

DTIC FILE COPY

2

MTL TR 88-30

AD-A203 671

AD

ANION CONTROLLED MICROSTRUCTURES IN THE Al_2O_3 -AIN SYSTEM

JAMES W. McCAULEY

MATERIALS SCIENCE BRANCH, U.S. ARMY MATERIALS TECHNOLOGY LABORATORY

K. M. KRISHNAN, R. S. RAI, and G. THOMAS

UNIVERSITY OF CALIFORNIA, LAWRENCE BERKELEY LABORATORY

A. ZANGVILL and R. W. DOSER

UNIVERSITY OF ILLINOIS

N. D. CORBIN

NORTON COMPANY

November 1988

Approved for public release; distribution unlimited.



US ARMY
LABORATORY COMMAND
MATERIALS TECHNOLOGY LABORATORY



DTIC
ELECTE
JAN 23 1988
S H D

U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
Watertown, Massachusetts 02172-0001

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Mention of any trade names or manufacturers in this report shall not be construed as advertising nor as an official indorsement or approval of such products or companies by the United States Government.

DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed.
Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MTL TR 88-30	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ANION CONTROLLED MICROSTRUCTURES IN THE Al ₂ O ₃ -AlN SYSTEM		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) James W. McCauley, K. M. Krishnan, R. S. Rai, G. Thomas, A. Zangvill, R. W. Doser, and N. D. Corbin		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Materials Technology Laboratory Watertown, Massachusetts 02172-0001 ATTN: SLCMT-EMS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS D/A Project: 1L161102AH42 AMCMS Code: 611102.H420011
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Laboratory Command 2800 Powder Mill Road Adelphi, Maryland 33203-1145		12. REPORT DATE October 1988
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 16
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Published in Ceramic Microstructures '86, ed., Pask & Evans, Plenum Publishing Corp., NY, 1988, p. 577-590.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Aluminum oxynitride; Microstructure; Aluminum nitride; Phase equilibria; Aluminum oxide; Electron microscopy; (KT)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (SEE REVERSE)		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Block No. 20

ABSTRACT

The phase equilibria of the pseudo-binary $\text{Al}_2\text{O}_3\text{-AlN}$ 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 polycrystalline 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 $\alpha\text{-Al}_2\text{O}_3$ /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;

*Contd
Raymondson
previous page*

41Pnq

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ANION CONTROLLED MICROSTRUCTURES IN

THE Al_2O_3 -AlN SYSTEM

James W. McCauley
U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172

K. M. Krishnan, R. S. Rai and G. Thomas
University of California
Lawrence Berkeley Laboratory
Berkeley, California

A. Zangvill and R. W. Doser
University of Illinois
Urbana, Illinois

N. D. Corbin
Norton Company
Northboro, Massachusetts

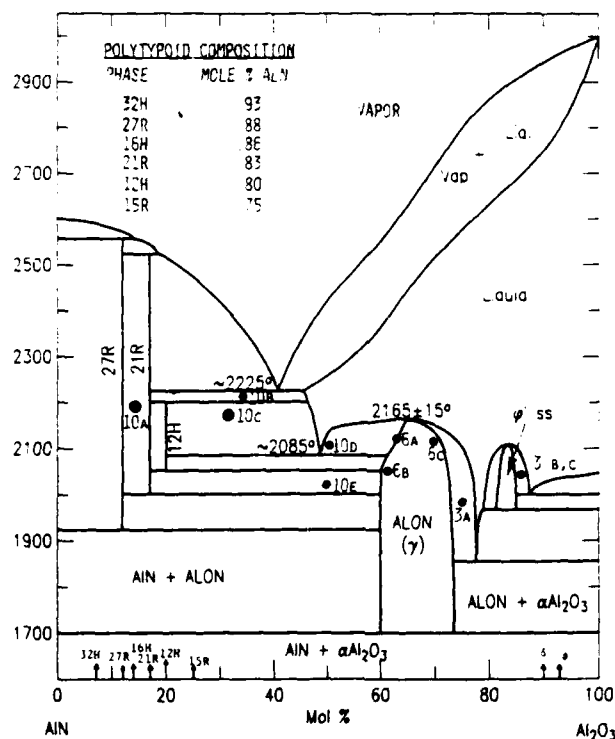
INTRODUCTION

McCauley and Corbin¹ 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 Taniguchi². 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 Ondik³ for the Phase Diagrams for Ceramists project. Compositions for the 32H and 16H AlN polytypoids⁴ and the $9\text{Al}_2\text{O}_3$. AlN phase⁵ 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) sublimes, while the other (Al_2O_3) melts resulting in solid/vapor, liquid/vapor and liquid/solid equilibria that add enormous



Where CN = coordination number of cation

Three levels of substitution illustrate the situation:

Case 1. N substitutes for O, no change in structure:

$$\text{Al}_3^{\text{VI}}\text{O}_3^{\text{IV}}\text{N}^{\text{IV}} \quad \zeta(\text{N}) = \frac{3}{6} + \frac{3}{6} + \frac{3}{6} + \frac{3}{6} = 2$$

But since $A(\text{N}) = -3$
Net charge on N = -1

Case 2. N substitutes for O, some Al goes into tetrahedral coordination:

$$\text{Al}_2^{\text{IV}}\text{Al}_2^{\text{VI}}\text{O}_3^{\text{IV}}\text{N}^{\text{IV}} \quad \zeta(\text{N}) = \frac{3}{4} + \frac{3}{6} + \frac{3}{6} + \frac{3}{6} = 2.25$$

Net charge on N = -0.75

Case 3. N substitutes for O, more Al goes into tetrahedral coordination:

$$\text{Al}_2^{\text{IV}}\text{Al}_1^{\text{VI}}\text{O}_3^{\text{IV}}\text{N}^{\text{IV}} \quad \zeta(\text{N}) = \frac{3}{4} + \frac{3}{4} + \frac{3}{6} + \frac{3}{6} = 2.50$$

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 $\alpha\text{-Al}_2\text{O}_3$. 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.

