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ANION CONTROLLED MICROSTRUCTURES IN THE Al_2O_3-AlN SYSTEM

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ABSTRACT

The phase equilibria of the pseudo-binary Al_2O_3-AlN composition join has been extensively investigated, especially with respect to the processing of ALON--a nitrogen stabilized aluminum oxide spinel phase that can be sintered into transparent polycyrstalline ceramics. The system exhibits a wide variety of features and resulting microstructures: two spinel phases, vapor-solid and liquid-solid eutectics, AlN polytype-like structures, and α-Al_2O_3/spinel modulated structures. This system provides a unique perspective to a series of quite different materials based on a constant cation chemistry, with a continuous variation in the O/N anion ratio. Keywords: Aluminum; Nitrogen; composit materials; ceramics;

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ANION CONTROLLED MICROSTRUCTURES IN THE Al_2O_3-AlN SYSTEM

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INTRODUCTION

McCauley and Corbin[1] have published a revised phase equilibrium diagram for the pseudo-binary Al_2O_3-AlN composition join for one atmosphere of flowing nitrogen. Since that time additional characterization of final reacted products has been carried out by transmission electron microscopy (TEM). Further, there has been much renewed interest in AlN ceramics since the methodology for processing of translucent polycrystalline AlN has been published by Kuramoto and Taniguchi[2]. The purpose of this paper is to relate microstructural development in this system to unified crystal chemistry and phase equilibria concepts, supplemented by TEM characterization of selected final products.

REVIEW

Figure 1 illustrates the proposed phase diagram as redrawn by Dennis and Ondik[3] for the Phase Diagrams for Ceramists project. Compositions for the 32H and 16H AlN polytypoids[4] and the $9Al_2O_3$. AlN phase[5] are also indicated on the diagram - the phase equilibrium relations for these phases are not yet completely understood.

This system can serve as a useful model for many other advanced ceramic systems where oxide sintering aids are added to nitride or carbide mixtures. For the conditions (one atmosphere of flowing nitrogen) studied, one end member (AlN) sublines, while the other (Al_2O_3) melts resulting in solid/vapor, liquid/vapor and liquid/solid equilibria that add enormous

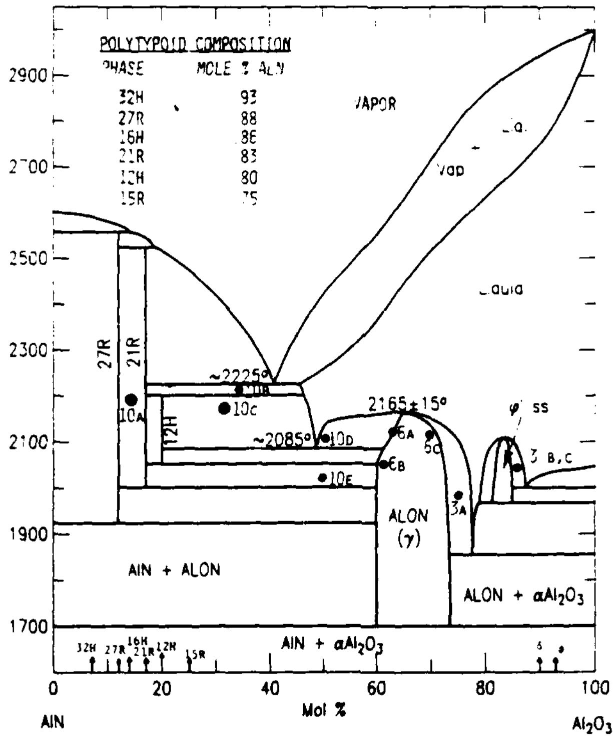


FIGURE 1. PROPOSED PHASE EQUILIBRIUM FOR THE PSEUDO-BINARY Al_2O_3-AlN COMPOSITION JOIN. (ONE ATMOSPHERE OF FLOWING NITROGEN).

potential complexities to processing of mixtures in these types of systems. Very small temperature of composition changes can result in dramatic changes in sintering mechanisms and resulting material. Besides the problems associated with equilibrium phenomena, there are also non-equilibrium aspects, including those associated with impurities in starting powders which can also alter the sintering mechanisms, especially if they result in impurity liquids that have differing wetting or vapor formation properties.

