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ALUMINUM OXYNITRIDE SPINEL (ALON): A REVIEW

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ABSTRACT

Aluminum oxynitride spinel (ALON) is a relatively new ceramic that can be processed into fully dense transparent material. There are a variety of applications where this material could replace alumina, especially where optical transparency and strength are important. This report reviews the current status of this material, including phase equilibria, processing, and properties.

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INTRODUCTION

Polycrystalline aluminum oxynitride spinel (ALON, also referred to as γ-ALON) is a relatively new ceramic that can be processed into fully dense transparent material,[1-4] as shown in Figure 1. Since it has an isotropic structure, it may have advantages over polycrystalline alumina for applications where true optical transparency and high strength are required. Alumina cannot be processed into a fully transparent material because of its anisotropic structure. This causes its refractive index to vary as a function of direction through a crystal. In a polycrystalline alumina body, the mismatch of the refractive indices at grain boundaries results in scattering.[5] This produces a material that is translucent and not transparent. Aluminum oxynitride spinel can also be thought of as a nitrogen stabilized alumina since only 9.1 atomic percent nitrogen is required to stabilize the spinel structure.[6] Current research on this material is involved with property evaluations to determine the potential applications for this material.[2,4,7,8]

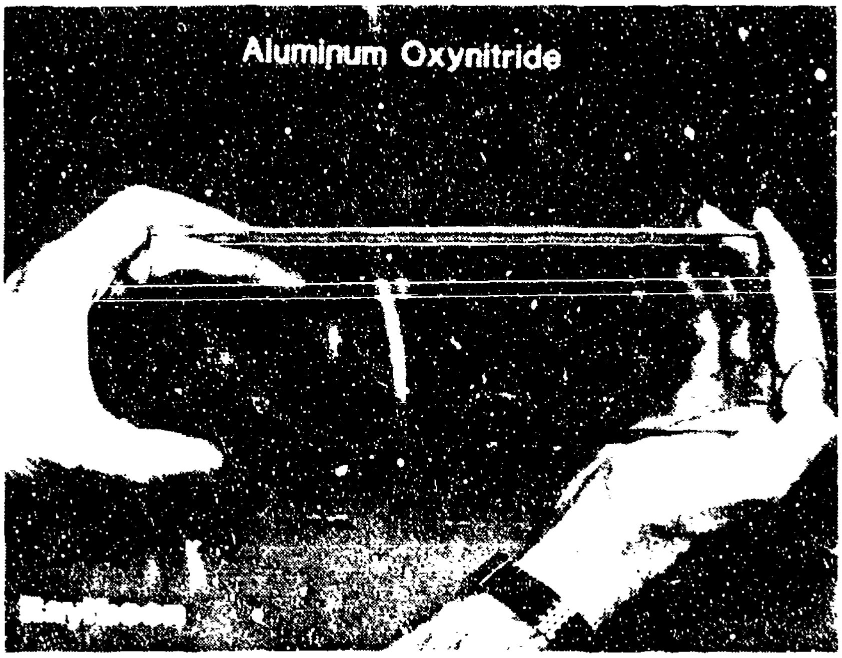

Figure 1. Transparent ALON plate (courtesy of Raytheon Company).

ALON HISTORY

It has been observed[9] since 1946 that a spinel form of Al_2O_3 can be stabilized at high temperatures (>1000°C). Initially, it was believed this phase was stabilized by reducing the aluminum[9-12] (Al^{+3} to Al^{+2}) as when producing Fe_3O_4 spinel from Fe_2O_3 (Fe^{+3} to Fe^{+2}). In 1959 Yamaguchi[13] reported that the spinel phase was stabilized not by Al^{+3} but by nitrogen. During the 1960s, French investigators studied different aspects of oxynitride materials including phase relations[14] and processing.[15-18] Adams et al[19] and Long and Foster[20] also studied various aspects of oxynitrides in the United States during this time. Not until interest was sparked in England on materials in the silicon-aluminum-oxygen-nitrogen chemical system "SIALONS"[21] did aluminum oxynitride materials become of major interest. The surge of interest that followed focussed on obtaining a better understanding of the $AlN-Al_2O_3$ phase diagram since it would give a better understanding of the Si-Al-O-N system. The first work reported on producing ALON spinel as a dense transparent material was published by McCauley and Corbin in 1979.[1] Since then, reports dealing with phase equilibria,[22-24] processing,[1,25,26] and properties[4,7,8] have been published.