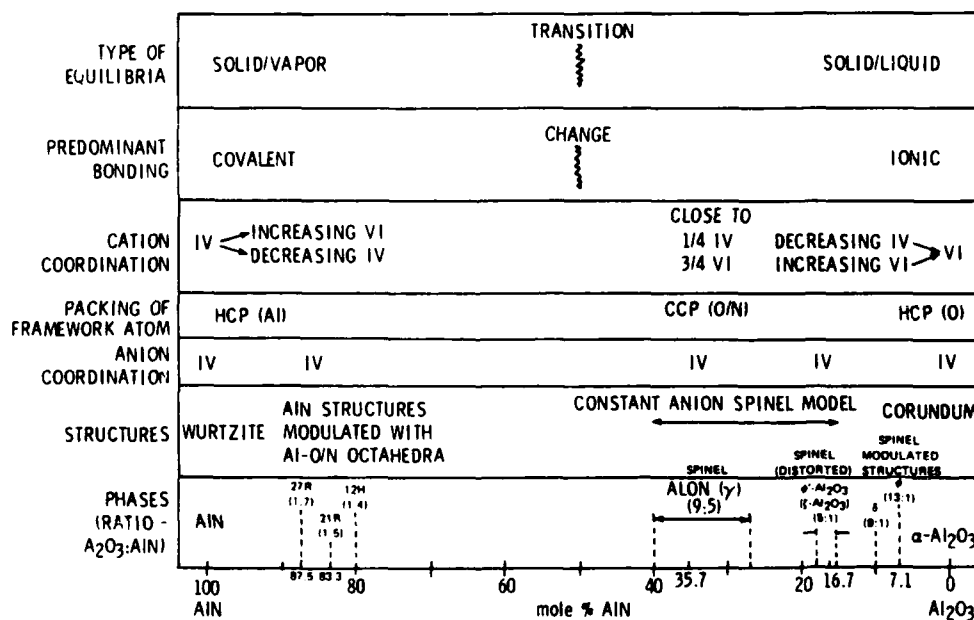


FIGURE 2. RELATION OF CRYSTAL CHEMISTRY TO COMPOSITION AND PHASE EQUILIBRIUM IN THE AlN-Al₂O₃ SYSTEM.

A model, assuming a constant anion spinel framework⁷, 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 $n\text{Al}'_2\text{O}_3$ and $m\text{Al}''\text{N}$.
- let $x = N$ then $\text{Al}'' = x$
- $y = 0$ then $\text{Al}' = \frac{2}{3} y$
- further if $N = x$ then $O = 32 - x$
- $\text{Al}' = \frac{2}{3} (32 - x)$
- $\text{Al}'' = x$
- 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 $\text{Al} \frac{64+x}{3} \square \frac{8-x}{3} \text{O}_{32-x} \text{N}_x$

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 Yanogida⁸.

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 phase⁹ referred to as ALON' or ϕ' and similar to ξ -Al₂O₃ or LiAl₅O₈¹⁰. The aforementioned model predicts a composition of Al₂₂O₃₀N₂ (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 authors¹¹⁻¹⁵. 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).

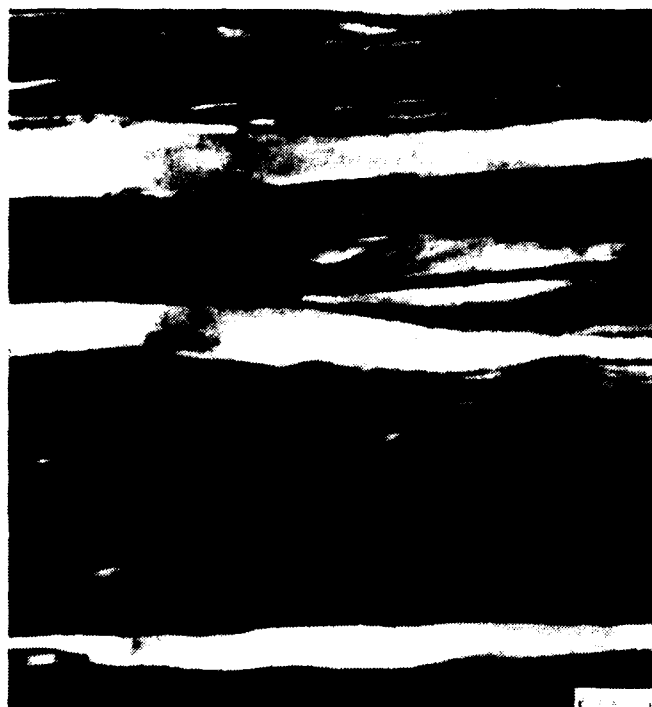


FIGURE 5. TEM OF ALON AND ALON' INTERGROWTH
MICROSTRUCTURE; SAME MATERIAL AS IN FIGURE 3(c).



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 reflective 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 ⁸	-	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)	~e	-	-
† 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

⁸Estimated by Corbin

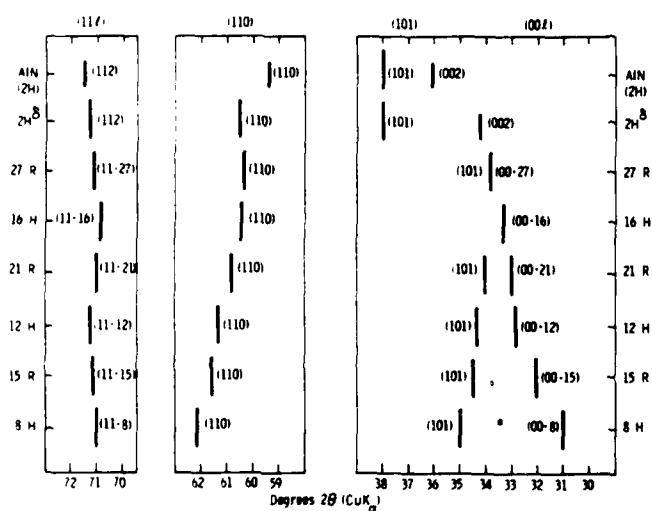


FIGURE 8. VARIATION OF SELECTED X-RAY POWDER DIFFRACTION PEAKS IN AlN POLYTYPOID PHASES.