The other important feature of this system involves the various crystal chemistry aspects involved in anion, rather than cation crystal chemistry. Traditional crystal chemistry normally involves cation substitutions in constant anion frameworks. However, in this system the aluminum cation does not change, while oxygen and nitrogen are continuously varied. Figure 2 is a schematic summary representation of the various crystal chemistry and phase equilibrium relationships observed in this system. As indicated in the figure, one of key factors in the formation of all the intermediate phases is the change in cation coodination caused by the substitution of nitrogen for oxygen or vice versa. Application of Pauling's[6] electrostatic valence rule clearly demonstrates that the addition of nitrogen anions to α-Al_2O_3 causes a local charge imbalance on the substituted nitrogen which can be minimized by an Al coordination shift from six to four anions. This rule is summarized as follows:

$\zeta e = Ae$ or $\zeta + A =$ net charge on anion
where $\zeta = \Sigma S$ = sum of bonds to anion

A = anion valence
and z = cation valence
ze = electrical charge on cation
Strength of electrostatic bond = $S = \frac{z}{CN}$

Where CN = coordination number of cation

Three levels of substitution illustrate the situation:

Case 1. <u>N substitutes for O, no change in structure</u>:

$$Al_3^{VI}O_3^{IV}N^{IV} \qquad \zeta(N) = \frac{3}{6} + \frac{3}{6} + \frac{3}{6} + \frac{3}{6} = 2$$

But since A(N) = -3
Net charge on N = -1

Case 2. <u>N substitutes for O, some Al goes into tetrahedral coordination</u>:

$$Al^{IV}Al_2^{VI}O_3^{IV}N^{IV} \qquad \zeta(N) = \frac{3}{4} + \frac{3}{6} + \frac{3}{6} + \frac{3}{6} = 2.25$$

Net charge on N = -0.75

Case 3. <u>N substitutes for O, more Al goes into tetrahedral coordination</u>:

$$Al_2^{IV}Al^{VI}O_3^{IV}N^{IV} \qquad \zeta(N) = \frac{3}{4} + \frac{3}{4} + \frac{3}{6} + \frac{3}{6} = 2.50$$

Net charge on N = -0.50

The converse is true for oxygen addition to AlN. Therefore, minor additions of nitrogen or oxygen to either end member results in a variety of modulated structures based on either AlN or α-Al_2O_3. Further, another indirect effect of this is that the viscosity or the glass forming tendency of a liquid with substantial aluminum may be increased with nitrogen additions because of the formation of higher strength tetrahedral bonds.

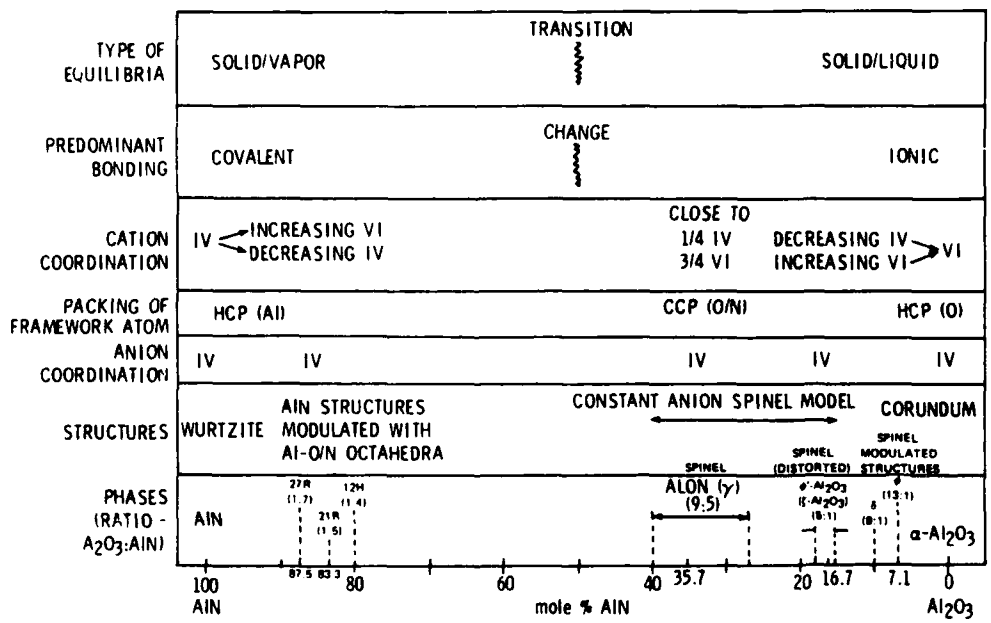


FIGURE 2. RELATION OF CRYSTAL CHEMISTRY TO COMPOSITION AND PHASE EQUILIBRIUM IN THE AlN-Al_2O_3 SYSTEM.