$AlN-Al_2O_3$-PHASE RELATIONS

In order to produce single phase ALON, it is important to understand the phase relationships in the Al-O-N system. To date, all studies have been along the AlN and Al_2O_3 join. Experimental results have shown that 13 different phases may occur. Table 1 lists these phases along with their nomenclature, approximate compositions, and investigators.[14,19,20,23,24,27,28]

Table 1. ALUMINUM OXYNITRIDE PHASES

	AlN	Polytypes of AlN						Spinel					
	2H	$2H^{\delta}$	20-H	27-R	16-H	21-R	12-H	γ	γ'	ϕ'	ϕ	δ	Al_2O_3
Mole % AlN	100	-	88.9	87.5	35.7	83.3	80.0	35.7	-21.0	16.7	7.1	4-10	0
References													
Adams (1962)	X	←	—	—	—	—	→	X				X	X
Lejus (1964)	X	←	—	—	—	—	→	X				X	X
Long (1961)	X									11.4		X	X
Henry (1969)	X	←	—	—	—	—	→	X		←	—	→	X
Michel (1972)								X		X	X	X	
Gauckler (1976)	X			X		X		X				X	X
Sakai (1978)	X	X		X	X	X	X	X					
McCauley (1981)	X			X		X	X	X		X			X
Goursat (1981)								X	X				X
Bartram (1979)	X		X	X									

←→ Identified that a phase or phases existed over this composition range

The commonly termed "Aluminum Nitride Polytypes" are phases based on the AlN structure.[21] Since these phases are compositionally controlled,[22,29] they are not true polytypes, as are SiC polytypes.[30] The different AlN polytypes are listed in Table 2 along with their compositions, assuming that they are stable only at specific metal-to-nonmetal ratios,[22,29] allowing for charge neutrality and assuming no silicon is in the structure. Most of the studies on these "polytype" phases are a result of work in the Si-Al-O-N system. As a result, all reported information on these phases show silicon to be present. Unreported data of Zangvil and Doser[31] have shown that several of these phases can be stabilized without silicon.

The composition of the spinel phases γ-ALON and ϕ'-ALON in Table 1 were taken from the spinel model evaluation of McCauley.[6] Phase γ'-ALON spinel was found upon the oxidation of ALON by Goursat.[32,33] Phase ϕ-ALON was observed by Michel[34] and determined to be monoclinic. The δ-ALON phase was observed by many investigators; its reported composition ranges from 10-4 mole % AlN, depending on the researcher.

Table 2. AlN "POLYTYPE PHASES"

Ramsdell Phase Notation	M : X	Formula	Mole % AlN
2-H	1 : 1	AlN	100
20-H*	10 : 11	$Al_{10}O_3N_8$	88.9
2-H$^{\delta}$†	>9 : 10	-	>87.5
27-R	9 : 10	$Al_9O_3N_7$	87.5
16-H†	8 : 9	$Al_8O_3N_6$	85.7
21-R	7 : 8	$Al_7O_3N_5$	83.3
12-H	6 : 7	$Al_6O_3N_4$	80.0

*Bartrom only
†Sakai only

M = Cation
X = Anion

The first phase diagram for this system was reported by Lejus.[14] Six phases were incorporated into the diagram, with a single phase designated "X" encompassing all the AlN polytype phases. The ALON solid solubility field was centered around 25 mole % AlN. Since this early work, the diagram has been modified by Sakai,[22] Gauckler,[23] and McCauley and Corbin.[1,24] For the most part all diagrams agree, with each newer version becoming more complex as it improves the preceding work.

Figure 2 is the most recent diagram as reported by McCauley and Corbin.[24] They incorporated the vapor phase because of its importance to the stability of AlN. The nitrogen-rich portion of the diagram agrees well with the temperature stability relationships reported by Sakai[22] and the composition relationships recorded in Table 2. The composition of the ALON solid solubility field was determined to be more nitrogen-rich than reported by Lejus (35.7 vs 25.0 mole % AlN). ALON was found to melt congruently at 2165°C in one atmosphere of nitrogen. Since their work did not focus on δ-ALON, it has not been entered on the diagram.

This phase diagram was thermodynamically evaluated by Dorner[35,36] and Kaufman[37] using thermodynamic data and assuming the stable ALON composition was equivalent to 25 mole % AlN. Both determined that ALON spinel phase was the only stable intermediate phase in this system. However, due to their different assumptions, which will be highlighted in the section on ALON-Free Energy of Formation, their results do not agree. Dorner has ALON incongruently melting at 2000°C and only stable above 1600°C, while Kaufman has it melting congruently at 1940°C and stable at room temperature. Kaufman's results better agree with experimental data on the stability of ALON.

ALON COMPOSITION

The true limits of ALON solid solubility have yet to be accurately determined by a detailed evaluation of the final reacted products. This is probably the major reason for the discrepancies between investigators as shown in Table 3. A major finding upon which all recent investigators agree is that the solid solubility limit does not include the ideal stoichiometric spinel composition Al_3O_3N (e.g., 1:1, as in $MgAl_2O_4$, Fe_3O_4, $FeAl_2O_4$). All models for this oxynitride spinel,[6,14,19] as shown in Table 3, assume a constant anion lattice of nitrogen and oxygen with a decrease in spinel cation vacancies with increasing nitrogen content.