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.

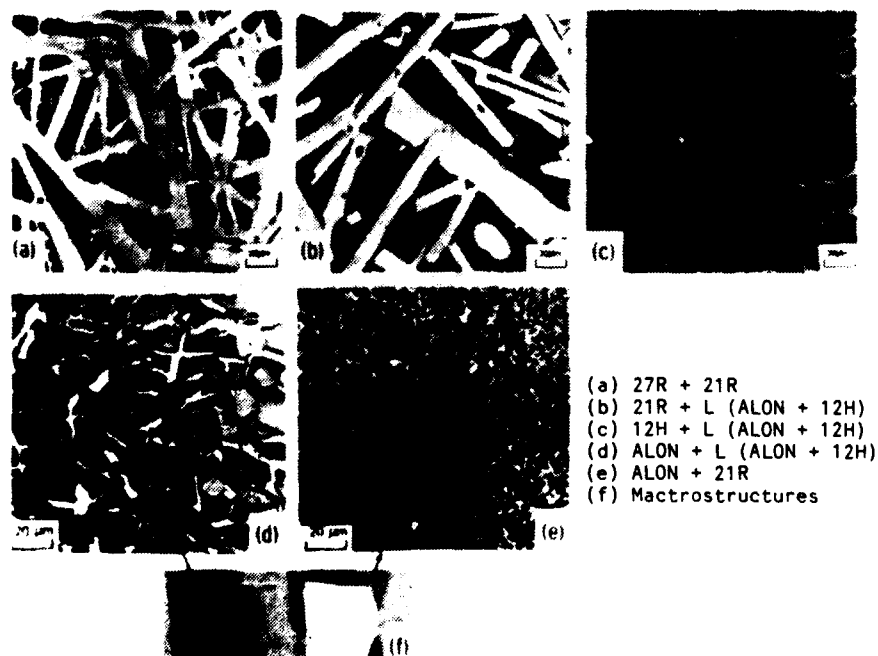


FIGURE 10. 50-0 MOLE % Al_2O_3 MICROSTRUCTURES.

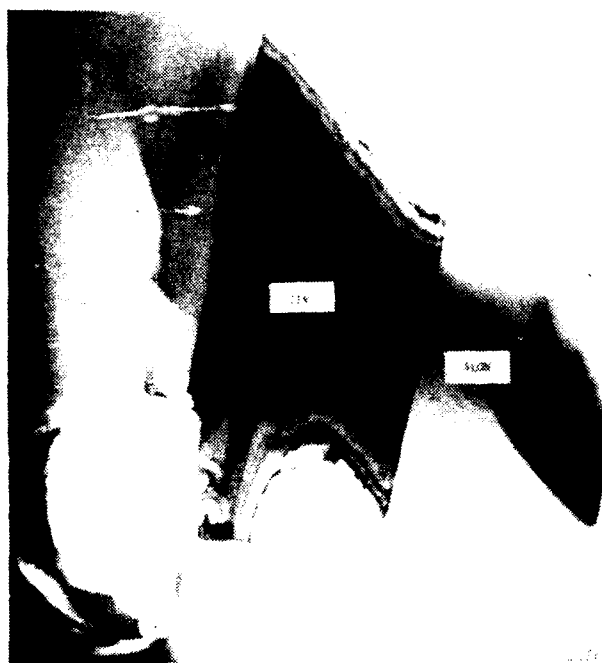


FIGURE 11. TEM MICROSTRUCTURE OF 21R PHASE SURROUNDED BY ALON; SAME MATERIAL AS IN FIGURE 10(e).



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) material⁴. 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 suggested¹⁴ 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.

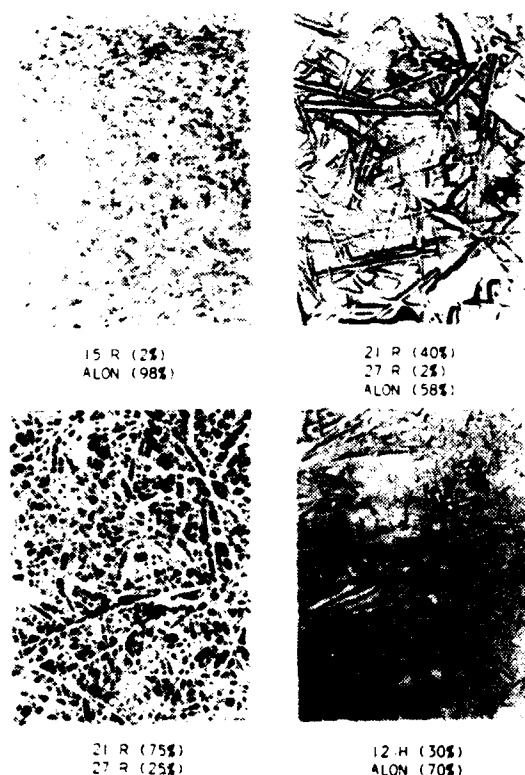


FIGURE 13.. LOW MAGNIFICATION PHOTOMICROGRAPHS OF VARIOUS MATERIAL ILLUSTRATED IN FIGURE 10.

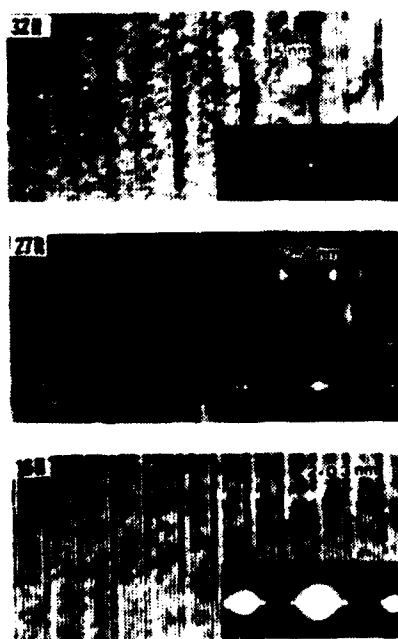


FIGURE 14. LATTICE IMAGES OF THE 32H, 27R AND 16H STRUCTURES FORMED BY THE SYMMETRICAL 001 REFLECTIONS.