A model, assuming a constant anion spinel framework[7], has been successfully used to describe and account for the unconventional compositions of both the ALON (x=5) and the φ'(ALON'; x = 2) phases. This model derives from the following considerations:

- Two end members are nAl'_2O_3 and $mAl''N$.
- let x = N then Al" = x

  y = O then $Al' = \frac{2}{3}y$

- further if N = x then $O = 32-x$

  $Al' = \frac{2}{3}(32-x)$

  $Al'' = x$

- then total cations $= \frac{2}{3}(32-x) + x = \frac{64+x}{3}$

- cation vacancies or interstitials $= 24 - \frac{64+x}{3} = \frac{8-x}{3}$

FINAL FORMULA $Al_{\frac{64+x}{3}} \square_{\frac{8-x}{3}} O_{32-x}N_x$

FOR x = 8 normal spinel structure
x > 8 cation interstitials
x < 8 cation vacancies

Using the above formula and substituting N = 11 to N = 0 the stoichiometries listed in Table 1 can be calculated.

Table 1. Stoichiometries calculated from constant anion spinel model

	N	O	Al	INTERSTITIALS	VACANCIES	Mole % AlN	
*	11	21	25.00	1.00	-	61.1	
	10	22	24.67	0.67	-	57.7	
	9	23	24.33	0.33	-	54.0	
*	8	24	24.00	0	0	50.0	Normal
	7	25	23.67	-	0.33	45.7	
	6	26	23.33	-	0.67	40.9	
*	5	27	23.00	-	1.00	35.7	ALON (γ)
	4	28	22.67	-	1.33	30.0	
	3	29	22.33	-	1.67	23.7	
*	2	30	22.00	-	2.00	16.7	ALON'(φ')
	1	31	21.67	-	2.33	8.8	
	0	32	21.33	-	2.67	0	

* = stoichiometric compounds - integral numbers of atoms

Basically the reasoning behind using the above model for describing these spinel materials is that in any unit cell an atom is either there (integral) or not there (zero); fractions of atoms can not exist in an actual unit cell. The model also helps to clarify the two ALON spinel compositions since first proposed by Yamaguchi and Yanogida[8].

MICROSTRUCTURAL DEVELOPMENT

ALON' (ϕ') REGION

Figure 3 illustrates reflected light optical photomicrographs of mixtures processed in the region of 20 mole % AlN. For these figures, and also the succeeding ones, the figure numbers refer directly to the black dots on the phase diagram in figure 1 for quick location and reference. The apparent deep eutectic at about 25 mole % AlN results in the formation of a liquid phase as depicted in 3(a). Figures 3(b) and 3(c) illustrate analogous structures for a distorted spinel phase[9] referred to as ALON' or ϕ' and similar to ξ - Al_2O_3 or $LiAl_5O_8$[10]. The aforementioned model predicts a composition of $Al_{22}O_{30}N_2$ (16.7 mole% AlN) for this material. Figure 4 illustrates a transmission electron micrograph of the fine structure shown in figure 3(c). Figure 5 illustrates an analogous TEM micrograph showing bands of incompletely reacted or transformed ALON (bright bands) and bands (dark) of apparent ALON' (ϕ') material. Much more detailed work is needed on this material.

ALON Region

Optical (reflected light) photomicrographs of typical microstructures observed in the ALON solid solution field are illustrated in figure 6. A TEM photomicrograph of material identical to that in figure 6(c) is illustrated in figure 7 showing very clean grain boundaries for carefully processed 30 mole% AlN ALON material. Figure 6(b) illustrates an ALON microstructure having a significant amount of residual porosity. As the processing temperature approaches the liquid plus ALON phase boundary, porosity is dramatically reduced, but other phases appear as depicted by the microstructure in figure 6(a). This results from the formation of a liquid which quenches to 12H plus ALON. Other highly reflective phases can also be observed.

