section is $Al_nO3N_{(n-2)}$. In the Al_2O_3–Al_4C_3 pseudo-binary section, this formula becomes: $Al_{(x+4)}O_{(1.5x)}C_3$. When x is respectively equal to 8, 6, 5, 4.4 and 4 the ratio $M/X = n/n+1$ with $M = (n_{Al})$ and $X = (n_O + n_C)$ is equal to 4/5, 5/6, 6/7, 7/8 and 8/9. It must be noted that the compounds of the

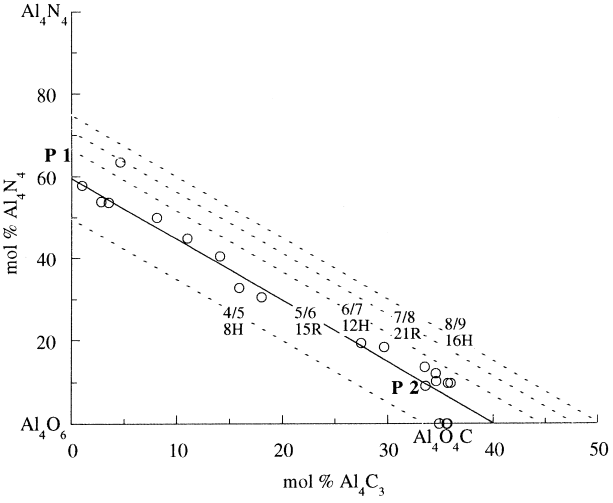

Fig. 3. Composition range of the "AlONC" phase in the pseudo-ternary section Al_4O_6–Al_4N_4–Al_4C_3.

Table 5
Weight fractions of C measured in the different samples

Sample no.	1	4	5	6	7(*)	7(**)
Total wt.% C (measured by chemical analysis)	0.26–0.43	0.72	0.57	0.35–0.15	0.94	< 0.94
wt.% C_{2H} (measured by neutron diffraction)	0.42	— [a]	0.07	0.29–0.21	–	0.06 (**)
Detected phase by X-ray and neutron diffractions	–	"AlONC"	"AlONC"	Al_4O_4C	–	-
Vol.% of precipitates detected by OM	0.0	–	~4	1 to 2	–	0.0

[a] Means not determined.

Al_2O_3–Al_4C_3 pseudo-binary section have not a polytype structure as R$\bar{3}$m or P6_3mc (see Table 3).

In order to plot the pseudo-ternary system Al_2O_3–AlN–Al_4C_3, it is interesting to use the Al_4O_6, Al_4N_4 and Al_4C_3 compounds. In fact, $M = n_{Al}$ is then a constant for the whole diagram and $X = (n_O + n_{C+} n_N)$. It is well known that the composition of the polytypes verifies the relation M/X = constant with $X = M + 1$ when they present a domain of solid solution. In Fig. 3, the parallel straight lines having the equation $M/X = 4/5$, 5/6, 6/7, 7/8, 8/9 (which corresponds respectively to the structures of the polytypes 8H, 15R, 12H, 21R, 16H) as well as the Al_4O_4C compound (which has not a polytype structure) have been plotted, see the Table 7. As an example, the intersection of the straight line (slope 5/6) representing the possible composition range of the 15R polytype ($Al_5O_3N_{(5-2)} = 3AlN + Al_2O_3$) in the AlN–$Al_2O_3$ pseudo-binary section is situated at (3/4) mol AlN, while in the Al_4N_4–Al_4O_6 pseudo-binary section ($Al_5O_3N_{(5-2)} = 3/4$ $Al_4N_4 + 1/2$ Al_4O_6), it is situated at (3/4)/((3/4) + (1/2)) that is 0.6 mol Al_4N_4. It can be noted that the domain of composition of the "AlONC" compound (noted with empty circles) is set in a parallel direction to these straight lines and is very near the one of the 15R polytype. The 15R polytype is not stable in the Al_2O_3–AlN pseudo-binary system but is observed in the Al_2O_3–AlN–SiO_2–Si_3N_4.pseudo-ternary system.[21] Furthermore it can be noted that the solid solution $Al_2OC_{(1-x)}AlN_x$ corresponds to a compound of the preceding type with a structure 2H and $M/X = 1$ (limite case of the polytypes with $X = M + 1$, M and X tending to infinity, see Table 3).

