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Structure and Properties of Aluminum Nitride and AlON Ceramics

by James W. McCauley

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Structure and Properties of Aluminum Nitride and AlON Ceramics

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Abstract

A brief review of aluminum nitride and AlON ceramics is presented in the context of the pseudobinary aluminum nitride-aluminum oxide phase equilibrium system. AlON is the name applied to the nitrogen stabilized cubic spinel in this system, with a composition centered at 35.7 mole-percent AlN. First, the phase equilibria and crystal chemistry of these phases are presented, focusing on a constant anion oxynitride spinel model and the various phases, including polytypoids, in this system. Then, a brief summary is given on the processing and microstructures of AlN and AlON, with comparisons to other microstructures in this system. Finally, selected properties of AlN and AlON are discussed and tabulated, with special reference to alumina. A comprehensive reference list is given.

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1. Introduction

The AlN-Al_2O_3 system contains three important materials: AlN, AlON, and Al_2O_3, which have a wide range of properties and uses. Excellent reviews for AlN can be found in Samsonov (1969), Dugger (1975), Sheppard (1990), and Prohaska and Miller (1990), in Corbin (1989) for AlON, and in Munro (1997) for polycrystalline α-alumina. Some discussion and references are provided in this review for alumina for ease of comparison to the other two materials.

2. Phase Equilibria and Crystal Chemistry

Substitution of nitrogen for oxygen in Al_2O_3 or, conversely, substitution of oxygen into AlN stabilizes new phases with significantly different crystal structures and symmetry (space group): α-Al_2O_3 = R $\bar{3}$c, AlON = Fd3m, and AlN = $P6_3mc$—rhombohedral, cubic, and hexagonal, respectively.

AlON, having the cubic spinel structure, can be thought of as a nitrogen stabilized cubic aluminum oxide. It has many properties comparable to α-A_2O_3, but because of its cubic crystal structure, fully dense, polycrystalline bodies can be completely transparent if processed properly (McCauley and Corbin 1979). Other properties, like dielectric loss tangent, can be extremely low because of the lack of thermal expansion-induced residual strain at grain boundaries. AlN is an intriguing material because of its theoretical thermal conductivity of about 320 W/mK at room temperature—extremely high for a dielectric material and comparable or higher than many metals.

Figure 1 illustrates the proposed phase equilibrium diagram for the pseudobinary Al_2O_3-AlN composition join determined experimentally by McCauley et al. (1988). In a recent series of papers (Willems et al. 1992a, 1992b, 1993; Dumitrescu and Sundman 1995; Qiu and Metselaar 1997), the thermodynamics of AlON have been worked out and the phase relations calculated, confirming the main aspects of the experimental diagram. Tabary and Servant (1998) have also reassessed the phase relationships in this system. Fukuyama et al. (1999), in using plasma arc melting to produce AlON powder, seem to have confirmed the vapor-liquid relationship in the extreme temperature region. Besides the three primary phases, there are also many intermediate phases, listed in the following subsections.