From this composition towards the AlN side many AlN polytype-like phases (polytypoids) occur as a function of temperature and starting composition. These are not properly called polytypes since their composition vary. Table 2 is a summary of many of these polytypoid phases with the corresponding nomenclature used by other authors[11-15]. Figure 8 shows the summarized X-ray diffraction data used in this study to differentiate them.[16]

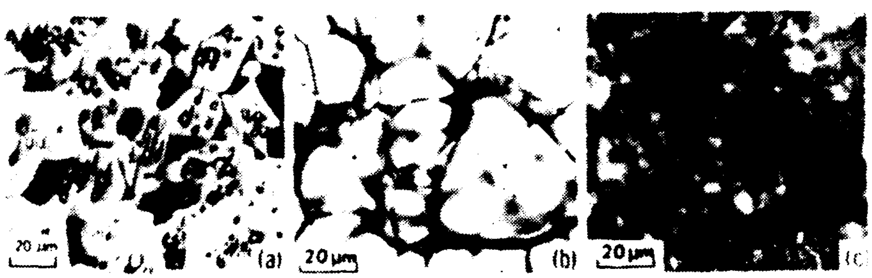


FIGURE 3. ϕ'(ALON') REGION MICROSTRUCTURES.
(a) ALON + L (REFLECTED LIGHT)
(b) ϕ' + L (TRANSMITTED LIGHT)
(c) ϕ' + L ((B) IN CROSSED POLARS)

FIGURE 4. TEM OF ϕ' (ALON') FINE MICROSTRUCTURE; SAME MATERIAL AS IN FIGURE 3(c).

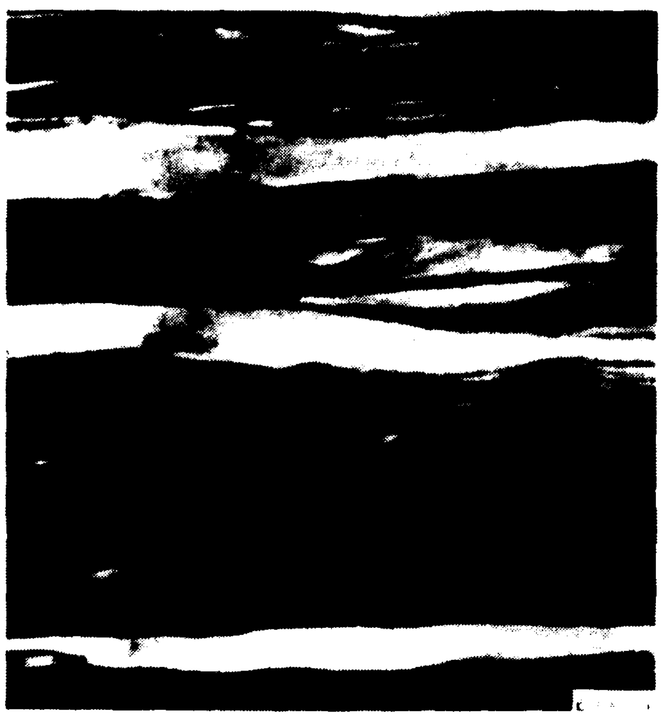


FIGURE 5. TEM OF ALON AND ALON' INTERGROWTH MICROSTRUCTURE; SAME MATERIAL AS IN FIGURE 3(c).

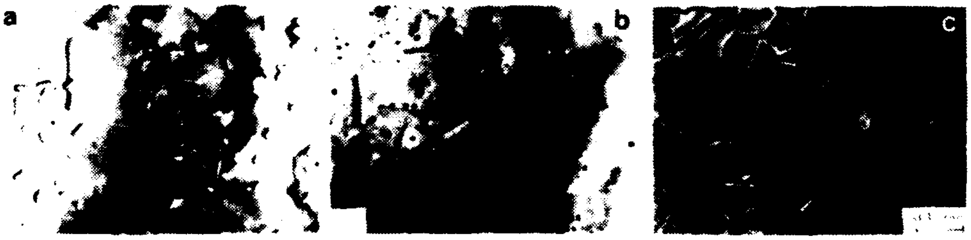


FIGURE 6. ALON REGION MICROSTRUCTURES REFLECTED LIGHT.
(a) ALON + L (ALON + 12H) (b) ALON

FIGURE 7. TEM MICROSTRUCTURE OF 30 MOLE % AlN ALON MATERIAL; SAME MATERIAL AS IN FIGURE 6(c).

Using the criteria described above, the lenticular phase in figure 6(a) was identified as 12H material. Figure 9, however, illustrates a TEM photograph of this same phase (apparently) identified in this case as a highly strained 15R polytypoid. This discrepancy has not been resolved yet and, therefore, not used to change the phase diagram. X-ray fluorescence energy analysis of 15R and the ALON matrix clearly shows that Si impurities from the starting powders preferentially substitutes into 15R. The other highly reflecftive impurity phases were identified as metallic Si-Fe inclusions by the same technique.