Table 6
Characteristic of the eutectics numbered 1 and 3

Eutectic no.	Matrix	%AlN("AlONC")
1	γ	> 55
1	γ + ϕ′	35–55
1	γ + ϕ′	20–35
3	ϕ′, δ	20–35

3.4. Crystalline cell (X-ray and neutron diffractions)

With the help of the X-ray diffraction, in Samples 4 and 5, some reflections of phases containing carbon (in particular the interdistances $d = 1.575$ and 2.734 Å) are observed. Furthermore, the refinement of the neutron diffraction spectrum of Sample 1 allowed the determination of the reflections of AlN in particular: $(002)_{AlN}$ (d_1 = 2.490 Å) and $(100)_{AlN}$ (d_2 = 2.695 Å), see Fig. 4. In the case of Sample 4, AlN is also present but in addition there are peaks preceding the AlN reflections which are well taken into account by considering a phase containing carbon having a hexagonal cell with parameters: (**a**,**c**) = (3.153 Å, 4.980 Å) and interdistance of (hkl) planes: d((110), (002), (100)) = (1.576 Å, 2.490 Å, 2.731 Å). These parameters are not consistent with those of the $Al_2OC_{(1-x)}AlN_x$ solid solution but are very near those of a phase having the composition Al_2OC (distinct of the "classical" Al_2OC phase), and identified by Fujishige et al.,[9] and having the parameters: (**a**,**c**) = (3.153 Å, 4.987 Å).

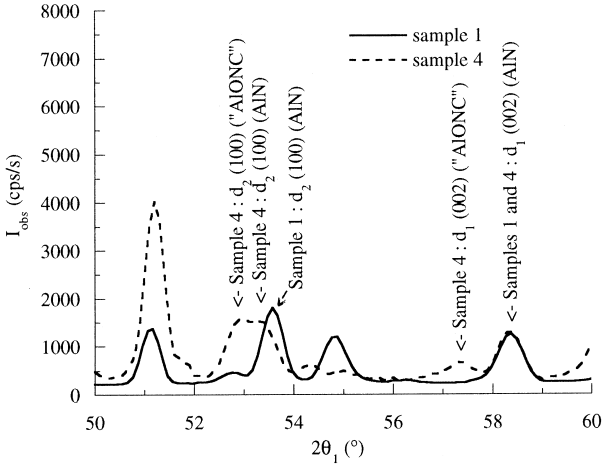

Fig. 4. Neutron diffraction spectra of Samples 1 and 4. Comparative intensities of the (002) and (100) reflections of AlN and "AlONC".

Table 7
Coordinates of the intersections (with the axis of pseudo-binary sections differently plotted) of the straight lines corresponding to the possible composition range of some polytypes 2nH and 3nR

$M/X = n/n+1$	Polytype 2nH or 3nR	Section AlN–Al_2O_3	Section Al_4N_4–Al_4O_6	Section Al_2O_3–Al_4C_3	Section Al_4O_6–Al_4C_3
		Formula — mol% AlN	Mol% Al_4N_4	Formula — mol% Al_4C_3	Mol% Al_4C_3
4/5	8H	$Al_4O_3N_2$:66.67	50	$Al_{12}O_{12}C_3 = Al_4O_4C$: 20.0	33.33
5/6	15R	$Al_5O_3N_3$:75	60 (P1)	$Al_{10}O_9C_3$: 25.0	40.0
6/7	12H	$Al_6O_3N_4$:80	66.67	$Al_9O_{7.5}C_3$: 28.57	44.44
7/8	21R	$Al_7O_3N_5$:83.33	71.38	$Al_{8.4}O_{6.6}C_3$: 31.25	47.61
8/9	16H	$Al_8O_3N_6$:85.71	75	$Al_8O_6C_3$: 33.33	50.0
				$Al_6O_3C_3 = Al_2OC$: 50	66.67

4. Conclusion

Due to the presence of impurities in the start material, precipitation of intermetallic phases (specially phases containing carbon) occurs at the grain-boundaries of the matrix of the samples. Three different eutectics can precipitate as a function of the average chemical composition of C in the sample. The chemical composition of the components of each eutectic has been determined.

Two of these eutectic contain a phase belonging to the quaternary system Al–O–N–C. This phase has a wide homogeneity range. From the data determined with the help of the X-ray and neutron diffraction spectra, we have proposed a hexagonal crystalline cell for this phase.

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