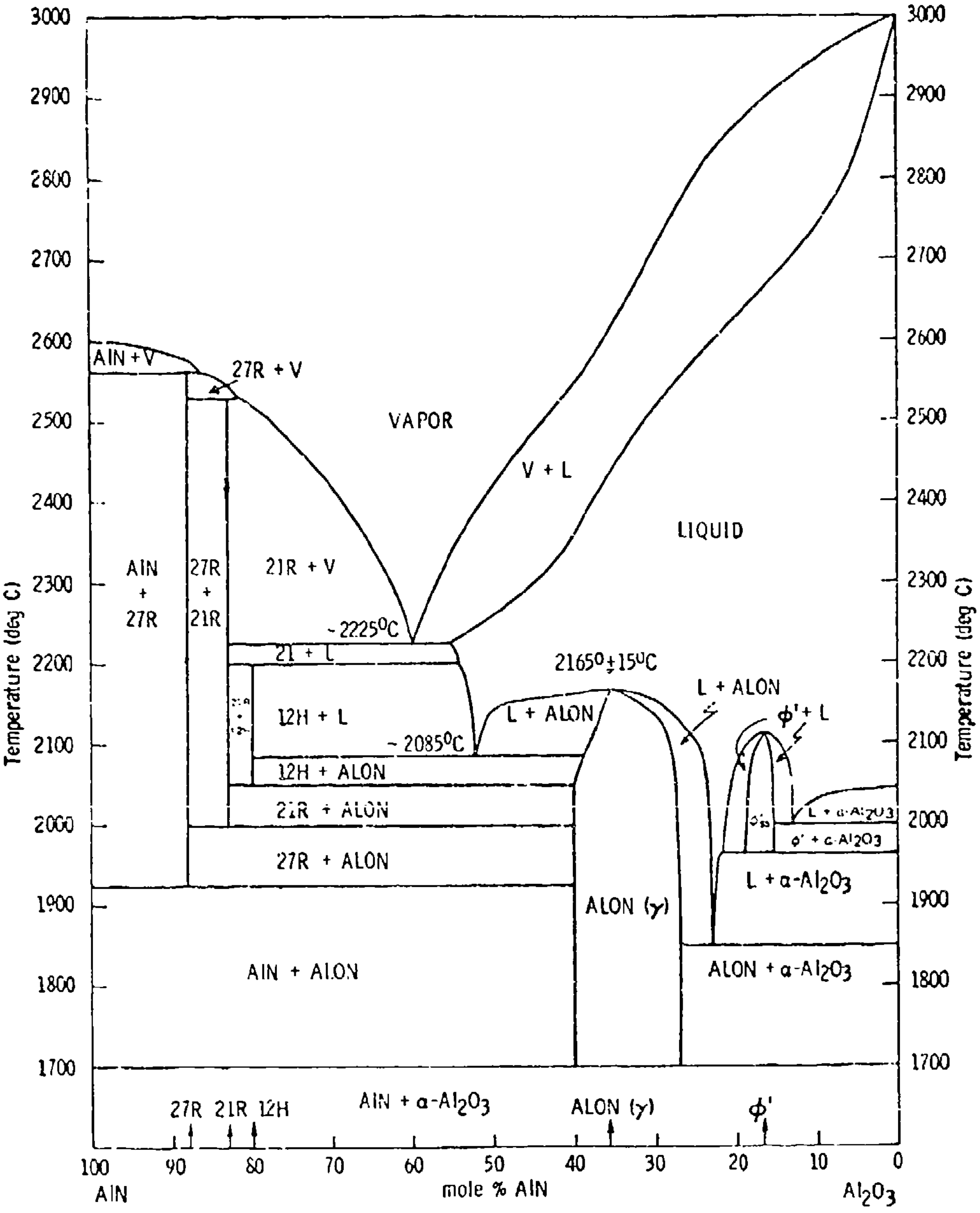

Figure 2. Phase diagram for the Al_2O_3-AlN pseudo-binary (McCauley, 1981).

ALON CRYSTAL STRUCTURE

From the very early results of Yamaguchi,[13] it was known that nitrogen would stabilize a spinel form of Al_2O_3. Recently, Goursat, et al[32,33] have determined the crystal structure of ALON by neutron diffraction to be (Fd3m) spinel. They confirmed that oxygen and nitrogen occupy the anion sites of a spinel lattice. The aluminum cations were found to occupy both octahedral and tetrahedral sites of the spinel structure. This spinel phase was found to be stable only when a disordered vacancy is in the spinel octahedral position. Since a trivalent ion (Al^{+3}) is in the tetrahedral positions of the spinel structure, ALON can be considered as an

Table 3. γ-ALON COMPOSITIONS

Oxynitide Spinel Formulas	Experimental Range Mole % AlN	References
$Al_{\frac{(64+x)}{3}} \boxed{S}_{\frac{(8-x)}{3}} O_{32-x} N_x$ $(0 \leq x \leq 8)$	40-27	McCauley (1978)
$Al_{\frac{(8+x)}{3}} \boxed{S}_{\frac{(1-x)}{3}} O_{4-x} N_x$ $(0 \leq x \leq 1)$	33-16	Lejus (1964)
$Al_{(2+\frac{x}{3})} \boxed{S}_{\frac{(3-4x)}{12}} O_{(3-x)} N_x$ $(0 \leq x \leq 3/4)$	50-33	Adams (1962)
$Al_7O_9N_1$	25	Kaufman (1979) Dormer (1981)
Al_3O_3N	50	Yamaguchi (1959) Henry (1969)
Al_3O_4	Misinterpreted	Yamaguchi (1950) Filonenko (1957) Vert (1957)