Table 2. AlN polytypoid nomenclature

Hexagonal Unit Cell Dimensions in Å				Authors						
a	c	c/n	Atom% Oxygen (Jack)	Jack (Thompson)	Gauckler	Sakai	Land	Layden	Lejus
† 3.11	4.99	2.49	0	2H	AlN	AlN	AlN	AlN	AlN
3.08	5.30	2.65	<15.8	$2H^{\delta}$	-	X_1	-	-	-
† 3.06	71.98	2.67	15.8	27R	X_7	X_2	-	-	-
3.06	43.07	2.69	17.6‡	-	-	X_3(16H)	~ε	-	-
† 3.05	57.19	2.72	20.0	21R	X_6	X_4	-	U	~X
† 3.03	32.91	2.74	23.1	12H	X_5	X_5	ζ	-	-
† 3.01	41.81	2.79	27.3	15R(Y)	X_2	-	η	Y	-
2.99	23.02	2.88	33.3	8H	X_4	-	~θ	-	-

n=number of layers per unit cell
Ramsdell notation
†Phases observed in current work
‡Estimated by Corbin

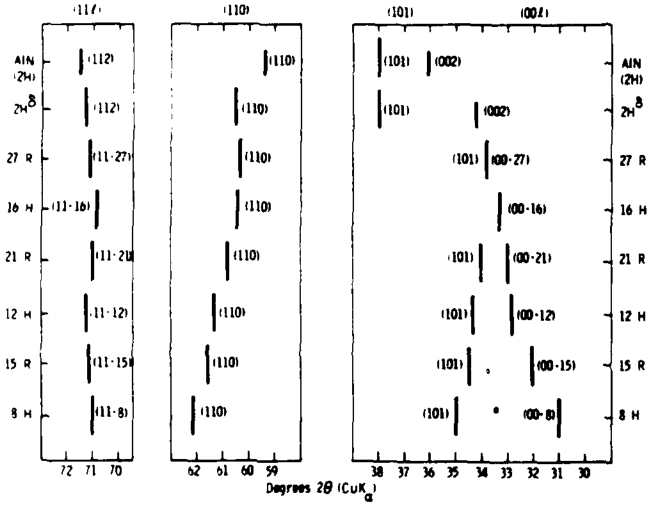


FIGURE 8. VARIATION OF SELECTED X-RAY POWDER DIFFRACTION PEAKS IN AlN POLYTYPOID PHASES.

FIGURE 9. TEM MICROSTRUCTURE OF STRAINED 15R PHASE AT ALON GRAIN BOUNDARIES; SAME MATERIAL AS IN FIGURE 6(a).

50-0 Mole % Al_2O_3 Region

The dramatic effect of liquid on the microstructure of reacted material is nicely demonstrated by figures 10(d) and (e), photomicrographs of material reacted above and below the eutectic temperature, respectively. Figure 10(f) illustrates the macroscopic appearance of these same samples. Figure 11 illustrates a TEM photograph of the 21R phase identified by X-ray diffraction in figure 10(e). The identification of 12H (figure 12) is also confirmed for material shown in figure 10(c). The comparison of the microstructures in figure 10(c) and 10(d) deserves special attention. X-ray powder diffraction of both of these samples indicated very similar percentages of ALON and 12H. However, microstructural interpretation of these same samples definitely suggests that 12H formed first in the 10(c) material with ALON (gray matrix material) forming last. Whereas, ALON formed first in 10(d), with 12H forming last at the ALON boundaries. This nicely shows the importance of detailed microstructural information in the interpretation of phase equilibrium relationships. Preferential substitution of Si into 21R and 12H was also confirmed by TEM analysis in these samples as well.

This part of the phase diagram is extremely complicated because of the presence of both the solid/vapor and solid/liquid eutectics. Material processed in the 27R + 21R region (figure 11(a)) exhibited much less weight loss than material reacted in the 21R + Liquid region.

A series of low magnification photomicrographs of identical material as illustrated in figure 10 is shown in figure 13. It is clear that the microstructures labeled 21R(40%) - 27R(2%) - ALON(58%) and 21R(75%) - 27R(25%), the latter being identical to figure 10(a), suggest that the fracture energy or toughness of these materials should/could be very large based on the interlocking fibrous/lamellar network of polytypoid phases.