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 Corbin¹⁷ 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 Company¹⁹ 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.

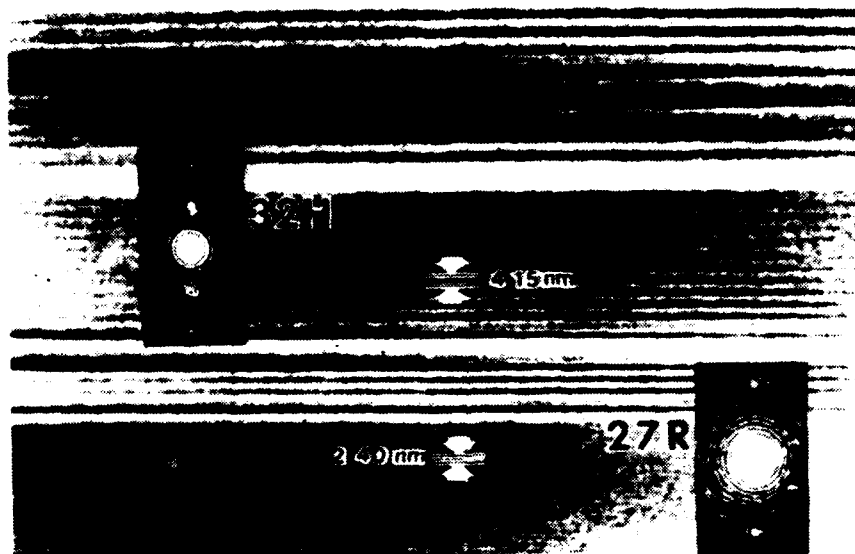


FIGURE 15. LOW RESOLUTION LATTICE IMAGES SHOWING THE COEXISTENCE OF THE 32H AND 27R POLYTYPIC STRUCTURES.

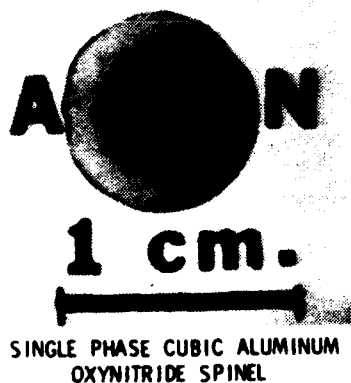
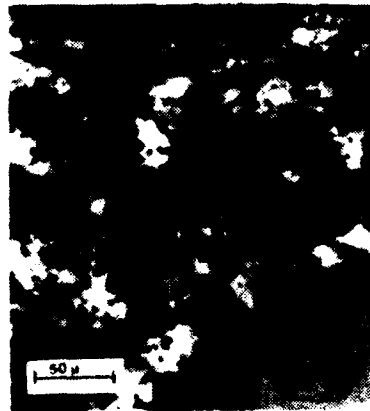


FIGURE 16. FIRST TRANSLUCENT ALON MATERIAL, ABOUT 1976.

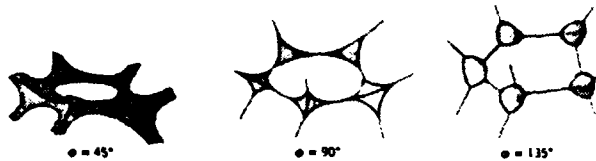
ALON GRAIN BOUNDARY PHASE WETTING CHARACTERISTICS



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.

REFERENCES

1. J. W. McCauley and N. D. Corbin, "High Temperature Reactions and Microstructures in the Al_2O_3 -AlN System," F. L. Riley, ed., Progress in Nitrogen Ceramics, Martinus Nijhoff Publishers, the Netherlands (1983), 111-118.
2. N. Kuramoto and H. Taniguchi, "Transparent AlN Ceramics," Journal of Materials Science Letters. (1984) 3, 471-474.
3. J. R. Dennis and H. Ondik, National Bureau of Standards, Gaithersburg, Maryland. Personal Communication.
4. K. M. Krishnan, R. S. Rai, G. Thomas, N. D. Corbin and J. W. McCauley, "Characterization of Long Period Polytypoid Structures in the Al_2O_3 -AlN Systems," Laurence Berkeley Laboratory Report LBL-20644, December 1985.
5. A. Lefebvre, J. C. Gilles and R. Collongues, "Antiphases Periodiques Dans un Spinel Non-Stoechiometrique ($9\text{Al}_2\text{O}_3$ -AlN) Prepare a Haute Temperature," Mat. Res. Bull. (1972) 7, 557-566.
6. L. Pauling, The Nature of the Chemical Bond. Cornell University Press, Ithaca, New York (1960).
7. J. W. McCauley, "A Simple Model for Aluminium Oxynitride Spinel," J. Am. Ceram. Soc. (1978) 61, 372-373.
8. G. Yamaguchi and H. Yanagida, "Study on the Reductive Spinel - A New Spinel Formula $\text{AlN-Al}_2\text{O}_3$ instead of the Previous One Al_2O_4 ," Chemical Society of Japan Bulletin (1959) 32, 1264-1265.
9. D. Michel, "Contribution a l'etude de phenomenes d'ordonnement de defaults dans les monocristaux de materiaux refractaires a base d'alumine et de zircone," Rev. Int. Hautes Temper. et Refract. (1972) 9, 225-242.
10. G. Long and L. M. Foster, "Crystal phases in the system Al_2O_3 -AlN," J. Am. Ceram. Soc. (1961) 44, 255-258.
11. A. Lejus, "Sur la formation a haute temperature de spinelles non stoechiometriques et de phases derivees dans plusieurs systemes d'oxydes a base d'alumina et dans systeme aluminenitride d'aluminum," Rev. Hautes Temper. et Refract. (1964) 1 53-95.
12. T. Sakai, "Hot Pressing of the $\text{AlN-Al}_2\text{O}_3$ System," Yogyo-Kyokai-Shi (1978) 86, 125-130.
13. L. J. Gauckler and G. Petzow, "Representation of Multi-Component Silicon Nitride Based Systems," F. L. Riley (ed), Nitrogen Ceramics, Noordhoff, Leyden (1977) 41-62.
14. K. H. Jack, "Review; Sialons and Related Nitrogen Ceramics," Jour. Materials Science. 11, 1135-1158.
15. P. L. Land, J. M. Wimmer, R. W. Burns and N. S. Choudhury, "Compounds and Properties of the System Si-Al-O-N," Jour. Amer. Ceramic Soc. (1978) 61, 56-60.
16. N. D. Corbin and J. W. McCauley, Unpublished work at the U. S. Army Materials Technology Laboratory, Watertown, MA.
17. J. W. McCauley and N. D. Corbin, "Phase Relations and Reaction Sintering of Transparent Cubic Aluminium Oxynitride Spinel (AlON)," J. Am. Ceram. Soc. (1979) 62, 476-479.
18. N. D. Corbin, Unpublished Work at the U. S. Army Materials Technology Laboratory, Watertown, MA.
19. T. M. Hartnett, E. A. Maguire, R. L. Gentilman, N. D. Corbin and J. W. McCauley, "Aluminium Oxynitride Spinel (AlON) - A New Optical and Multimode Window Material," Ceramic Eng. and Science Proceedings, (1982) 3, 67-76.