$\boxed{S}$ = Spinel cation vacancies
x = Limits from Al_3O_3N to Al_2O_3

inverse spinel. Table 4 compares stoichiometric spinels to nonstoichiometric oxynitride spinels.[6,14,32,38]

The variation of lattice parameter with composition of this material has previously been reported[1,14] and ranges from 7.951 Å (nitrogen rich) to 7.938 Å (oxygen rich). Figure 3 shows the variation of lattice parameter as a function of oxygen content (determined by neutron activation analysis) for fully reacted specimens.[39]

Table 4. SPINEL STRUCTURES

Type	Stochiometric			Nonstochiometric		
	Normal	Inverse	Oxynitride*	γ-Oxynitride	γ-Oxynitride	γ-Alumina
Formula†	AB_2O_4	$B(AB)O_4$	BB_2O_3N	33.3 m/o AlN	35.7 m/o AlN	$B_{8/3}O_4$
Example	$MgAl_2O_4$	$MgFe_2O_4$	Al_3O_3N	Al_5O_6N	$Al_{23}O_{27}N_5$	Al_2O_3
Anion Sites 32 Total	(32) O^{-2}	(32) O^{-2}	(24) O^{-2} (8) N^{-3}	(27.44) O^{-2} (4.56) N^{-3}	(27) O^{-2} (5) N^{-3}	(32) O^{-2}
Cation Sites 16 (oct.)	(16) Al^{+3}	(8) Fe^{+3} (8) Mg^{+2}	(16) Al^{+3}	(14.88) Al^{+3} (1.12) $\boxed{S}$	(15) Al^{+3} (1) $\boxed{S}$	(13.3) Al^{+3} (2.7) $\boxed{S}$
8 (tet.)	(8) Mg^{+2}	(8) Fe^{+3}	(8) Al^{+3}	(8) Al^{+3}	(8) Al^{+3}	(8) Al^{+3}
Reference	Kingery (1976)		-	Goursat (1981)	McCauley (1978)	Lejus (1964)

*Not stable
†A = A^{+2}; B = B^{+3}; O = O^{-2}; N = N^{-3}

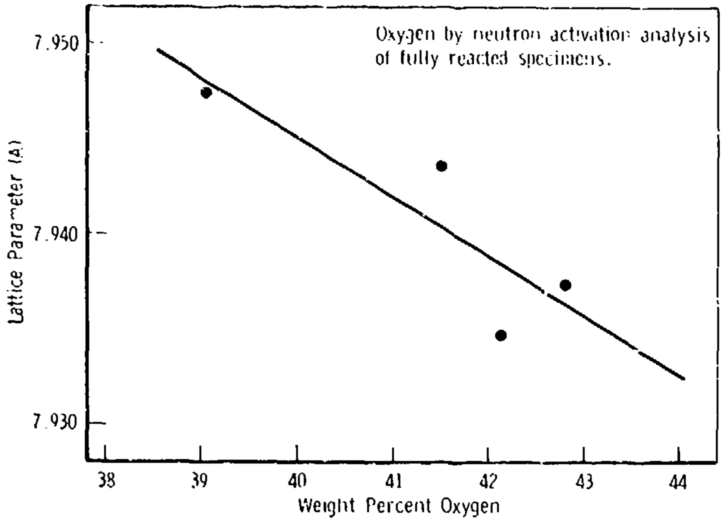

Figure 3. ALON lattice parameter as a function of oxygen content.

ALON PROCESSING

Three basic methods have been used to produce aluminum oxynitride phases. The most common of these involves the simultaneous reduction and nitridation of Al_2O_3. A second method uses aluminum metal, and oxynitrides it by a combustion-type reaction. Finally, these phases have also been produced by the reaction of gases. Table 5 lists the reactions used to produce these phases, along with references.