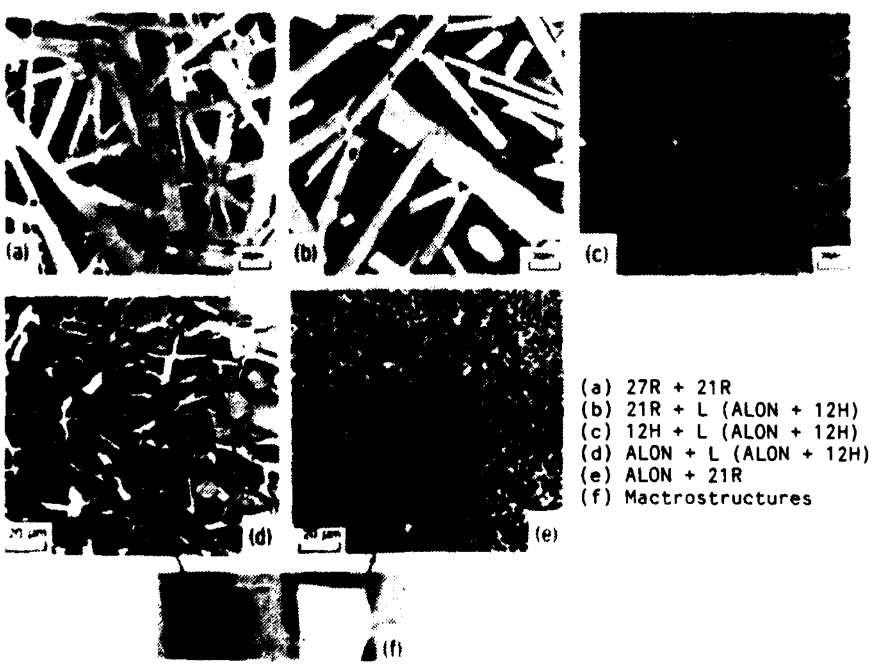


FIGURE 10. 50-0 MOLE % Al_2O_3 MICROSTRUCTURES.

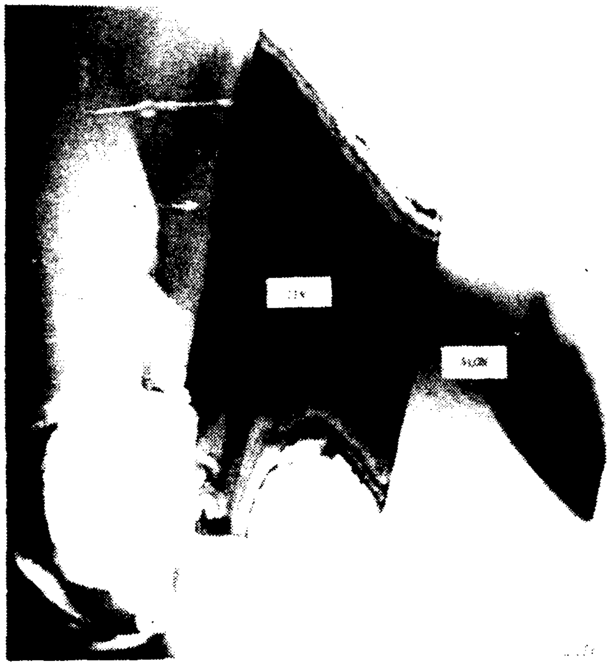


FIGURE 11. TEM MICROSTRUCTURE OF 21R PHASE SURROUNDED BY ALON; SAME MATERIAL AS IN FIGURE 10(e).