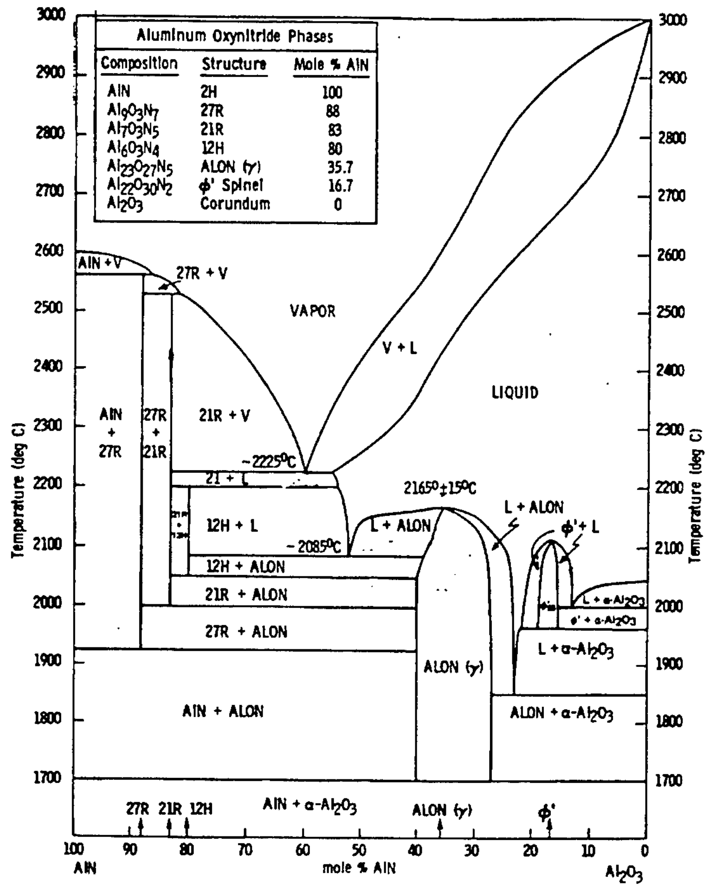


Figure 1. Proposed experimental phase equilibrium diagram for the pseudobinary Al_2O_3-AlN composition join at one atmosphere of flowing nitrogen (McCauley and Corbin 1983).

2.1 AlON–Al_2O_3 Region

- 13 Al_2O_3:1 AlN = ϕ - Al_2O_3 (Michel 1972).
- 9 Al_2O_3:1AlN = δ - Al_2O_3 (Long and Foster 1961; Lefebvre et al. 1972; Tabary and Servant 1999b).
- 10 Al_2O_3:2AlN = ζ - Al_2O_3 or ϕ' - Al_2O_3 (Long and Foster 1961; Michel 1972); $Al_{22}O_{30}N_2$ = AlON′ or ϕ' (McCauley 1978; Tabary et al. 1999).

2.2 AlON Region

- 9Al_2O_3:5AlN = $Al_{23}O_{27}N_5$ = AlON (McCauley 1978; Tabary and Servant 1999a).

2.3 AlN Polytypoids (Corbin 1989; Tabary and Servant 1999a; Tabary et al. 2000)

- $1Al_2O_3$:4AlN = 12H.
- $1Al_2O_3$:5AlN = 21R.
- $1Al_2O_3$:7AlN = 27R (Krishnan et al. 1985).
- $1Al_2O_3$:14AlN = 32H (Krishnan et al. 1985).

Other polytypoids have also been identified: 8H, 15R, 16H, 33R, 24H, and 39R. However, the phase equilibria have not yet been clarified. Tabary and Servant (1999a) and Tabary et al. (2000) have carried out a fairly detailed microstructural characterization of the polytypoids in this system.

Figure 2 (McCauley and Corbin 1983) summarizes selected phase equilibria, bonding and atomic structure changes in this system. The bonding changes from primarily ionic in α-Al_2O_3 to covalent in AlN. The electronegativities of Al = 1.5, O = 3.5, and N = 3.0 result in predicted ionic character of α-Al_2O_3 at 63%, AlN at 43%, and AlON at about 56% (Pauling 1963). With a magnesium electronegativity of 1.2, $MgAl_2O_4$ has a predicted ionic character of about 68%. Structurally, the substitution of oxygen into AlN or nitrogen into Al_2O_3 destabilizes the parent structures with the resulting formation of modulated structures. Conceptually, nitrogen substitution into Al_2O_3 causes a local charge imbalance on the substituted nitrogen. This can be reduced by a shift in anion coordination around Al from six to four, driving the α-Al_2O_3-based phase toward a spinel ($MgAl_2O_4$)-type structure, where the cations are distributed between octahedral and tetrahedral coordination. This has been confirmed by crystal structure analysis of AlON, first determined by Goursat et al. (1981) and more recently refined by Tabary and Servant (1999a), confirming the predictive model of McCauley (1978). Basically, in the AlON spinel unit cell, there are 8 Al cations in tetrahedral sites and 15 Al and 1 vacancy in the 16 octahedral sites. The model proposed by McCauley (1978), which assumes a constant number (32) of anions in a spinel unit cell, has successfully been used to describe and account for the unconventional (seemingly nonstoichiometric) composition of both the AlON (N = 5) and the ϕ' (N = 2) phases. The model assumes the following formula: $Al_{(64+x)/3}\text{Cation Vacancy}_{(8-x)/3}\,O_{(32-x)}N_x$.