DISTRIBUTION LIST

No. of Copies	To	No. of Copies	To
	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301		Director, U.S. Army Research & Technology Labs, Ames Research Center, Moffet Field, CA 94035
1	ATTN: Mr. J. Persh	1	ATTN: DAVDL-D, Dr. R. Carlson
1	Dr. L. Young	1	DAVDL-AL-D, Dr. I. C. Statler, MS215-1, Aeromechanics Laboratory
1	Mr. K. R. Foster		
	Commander, U.S. Army Laboratory Command, 2800 Powder Mill Road, Adelphi, MD 20783-1145		Commander, U.S. Army Missile Command, Redstone Scientific Information Center, Redstone Arsenal, AL 35898-5241
2	ATTN: AMSLC-IM-TL	1	ATTN: AMSMI-RD-CS-R/ILL Open Lit
1	AMSLC-TD	1	AMSMI-RL, Dr. J. J. Richardson
1	AMSLC-TD-A	1	AMSMI-R, Dr. W. C. McCorkle
1	AMSLC-PA		
1	AMSLC-TP		Commander, U.S. Army Aviation Systems Command, P.O. Box 209 St. Louis, MO 63120
	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22304-6145	1	ATTN: AMSAV-NS, Mr. M. L. Bauccio
2	ATTN: DTIC-FDAC	1	Technical Library
	National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161		Commander, U.S. Army Natick Research, Development, and Engineering Center, Natick, MA 01760
1	Director, Defense Advanced Research Projects Agency, 1400 Wilson Boulevard, Arlington, VA 22209	1	ATTN: Technical Library
1	ATTN: Dr. P. Parrish	1	Dr. J. A. Sousa
1	Dr. B. Wilcox	1	Dr. R. J. Byrne
1	Dr. K. Hardmann-Rhyne	1	Dr. R. Lewis
	Battelle Columbus Laboratories, Metals and Ceramics Information Center, 505 King Avenue, Columbus, OH 43201		Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1	ATTN: Mr. W. Duckworth	1	ATTN: Technical Document Center
1	Dr. D. Niesz		Commander, U.S. Army Science and Technology Center Far East Office, APO San Francisco, CA 96328
	Department of the Army, Office of the Assistant Secretary of the Army (RDA), Washington, DC 20310	1	ATTN: Terry L. McAfee
1	ATTN: Dr. J. G. Prather, Dep for Sci & Tech		Commander, U.S. Army Communications and Electronics Command, Fort Monmouth, NJ 07703
1	Dr. J. R. Sculley, SARD	1	ATTN: AMSEL-TDD, Mr. T. A. Pfeiffer, Technical Dir.
	Deputy Chief of Staff, Research, Development, and Acquisition, Headquarters, Department of the Army, Washington, DC 20310		Director, Electronic Technology and Devices Lab, Fort Monmouth, NJ 07703
1	ATTN: DAMA-ZE, Mr. C. M. Church	1	ATTN: DELET-D, Dr. C. G. Thornton
	Commander, U.S. Army Research and Development Office, Chief Research and Development, Washington, DC 20315		Commander, U.S. Army Tank-Automotive Command, Warren, MI 48090
1	ATTN: Physical and Engineering Sciences Division	1	ATTN: Dr. W. Bryzik
	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211	1	D. Rose
1	ATTN: Information Processing Office	1	AMSTA-RKA
1	Dr. G. Mayer	1	AMSTA-UL, Technical Library
1	Dr. J. Hurt	1	AMSTA-R
1	Dr. A. Crowson	1	AMSTA-NS, Dr. H. H. Dobbs
1	Dr. R. Reeber		Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
1	Dr. R. Shaw	1	ATTN: Mr. J. Lannon
1	Dr. R. E. Weigle	1	Mr. H. E. Peibly, Jr., PLASTEC, Director
	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333	1	Technical Library
1	ATTN: AMCLD, Dr. L. Hagan	1	Dr. T. Davidson
1	AMCDE, Mr. D. L. Griffin	1	Dr. B. Ebihara
1	AMCQA-EQ, Mr. H. L. Light	1	AMSMC-LC(D), Dr. J. T. Frasier
1	AMCQA, Mr. S. J. Lorber		Commander, U.S. Army Armament, Munitions and Chemical Command, Rock Island, IL 61299
	Commander, U.S. Army Electronics Research and Development Command, Fort Monmouth, NJ 07703	1	ATTN: Technical Library
1	ATTN: AMDET-ES, Dr. A. Tauber		Commander, U.S. Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, MD 21010
	Director, Electronics Warfare Laboratory, Fort Monmouth, NJ 07703	1	ATTN: AMSMC-CLN-ST, Mr. S. Shukis
1	ATTN: AMDEW-D, Mr. M. Adler		Commander, Aberdeen Proving Ground, MD 21005
	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005	1	ATTN: AMDAR-CLB-PS, Mr. J. Vervier
1	ATTN: AMXSY-MP, H. Cohen		U.S. Army Corps of Engineers, Construction Engineering Research Lab, P.O. Box 4005, Champaign, IL 61820
	Commander, U.S. Army Night Vision Electro-Optics Laboratory, Fort Belvoir, VA 22060	1	ATTN: Dr. Robert Quattrone
1	ATTN: DELNV-S, Mr. P. Travesky		Commander, U.S. Army Belvoir RD&E Center, Fort Belvoir, VA 22060-5606
1	DELNV-L-D, Dr. R. Buser	1	ATTN: STRBE-FS, Mr. W. McGovern, Fuel & Wtr Sup Div
1	DELNV-D, Dr. L. Cameron	1	AMDME-V, Mr. E. York
	Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783	1	AMDME-HS, Dr. K. H. Steinbach
1	ATTN: Technical Information Office	1	AMDME-ZT, Mr. T. W. Lovelace, Tech Dir
1	AMSLC-RAE	1	Mr. M. Lepera
			Director, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005
		1	ATTN: AMDAR-BLT, Dr. A. M. Dietrich
		1	AMDAR-BLF, Dr. A. Niller
		1	AMDAR-BLI, Mr. L. Watermeier
		1	AMSMC-BL(A), Dr. R. J. Eichelberger