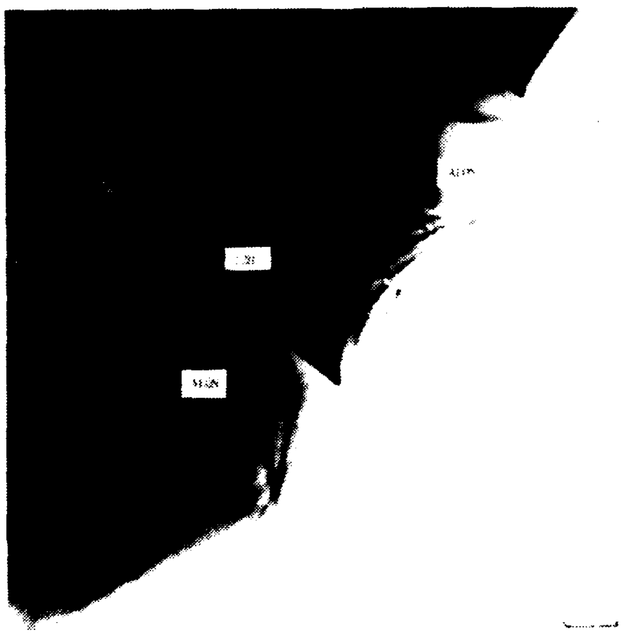


FIGURE 12. TEM MICROSTRUCTURE OF 12H PHASE IN ALON MATRIX; SAME MATERIAL AS IN FIGURE 10(c).

For this reason additional characterization was carried out on the figure 10(a) material[4]. In the detailed TEM study 21R was not found, but a new phase, 32H, was identified; figure 14 illustrates lattice images of the polytypoids identified in this material. It has been suggested[14] that the composition of the polytypoids can be calculated from the number of layers in the repeat unit cell which originates from the various cation/anion ratios. So far quantitative confirmation of the calculated polytypoid compositions has not been successful; qualitative differences, however, have been observed and confirm the trends. The 32H and 27R polytypoids are known to co-exist as depicted in figure 15. This TEM photomicrograph dramatically illustrates the two co-existing phases connected to each other by a disordered region. It is our assumption that this is due to the counter diffusion of ions during the reaction sintering process.

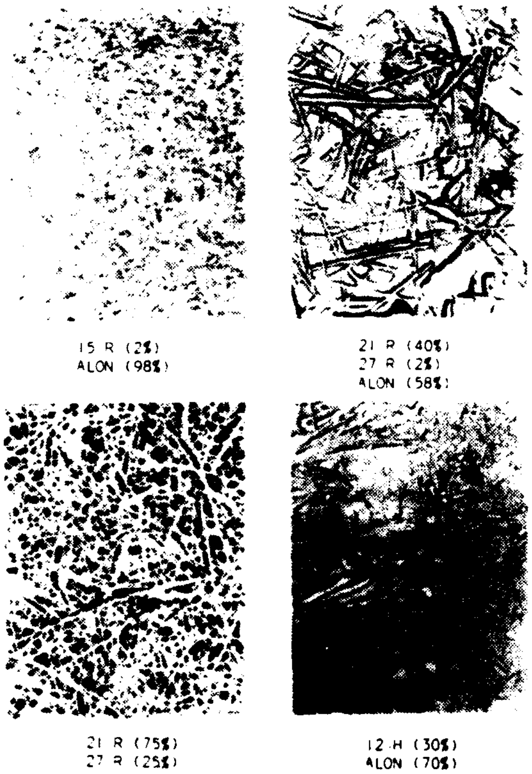


FIGURE 13. LOW MAGNIFICATION PHOTOMICROGRAPHS OF VARIOUS MATERIAL ILLUSTRATED IN FIGURE 10.

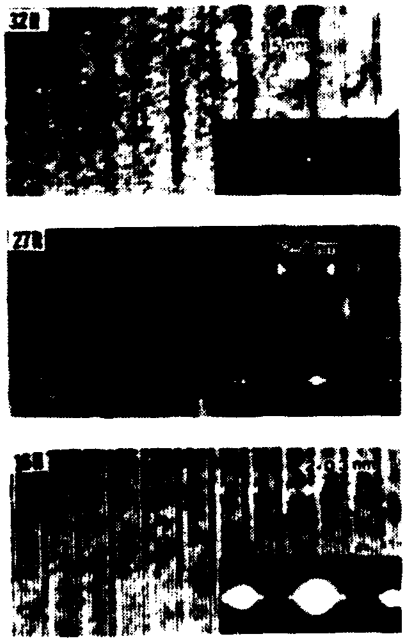


FIGURE 14. LATTICE IMAGES OF THE 32H, 27R AND 16H STRUCTURES FORMED BY THE SYMMETRICAL 001 REFLECTIONS.