Table 5. ALUMINUM OXYNITRIDE SPINEL REACTIONS

	General Equations	T°C Required	References
1	$Al_2O_{3(s)} + AlN_{(s)} \rightarrow \gamma\text{-}ALON_{(s)}$	$\geq 1650^{\circ}C$	McCauley (1979) Harnett (1981) Goursat (1976) Sakai (1978, 1982) Lejus (1964) Adams (1962)
2	$Al_2O_{3(s)} + C_{(s)} + N_{(g)} \rightarrow \gamma\text{-}ALON_{(s)} + CO_{(g)}$	$\geq 1700^{\circ}C$	Rafaniello (1981) Ish-Shalom (1980)
3	$Al_2O_{3(s)} + C_{(s)} + Air \rightarrow \gamma\text{-}ALON_{(s)} + CO_{(g)}$	$\geq 1700^{\circ}C$	Filonenko (1957) Vert (1957) Yamaguchi (1959)
4	$Al_2O_{3(s)} + Al_{(\ell)} + N_{2(g)} \rightarrow \gamma\text{-}ALON_{(s)}$	$>1500^{\circ}C$	Michel (1966)
5	$Al_2O_{3(s)} + Al_{(\ell)} + Air \rightarrow \gamma\text{-}ALON_{(s)}$	$>2045^{\circ}C$	Michel (1972) Collongues (1967)
6	$Al_2O_{3(s)} + NH_{3(g)} + H_{2(g)} \rightarrow \gamma\text{-}ALON_{(s)} + H_2O$?	$\geq 1650^{\circ}C$	Collongues (1962)
7	$Al_{(\ell)} + Air \rightarrow \gamma\text{-}ALON_{(s)}$	$\sim 1500^{\circ}C$	Michel (1972) Bouriannes (1974)
8	$AlCl_{3(g)} + CO_{2(g)} + NH_{3(g)} + N_{2(g)} \rightarrow \gamma\text{-}ALON_{(s)} + CO_{(g)} + N_{2(g)} + HCL_{(g)}$	$900^{\circ}C$	Silvestri (1975)

Using Alumina

It has been reported by Collongues[17] that alumina is stable in nitrogen unless a reducing agent is present. In the presence of both a reducing agent and nitrogen, aluminum oxynitrides and aluminum nitride will form. Reducing agents that have been successful include aluminum, carbon, ammonia, and AlN (see Table 5, Eqs. 1-6).

The development of vapor species may be an important part of this reduction/nitridation process. It has been reported that the volatility of alumina is much greater in reducing conditions.[40,41] The formation of vapor species also appears to play a key role in the reaction/sintering of this material.[42] Pasco and Doremus[43] have reported that, during the formation of aluminum oxycarbides by alumina/carbon reactions, vapor transport is important. It is anticipated that the same follows for oxynitride formation from alumina.

Reacting AlN and Al_2O_3 powder mixtures above 1650°C has been used to produce ALON powders,[2,33,34] reaction sintered samples,[1] and reaction hot pressed specimens.[3,22,27,44,45] The major difficulty in this technique is to obtain AlN powder having high purity and a fine particle size. It has been shown that the characteristics of the AlN powder (especially unreacted Al, metal impurities, and particle size) are important for sintering ALON.[46]

Rafaniello and Cutler[25] and Ish-Shalom[26] have produced ALON by heating mixtures of Al_2O_3 and carbon in nitrogen above 1700°C. This process has also been used for producing AlN by adding enough carbon to remove all the oxygen in Al_2O_3.[26] Early studies, in which these mixtures were heated in air, also produced the spinel phase.[11-13] This author has observed the formation of the spinel phase on the surface of α-Al_2O_3 powder pellets when heated in an atmosphere of nitrogen while exposed to the carbon heating elements above 1800°C. Thus, carbon need not be in direct contact with the alumina in order to produce ALON.[42]

Aluminum oxynitride phases have also been produced by reacting alumina and aluminum mixtures in air[15,16] and in nitrogen[42] Collongues, et al[17,18] produced ALON and δ-ALON by reacting alumina with an ammonia plus hydrogen gas mixture above 1650°C.

Vardelle and Besson[47] have produced a spinel phase by arc-plasma spraying α-Al_2O_3 in both hydrogen/nitrogen and hydrogen/argon plasma-gas mixtures. This author believes there is a good possibility that the material produced in the H_2/N_2 plasma could be ALON.

The production of ALON from an alumina precursor is desirable because of the low-cost, high-purity, fine-particle alumina powder readily available. The major problem with using alumina as a starting component is due to the high temperatures (>1650°C) required for synthesis.

Using Aluminum

Aluminum oxynitrides have been produced from aluminum metal by Michel and Huber[48] and Bouriannes.[49,50] Michel noted that, at high temperatures, aluminum liquid can react with air to form various aluminum oxynitrides. Bouriannes formed ALON by rapidly induction-heating aluminum spheres in air until combustion occurred (initiated ~1500°C). The resulting phases were found to depend on the air pressure used (pressure > 70 Bar = ALON, < 70 Bar = α-Al_2O_3). This method of synthesis is in many ways similar to a technique, termed Self-Propagating High-Temperature Synthesis (SHS), used to produce a variety of refractory materials including borides, carbides, and nitrides.[51,52]

Using Gases

Various aluminum oxynitride compositions have been successfully deposited by chemical deposition techniques.[53-58] Irene[53] and Silvestri[54] were able to use Reaction 8 in Table 5 to produce thin polycrystalline spinel layers on silicon substrates. The ALON phase was observed at 900°C, while, at 770°C, a zeta-Al_2O_3-type structure was observed (possibly zeta-ALON). This work produces ALON spinel at the lowest temperatures.