Table 1 lists the various compositions predicted by this model from N = 0 to 11. The "normal" spinel composition (N = 8) does not seem to be a stable phase, whereas AlON (N = 5) and ϕ' (N = 2) are seemingly stable stoichiometric phases verified by many investigators. Yamaguchi and Yanagida (1959) were the first investigators to propose that nitrogen additions to Al_2O_3 would stabilize a spinel-type material.

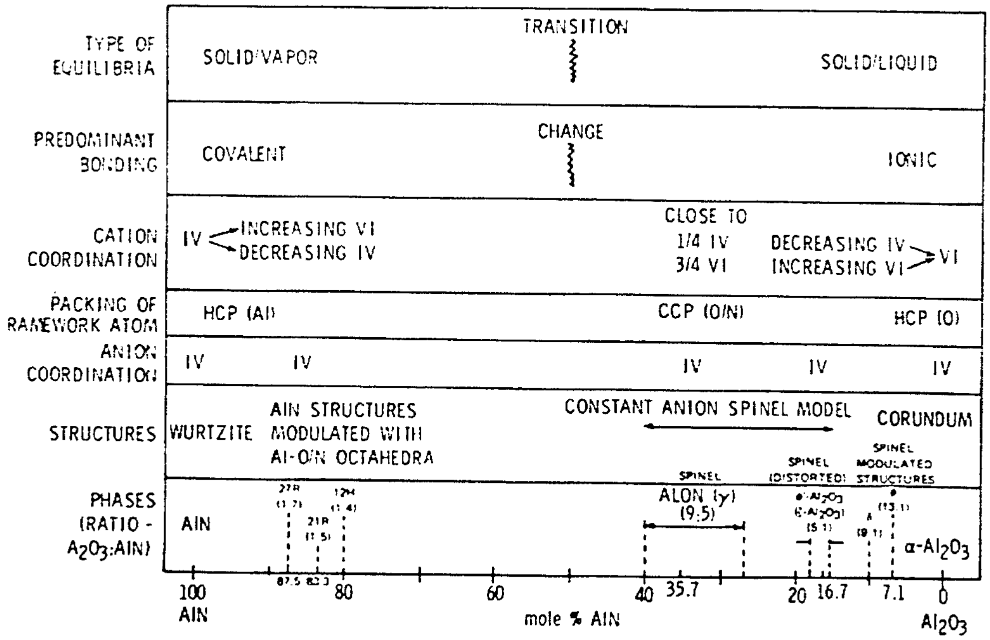


Figure 2. Crystal chemistry relationships in the Al_2O_3-AlN system (McCauley and Corbin 1983).

Table 1. Stoichiometries calculated from the constant anion model (McCauley 1978).

N	O	Al	Interstitials	Vacancies	Mole-Percent AlN
11[a]	21	25.00	1.00	—	61.1
10	22	24.67	0.67	—	57.7
9	23	24.33	0.33	—	54.0
8[a]	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[a]	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[a]	30	22.00	—	2.00	16.7AlON' (ϕ')
1	31	21.67	—	2.33	8.8
0	32	21.33	—	2.67	0

[a] Stoichiometric compounds - integral numbers of atoms.

As indicated in Figure 2, AlN has the hexagonal, wurtzite structure, where Al is tetrahedrally coordinated with nitrogen. The substitution of oxygen for nitrogen in the wurtzite AlN structure results in structural irregularities (Dorignac et al. 1994) and the formation of many polytype-like (polytypoid) phases. This is apparently different than SiC, which has a vast array of polytypes. Recently, however, Ueno et al. (1992) and Xia et al. (1993) have confirmed that at pressures of about 16–20 GPa, AlN transforms into an octahedrally coordinated rock salt structure (O^5_h).