ALON HISTORICAL PERSPECTIVE

At this point in time in the development and commercialization of ALON ceramics it is worthwhile to revisit the evolution of this material. The approach taken by McCauley and Corbin[17] involved reaction sintering of ALON from starting Al_2O_3 and AlN powders. It was and still is our opinion that significant cost reduction can be achieved by this one step process. Figure 16 shows a macrophotograph of the first translucent disc of ALON fabricated in 1976. The main problems associated with this process involved uncontrolled grain growth of reacted material and impurities in the starting powders. Figure 17 illustrates the segregation of impurity liquids at the ALON Grain boundaries.[18] Since that time Raytheon Company[19] has used modified processes involving traditional sintering of pre-reacted and conditioned ALON powders. Figure 18 is the latest stage in the evolution of this material. So even in this case which included some luck and fortuitous happenings along the way the commercialization of ALON has taken about ten years.

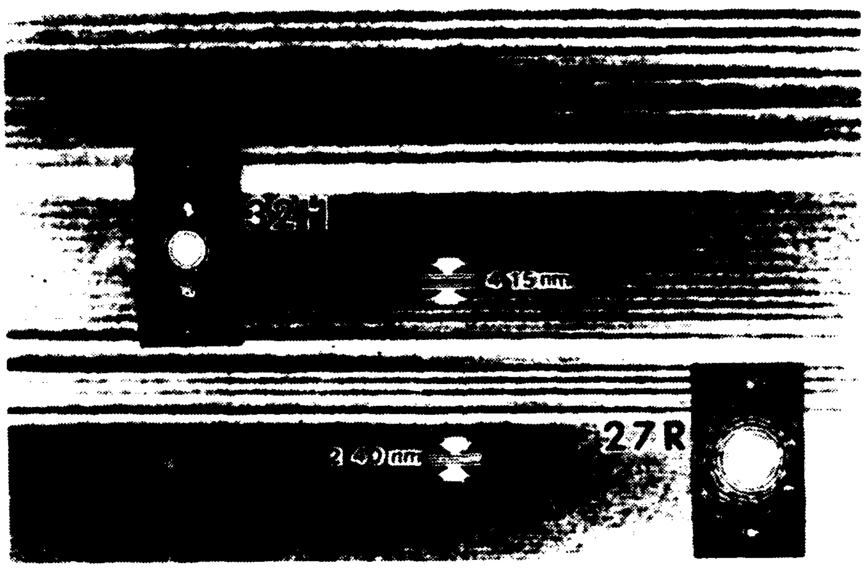


FIGURE 15. LOW RESOLUTION LATTICE IMAGES SHOWING THE COEXISTENCE OF THE 32H AND 27R POLYTYPOID STRUCTURES.

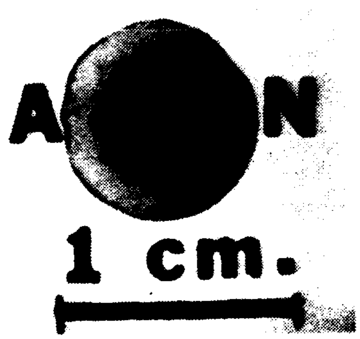
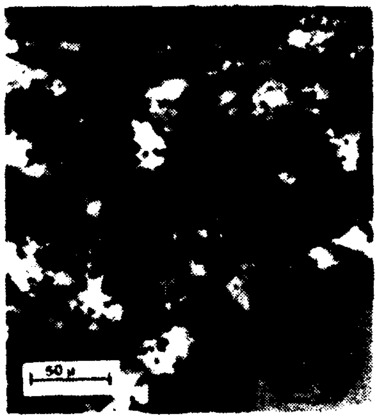


FIGURE 16. FIRST TRANSLUCENT ALON MATERIAL, ABOUT 1976.

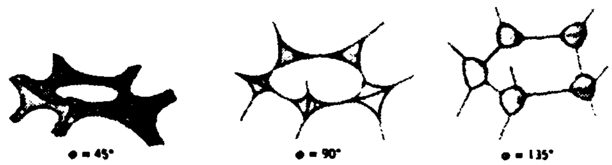
ALON GRAIN BOUNDARY PHASE
WETTING CHARACTERISTICS



Transmitted Light With Ultra Microscope Lens

$SS/SL = 2\cos\phi/2$

SS = Solid-Solid Surface Energy
SL = Solid-Liquid Surface Energy
ϕ = Dihedral Angle



Second Phase Distributions for Various Dihedral Angles

FIGURE 17. ULTRAMICROSCOPIC PHOTOGRAPH OF TRANSLUCENT ALON SHOWING POROSITY AND DARK CONTINUOUS GRAIN BOUNDARY PHASE.

FIGURE 18. STATE-OF-THE-ART COMMERCIAL ALON PRODUCED BY RAYTHEON COMPANY.

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