ALON PROPERTIES

Recently, several reports dealing exclusively with the properties of aluminum oxynitride spinel (ALON) have been published.[2,4,7,8] Data from these and earlier works were used to produce Table 6. Currently, all property data available on ALON is on polycrystalline material or powders. Because of this, none of the data are intrinsic to this material. Essentially, all property data are extrinsic, limited by such variables as grain size, residual porosity, and impurities. Future studies with single crystals of ALON would be valuable in determining the intrinsic limitations of this new material.

Table 6. ALUMINUM OXYNITRIDE SPINEL PROPERTIES

OPTICAL/DIELECTRIC		
IR Cut-Off	5.2 μm	Hartnett (1981)
Refractive Index	1.77 → 1.80	Corbin (1981)
Loss Tangent	0.004 (25^0, 10^7 Hz)	Corbin (1981)
Dielectric Constant	8.5 (25^0, 10^2 Hz)	Corbin (1981)
Magnetic Susceptibility	-0.34×10^{-6}/g (1300 Gauss.)	Yamaguchi (1959)
MECHANICAL		
Hardness	1650 → 1800 Kg/mm^2	R faniello (1981)
Elastic Modulus	47×10^6 psi	Corbin (1981)
Poisson Ratio	0.249 → 0.263	Corbin (1981)
Fracture Strength	35 → 50×10^3 psi	Corbin (1981)
Fracture Toughness	2.5 2.9 MN/m$^{1.5}$	Quinn (1984)
THERMAL		
Thermal Shock (ΔT_c)	175 ± 5^0C	Quinn (1984)
Thermal Conductivity (RT)	0.030 cal (cm·S·$K^0)^{-1}$	Hartnett (1984)
Thermal Expansion Coeff.	$7.59 \times 10^{-6}/^0$C (25^0-1000^0)	Sakai (1980)
	$5.23 \times 10^{-6}/^0$C (20^0-200^0)	Corbin (1981)
Thermal Diffusivity	0.040 to 0.037 cm^2/S (RT)	Quinn (1984)
	0.027 cm^2/S (400^0K)	Sakai (1978)
Specific Heat	0.169 cal/g·^{0}K (300^0K)	Sakai (1978)
	0.252 cal/g·^{0}K (450^0K)	Sakai (1978)
CHEMICAL		
Melting Point in N_2	2165 ± 15^0C	McCauley (19[illegible]
Oxidation Resistance	Protective Layer 1200^0C	Corbin (19[illegible]
	Starts at 650^0C	Goursat [illegible]
Chemical Attack	Stable Versus Acids & Bases	Yamaguchi [illegible]

Optical and Dielectric

Since ALON is being considered as a potential electromagnetic window material, its optical and dielectric properties are of special interest. Hartnett, et al[2] have reported the inline transmission of a 2.4 mm thick specimen to have an infrared cutoff at 5.12 μm and an ultraviolet cutoff near 0.27 μm. They have also reported that samples >99% theoretical density show visible light transparency (Figure 1). The refractive indices for ALON vary with composition from 1.770 (30% AlN) to 1.875 (37.5% AlN).[1] Figure 4 shows the power absorption coefficient of a 3.43 mm thick specimen as a function of wavelength.[59] In the mm-wavelength region, ALON has very low absorption. The variation in the dielectric constant and loss tangent as a function of frequency and temperature have previously been reported.[7] Figures 5 and 6 are reproduced from this work. The magnetic susceptibility was determined by the Gouy method and found to be -0.34×10^{-6}/g with an applied field of 1300 G.[13]

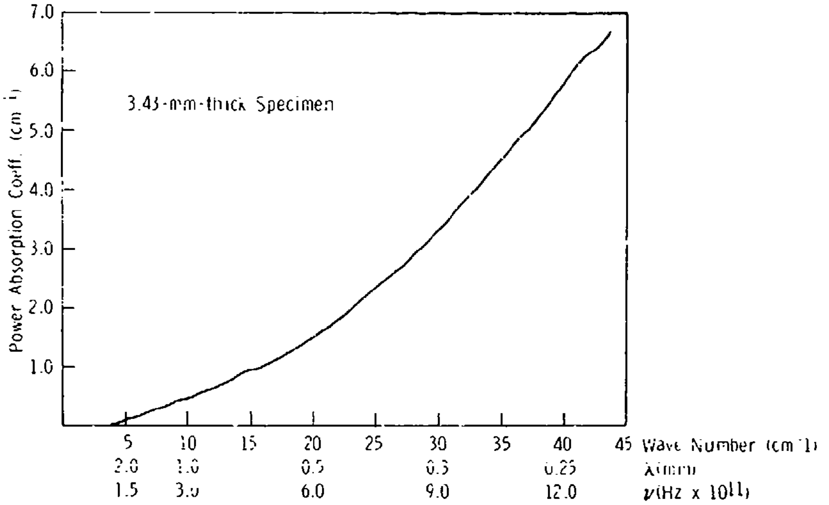

Figure 4. ALON power absorption coefficient U.S. wave number.