No. of Copies	To
1	Commander, Rock Island Arsenal, Rock Island, IL 61299 ATTN: SARRI-EN
1	Director, U.S. Army Industrial Base Engineering Activity, Rock Island, IL 61299 ATTN: AMXIB-MT, Mr. G. B. Ney
1	Chemical Research and Development Center, Aberdeen Proving Ground, MD 21010 ATTN: AMSMC-CLO(A), Dr. B. Richardson
1	Commander, U.S. Army Test and Evaluation Command, Aberdeen Proving Ground, MD 21005 ATTN: AMSTE-ME
1	AMSTE-TD, Mr. H. J. Peters
1	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901 ATTN: Military Tech
1	Mr. J. Crider
1	Ms. P. Durrer
1	Mr. P. Greenbawn
1	Chief, Benet Weapons Laboratory, Watervliet, NY 12189 ATTN: AMDAR-LCB-TL
1	Dr. G. D'Andrea
1	AMDAR-LCB, Dr. F. Sautter
1	Director, Eustis Directorate, U.S. Army Mobility Research and Development Laboratory, Fort Eustis, VA 23604 ATTN: SAVDL-E-MOS (AMCCOM)
1	Commander, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS 39180 ATTN: Research Center Library
1	Project Manager, Munitions Production Base, Modernization and Expansion, Dover, NJ 07801 ATTN: AMCPM-PBM-P
1	Technical Director, Human Engineering Laboratories, Aberdeen Proving Ground, MD 21005 ATTN: Technical Reports Office
1	AMXHE-D, Dr. J. D. Weisz
1	Chief of Naval Research Arlington, VA 22217 ATTN: Code 471
1	Dr. A. Diness
1	Dr. R. Pohanka
1	Naval Research Laboratory, Washington, DC 20375 ATTN: Code 5830
1	Headquarters, Naval Air Systems Command, Washington, DC 20360 ATTN: Code 5203
1	Headquarters, Naval Sea Systems Command, 1941 Jefferson Davis Highway, Arlington, VA 22376 ATTN: Code 035
1	Headquarters, Naval Electronics Systems Command, Washington, DC 20360 ATTN: Code 504
1	Commander, Naval Ordnance Station, Louisville, KY 40214 ATTN: Code 85
1	Commander, Naval Material Industrial Resources Office, Building 537-2, Philadelphia Naval Base, Philadelphia, PA 19112 ATTN: Technical Director
1	Commander, Naval Weapons Center, China Lake CA 93555 ATTN: Mr. F. Markarian
1	Commander, U.S. Army Wright Aeronautical Labs, Wright- Patterson Air Force Base, OH 45433 ATTN: Dr. N. Tallan
1	Dr. H. Graham
1	Dr. R. Ruh
1	Aero Propulsion Labs, Mr. R. Marsh
1	Dr. H. M. Burte
1	AFWAL/MLLP, Mr. D. Forney
1	AFML/MLLM, Mr. H. L. Gegel
1	AFSC/MLLM, Dr. A. Katz

No. Copies	To
1	Commander, Air Force Armament Center, Eglin Air Force Base, FL 32542 ATTN: Technical Library
1	National Aeronautics and Space Administration, Lewis Research Center, 21000 Brookpark Road, Cleveland, OH 44135 ATTN: J. Accurio, USAMRDL
1	Dr. H. B. Probst, MS 49-1
1	Dr. S. Dutta
1	National Aeronautics and Space Administration, Washington, DC 20546 ATTN: AFSS-AD, Office of Scientific and Technical Info.
1	National Aeronautics and Space Administration, Langley Research Center, Hampton, VA 23665 ATTN: Mr. J. Buckley, MS 387
1	Dr. J. Heyman, MS 231
1	Mr. R. L. Long, MS 266
1	Commander, White Sands Missile Range, Electronic Warfare Laboratory, OMEW, ERADCOM, White Sands, NM 88002 ATTN: Mr. Thomas Reader, AMSEL-WLM-ME
1	Department of Energy, Division of Transportation, 20 Massachusetts Avenue, N.W., Washington, DC 20545 ATTN: Mr. G. Tnur
1	Dr. R. J. Gottschall, ER-131, GTN
1	Department of Transportation, 400 Seventh Street, S.W., Washington, DC 20590 ATTN: Mr. M. Lauriente
1	Mechanical Properties Data Center, Belfour Stulen Inc., 13917 W. Bay Shore Drive, Traverse City, MI 49684
1	National Bureau of Standards, Washington, DC 20234 ATTN: E. S. Etz, Bldg. 222, Rm A-121
1	D. L. Hunston, Bldg. 224, Rm A-209
1	Dr. D. H. Reneker, Dep. Dir., Ctr for Mat'l's Sci.
1	Dr. Lyle Schwartz
1	Dr. Stephen Hsu
1	Dr. Allan Draggoo
1	U.S. Bureau of Mines, Mineral Resources Technology, 2401 E. Street, N.W., Washington, DC 20241 ATTN: Mr. M. A. Schwartz
1	National Bureau of Standards, Gaithersburgh, MD 20760 ATTN: Dr. S. Wiederhorn
1	Dr. J. B. Wachtman
1	Dr. N. Tighe
1	National Research Council, National Materials Advisory Board, 2101 Constitution Avenue, Washington, DC 20418 ATTN: Dr. K. Zwilsky
1	D. Groves
1	R. M. Spriggs
1	J. Lane
1	National Science Foundation, Materials Division, 1800 G Street, N.W., Washington, DC 20006 ATTN: Dr. L. Toth
1	Dr. J. Hurt
1	AiResearch Manufacturing Company, AiResearch Casting Company, 2525 West 190th Street, Torrance, CA 90505 ATTN: Mr. K. Styhr
1	AVCO Corporation, Applied Technology Division, Lowell Industrial Park, Lowell, MA 01887 ATTN: Dr. T. Vasilos
1	Case Western Reserve University, Department of Metallurgy, Cleveland, OH 60605 ATTN: Prof. A. H. Heuer
1	Defence Research Establishment Pacific, FMO, Victoria, B.C., VOS 1B0, Canada ATTN: R. D. Barer
1	European Research Office, 223 Old Marylebone Road, London, NW1 - 5th, England ATTN: Dr. I. Ahmad

No. of Copies	To
	Ford Motor Company, Turbine Research Department, 20000 Rotunda Drive, Dearborn, MI 48121
1	ATTN: Mr. A. F. McLean
1	Mr. J. A. Mangels
	Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121
1	ATTN: Dr. D. Compton, Vice President, Research
	General Electric Company, Research and Development Center, Box 8, Schenectady, NY 12345
1	ATTN: Dr. R. J. Charles
1	Dr. C. D. Greskovich
1	Dr. S. Prochazka
	Georgia Institute of Technology, EES, Atlanta, GA 30332
1	ATTN: Mr. J. D. Walton
	GTE Sylvania, Waltham Research Center, 40 Sylvania Road, Waltham, MA 02154
1	ATTN: Dr. W. H. Rhodes
	Martin Marietta Laboratories, 1450 South Rolling Road, Baltimore, MD 21227
1	ATTN: Dr. J. Venables
	Massachusetts Institute of Technology, Department of Metallurgy and Materials Science, Cambridge, MA 02139
1	ATTN: Prof. R. L. Coble
1	Prof. H. K. Bowen
1	Prof. W. D. Kingery
1	Prof. J. Vander Sande
	Materials Research Laboratories, P.O. Box 50, Ascot Vale, VIC 3032, Australia
1	ATTN: Dr. C. W. Weaver
	Midwest Research Institute, 425 Volker Boulevard, Kansas City, MO 64110
1	ATTN: Mr. G. W. Gross, Head, Physics Station
	Pennsylvania State University, Materials Research Laboratory, Materials Science Department, University Park, PA 16802
1	ATTN: Prof. R. Roy
1	Prof. R. E. Newham
1	Prof. R. E. Tressler
1	Dr. C. Pantano
1	Mr. C. O. Ruud
	State University of New York at Albany, Department of Physics, Albany, NY 12222
1	ATTN: Prof. W. A. Lanford
	State University of New York at Stony Brook, Department of Materials Science, Long Island, NY 11790
1	ATTN: Prof. F. F. Y. Wang
	Stanford Research International, 333 Ravenswood Avenue, Menlo Park, CA 94025d
1	ATTN: Dr. P. Jorgensen
1	Dr. D. Rowcliffe
	United Technologies Research Center, East Hartford, CT 06108
1	ATTN: Dr. J. Brennan
1	Dr. K. Prewé
	University of California, Lawrence Livermore Laboratory, P.O. Box 808, Livermore, CA 94550
1	ATTN: Mr. R. Landingham
1	Dr. C. F. Cline
1	Dr. J. Birch Holt
	University of Florida, Department of Materials Science and Engineering, Gainesville, FL 32611
1	ATTN: Dr. L. Hench
	University of Washington, Ceramic Engineering Division, FB-10, Seattle, WA 98195
1	ATTN: Prof. R. Bradt
	Westinghouse Electric Corporation, Research Laboratories, Pittsburgh, PA 15235
1	ATTN: Dr. R. J. Bratton
	Battelle Pacific Northwest Lab, NDT Section, Richland, WA 99353
1	ATTN: Mr. A. Birks, Associate Manager