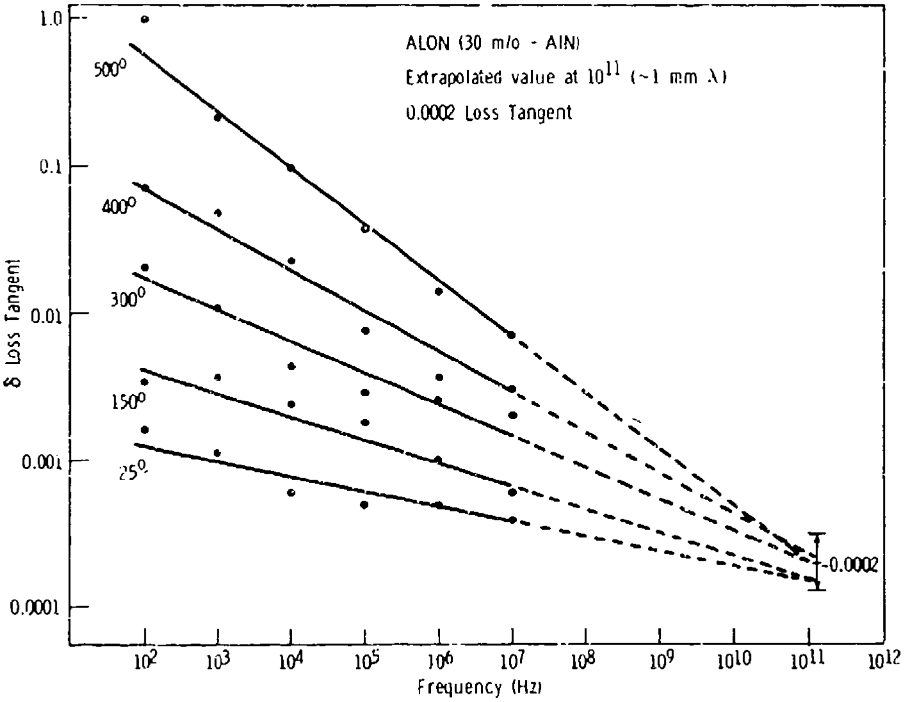

Figure 5. Loss tangent vs frequency (Corbin, 1981).

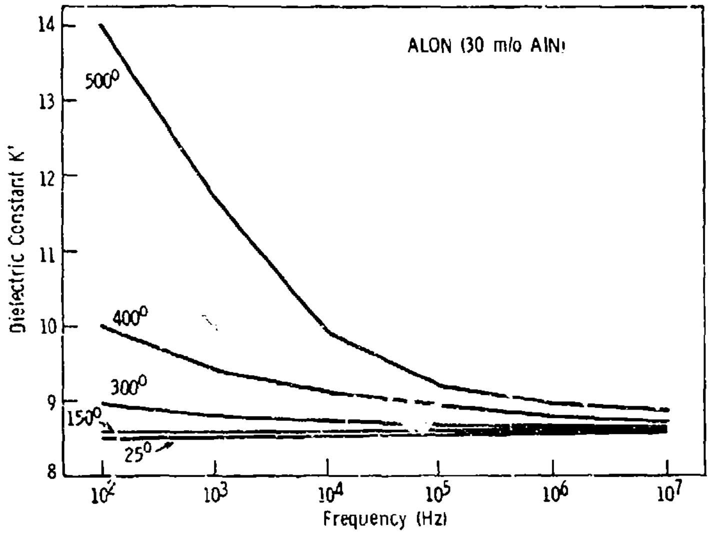

Figure 6. Dielectric constant vs frequency (Corbin, 1981).

Mechanical

Microhardness values of 1650-1800 Kg/mm^2 were obtained when using a 100-g load with a knoop indenter.[1,25] Quinn, et al[8] have reported a variety of mechanical properties on polycrystalline material, including an elastic modulus of 47.3 × 10^6 psi, a Poisson ratio of 0.263, and a K_{Ic} of 2.5 MN/m$^{1.5}$. Their four-point fracture strengths range from 44.4 × 10^3 psi at room temperature to 38.7 × 10^3 psi at 1000°C. In most cases, a critical flaw (large grain or pore) limited the strength of this material. All the data was obtained on relatively coarse-grained material (25-100 μm).

Thermal

The thermal expansion coefficient of ALON varies from 5.23 × 10^{-6}/°C (25-200°C) to 7.0 × 10^{-6} (20-980°C) for reaction sintered materials,[8] while, for hot pressed specimens,[60] it is 7.59 × 10^{-6}/°C (25-1000°C). The values for its room temperature thermal conductivity, thermal diffusivity, and specific heat are listed in Table 6.[8,61] Results from water quench experiments have determined the critical thermal shock temperature (ΔT_c) to be 175°C ± 5°C.[7,8] This is somewhat lower than the value determined for α-Al_2O_3 in the same study. Quinn[8] has proposed this is a result of the differences in the termal conductivities between these two materials (ALON/α-Al_2O_3 = 1/3).

Oxidation and Chemical Resistance

There is some disagreement on the stability of ALON in an oxidizing environment. Corbin and McCauley,[7] testing bulk samples in air, found the oxidation to produce a protective oxide layer up to ~1200°C. Billy,[62] however, found the oxidation of ALON to start as low as ~650°C in oxygen (p = 32 torr) and not produce a protective layer. It is reasonable to expect that the partial pressure of oxygen and nitrogen plays an important role on the stability of ALON at elevated temperatures. For example, in air, $P_{N_2} \cong 0.7$, while in the oxygen environment it is an order of magnitude less.

Work by Goursat[32,33] investigated the oxydation kinetics of ALON and the formation of a new phase, γ'-ALON, during the oxidation process. Figure 7 is a thermogravimetric analysis (TGA) trace taken from their work, showing the oxidation behavior of a 20-50 μm powder. Oxidation starts near 650°C and reaches a maximum weight gain at 1150°C. Heating beyond this temperature reduces the total sample weight gain. They attribute this to the oxidation of ALON below 1150°C with no loss of nitrogen. This results in the formation of the oxygen-rich phase γ'-ALON. Above 1150°C, oxidation occurs with the loss of nitrogen resulting in α-Al_2O_3. They also found that when a nitrogen-rich ALON composition is used as starting material, the γ'-ALON phase is not observed.

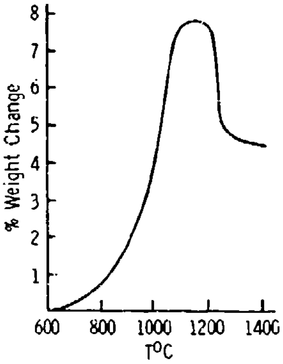

Figure 7. Thermogravametric analysis (TGA) of -ALON in oxygen (32 torr) (Goursat, 1976).

Resistance of this material to other forms of chemical attack have also been investigated.[11-13,63] The results show that ALON is resistant to various acids, bases, and H_2O.

ALON-Free Energy of Formation

The free energy of formation for ALON can be evaluated from the data of Dorner, et al[35,36] and Kaufman.[37] Dorner tabulated enthalpies and entropies of formation for ALON as a function of temperature. He determined these values by using the eutectoid decomposition of ALON into α-Al_2O_3 and AlN at 1600°C, as determined by Lejus,[14] and assuming a small positive value (1 Joule/°K-gram atom) for the entropy of formation from α-Al_2O_3 and AlN. Kaufman listed the free energy of reaction as a function of temperature for producing ALON by reacting α-Al_2O_3 and AlN. He calculated his values by using lattice stability information along with solution and compound phase parameters which he selected from observed thermochemical properties and phase diagrams. Both researchers assumed the composition for ALON to be at 25 mole % AlN (Al_7O_9N). This composition actually lies outside the experimentally determined solid solubility field of ALON.[24]

Table 7 was determined by using their data along with thermochemical information in the JANAF tables.[64] Under column (Δ), the differences between the free energy of formations when using Dorner vs Kaufman data are listed. Even though these differences appear small, they are extremely influential in evaluating the stability of ALON below 1600°C. When using these values to determine the stability of ALON below 1600°C, Dorner's data projects ALON as unstable, whereas Kaufman's show it to be stable at room temperature. As previously discussed, the predictions of Kaufman are in better agreement with the experimental data.

Table 7. γ-ALON* FREE ENERGY OF FORMATION (ΔG_f^0)

		Kcal mole^{-1}		
T^0K	T^0C	Dorner	Kaufman	Δ
1700	1427	-841.905	-843.242	-1.337
1900	1627	-791.497	-791.667	-0.170
2100	1827	-741.090	-740.455	+0.635
2300	2027	-690.683	-689.568	+1.115
2500	2227	-640.276	-638.998	+1.278

*$7\ Al_{(\ell)} + 9/2\ O_2 + 1/2\ N_2 \cdot Al_7O_9N$ (25 m/o AlN)

FUTURE ALON RESEARCH

Since aluminum oxynitride spinel is a relatively new material, very little information on its intrinsic properties is available. In order to fully utilize and find new application for this material, a series of basic research studies would be in order for the future. The following list highlights some critical areas for future ALON research:

- An experimental evaluation of ALON's thermodynamic properties, especially to determine its stability in a variety of different chemical environments.

- A determination of the oxygen, nitrogen, and aluminum diffusion coefficients in ALON, as a function of temperature and pressure.

- An evaluation of the effects of impurities and dopants on the sintering behavior of ALON.

- Studies involved with producing high purity ALON powders.

CONCLUSIONS

Aluminum oxynitride spinel (ALON) is a new material that has the potential to replace α-Al_2O_3 in a variety of applications where optical transparency, high strength, and isotropic properties are important. This material has been sintered into fully dense, transparent material by a variety of researchers using different techniques. Current property evaluations of this material show it to be optically transparent from 5.12 to 0.27 μm, have high strength (4 point = 44.4×10^3 psi), and oxidation-resistant in air to 1200°C Future studies should evaluate the stability of this material in a variety of environments to open up new areas where ALON can be utilized.

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