No. of Copies	To
	Rensselaer Polytechnic Institute, Department of Materials Engineering, Troy, NY 12181
1	ATTN: R. J. Diefendorf
	Oak Ridge National Laboratory, P.O. Box X Oak Ridge, TN 37830
1	ATTN: P. F. Becher
1	V. J. Tennery
1	R. Johnson
	Sandia Laboratories, Albuquerque, NM 87185
1	ATTN: Dr. F. Gerstle, Div 5814
	The John Hopkins University, Department of Civil Engineering/ Materials Science and Engineering, Baltimore, MD 28218
1	ATTN: Dr. R. E. Green, Jr.
	Director, Office of Science and Technology Policy, Old Executive Office Building, Washington, DC 20223
	Subcommittee on Science, 2319 Rayburn House Office Building, Washington, DC 20515
1	ATTN: Mr. P. C. Maxwell
	Aerospace Corporation, Materials Science Laboratory, 2350 East El Segundo Boulevard, El Segundo, CA 90245
1	ATTN: Dr. L. R. McCreight
	IBM Corporation, Thomas B. Watson Research Center, Yorktown Heights, NY 10598
1	ATTN: Dr. G. Onoda
	Corning Glass Works, Research and Development Division, Corning, NY 14830
1	ATTN: Dr. W. R. Prindle
	3M Company, New Products Department, 219-01-01, 3M Center, St. Paul, MN 55144
1	ATTN: R. E. Richards
	Technology Strategies, Inc., 10722 Shingle Oak Ct., Burke, VA 22015
1	ATTN: Dr. E. C. Van Reuth
	Rutgers University, Center for Ceramics, Rm A274, P.O. Box 909, Piscataway, NJ 08854
1	ATTN: Prof. J. B. Wachtman, Jr., Director
	Syracuse University, 304 Administration Building, Syracuse, NY 13210
1	ATTN: Dr. V. Weiss
	Lehigh University, Materials Research Center #32, Bethlehem, PA 18015
1	ATTN: Dr. D. M. Smyth
	Alfred University, Center for Advanced Ceramic Technology, Alfred, NY 14806
1	ATTN: R. M. Spriggs
	Alfred University, New York State College of Ceramics, Alfred, NY 14802
1	ATTN: Dr. R. L. Snyder
	University of California, Center for Advanced Materials, 058, Hildebrand Hall, Berkeley, CA 94720
1	ATTN: Prof. G. Somorjai
	Boeing Aerospace Company, 11029 Southeast 291, Auburn, MA 98002
1	ATTN: W. E. Strobelt
	University of California, Materials Science and Mineral Engineering, Heart Mining Building, Rm 284, Berkeley, CA 94720
1	ATTN: Prof. G. Thomas
	Director, U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001
2	ATTN: SLCMT-TML
7	Authors

U.S. Army Materials Technology Laboratory,
Watertown, Massachusetts 02172-0001
ANION CONTROLLED MICROSTRUCTURES IN THE
Al₂O₃-AlN SYSTEM - James W. McCauley,
K. M. Krishnan, R. S. Rai, G. Thomas,
A. Zangwill, R. W. Doser, and N. D. Corbin
Technical Report MTL TR 88-30, October 1988, 16 pp -
illus, tables, D/A Project 1L161102AH42,
AMCMS Code 611102.H420011

AD
UNCLASSIFIED
UNLIMITED DISTRIBUTION
Key Words
Aluminum oxynitride
Aluminum nitride
Aluminum oxide

The phase equilibria of the pseudo-binary Al₂O₃-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 polycrystalline ceramics. The system exhibits a wide variety of features and resulting microstructures: two spinel phases, vapor-solid and liquid-solid eutectics, AlN polypolytype-like structures, and α -Al₂O₃/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.

U.S. Army Materials Technology Laboratory,
Watertown, Massachusetts 02172-0001
ANION CONTROLLED MICROSTRUCTURES IN THE
Al₂O₃-AlN SYSTEM - James W. McCauley,
K. M. Krishnan, R. S. Rai, G. Thomas,
A. Zangwill, R. W. Doser, and N. D. Corbin
Technical Report MTL TR 88-30, October 1988, 16 pp -
illus, tables, D/A Project 1L161102AH42,
AMCMS Code 611102.H420011

AD
UNCLASSIFIED
UNLIMITED DISTRIBUTION
Key Words
Aluminum oxynitride
Aluminum nitride
Aluminum oxide

The phase equilibria of the pseudo-binary Al₂O₃-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 polycrystalline ceramics. The system exhibits a wide variety of features and resulting microstructures: two spinel phases, vapor-solid and liquid-solid eutectics, AlN polypolytype-like structures, and α -Al₂O₃/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.

U.S. Army Materials Technology Laboratory,
Watertown, Massachusetts 02172-0001
ANION CONTROLLED MICROSTRUCTURES IN THE
Al₂O₃-AlN SYSTEM - James W. McCauley,
K. M. Krishnan, R. S. Rai, G. Thomas,
A. Zangwill, R. W. Doser, and N. D. Corbin
Technical Report MTL TR 88-30, October 1988, 16 pp -
illus, tables, D/A Project 1L161102AH42,
AMCMS Code 611102.H420011

AD
UNCLASSIFIED
UNLIMITED DISTRIBUTION
Key Words
Aluminum oxynitride
Aluminum nitride
Aluminum oxide

The phase equilibria of the pseudo-binary Al₂O₃-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 polycrystalline ceramics. The system exhibits a wide variety of features and resulting microstructures: two spinel phases, vapor-solid and liquid-solid eutectics, AlN polypolytype-like structures, and α -Al₂O₃/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.

U.S. Army Materials Technology Laboratory,
Watertown, Massachusetts 02172-0001
ANION CONTROLLED MICROSTRUCTURES IN THE
Al₂O₃-AlN SYSTEM - James W. McCauley,
K. M. Krishnan, R. S. Rai, G. Thomas,
A. Zangwill, R. W. Doser, and N. D. Corbin
Technical Report MTL TR 88-30, October 1988, 16 pp -
illus, tables, D/A Project 1L161102AH42,
AMCMS Code 611102.H420011

AD
UNCLASSIFIED
UNLIMITED DISTRIBUTION
Key Words
Aluminum oxynitride
Aluminum nitride
Aluminum oxide

The phase equilibria of the pseudo-binary Al₂O₃-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 polycrystalline ceramics. The system exhibits a wide variety of features and resulting microstructures: two spinel phases, vapor-solid and liquid-solid eutectics, AlN polypolytype-like structures, and α -Al₂O₃/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.