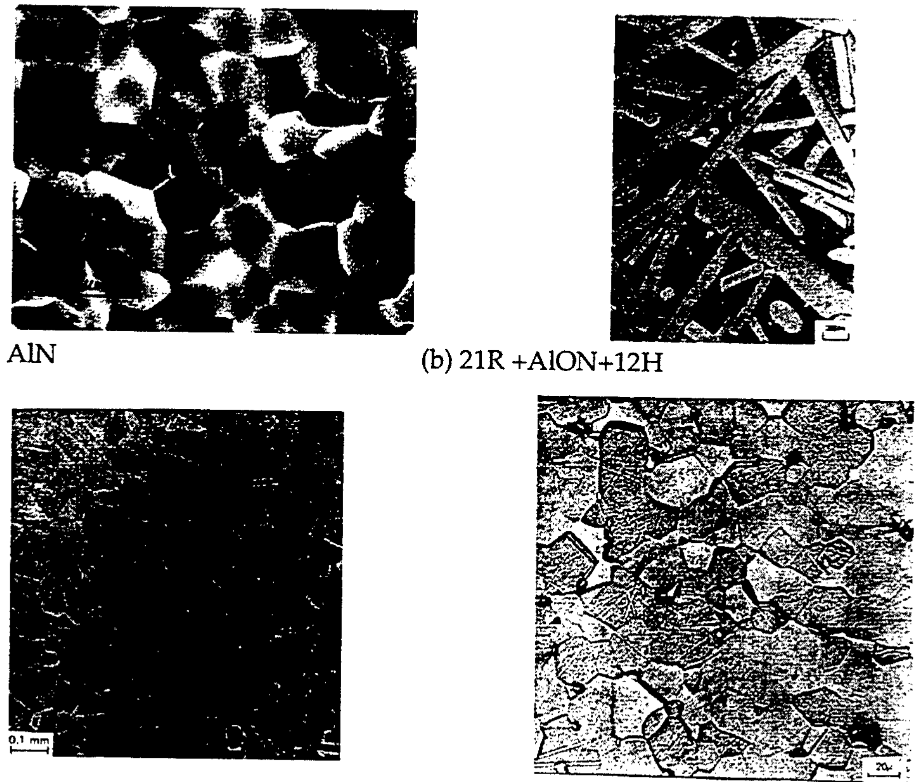
3. Processing and Microstructures of AlN and AlON

AlN powder can be produced by nitridation of Al metal powder or also by the reduction of alumina with admixed fine carbon particles in the presence of nitrogen or ammonia (Huseby 1983). AlON can be produced by the simple reaction of Al_2O_3 with AlN in nitrogen or by the carbothermal reduction of Al_2O_3 + carbon mixtures (Yawes et al. 1997a, 1997b; Ish-Shalom 1982).

Even though AlN is hexagonal, it can be sintered into translucent, almost transparent, polycrystalline ceramics (Kuramoto and Taniguchi 1984; Kuramoto et al. 1989). Coble (1962) demonstrated similar results for α-Al_2O_3, called Lucalox by the General Electric Company, Schenectady, NY. Both of these materials can never be truly transparent in polycrystalline bodies because of their anisotropic optical properties or birefringence, unless they have grain sizes significantly smaller than the wavelength of light. On the other hand, AlON, being optically isotropic, can be produced in completely transparent ceramic bodies (McCauley and Corbin 1979). Raytheon Corporation, Lexington, MA, manufactures AlON in sizes up to about 12 × 12 × 0.25 in for special high-performance applications, including transparent armor and radar windows and domes.

Figure 3 illustrates typical microstructures of AlN (Kuramoto 1984), AlON, and Lucalox. Of course, there are many variations of these microstructures, including grain size, shape, porosity, etc. The microstructure of AlON is hard to resolve optically because the lack of residual stress at the grain boundaries prevents the polishing treatment from preferentially eroding the boundaries for better contrast. (See McCauley et al. [1988] for a comprehensive review of microstructures in the Al_2O_3-AlN system, focusing on the AlON′, AlON, and polytypoid regions.)

Both pressureless sintering and hot pressing have been used to produce pore-free, fully dense AlN and AlON ceramics. Small amounts of additives (MgO in Al_2O_3 and CaO and Rare Earth compounds in AlN) are typically utilized to achieve fully dense, pore-free material. Various chemical vapor deposition techniques (e.g., Irene et al. [1975] and Silvestri et al. [1975]) can be used to produce $Al_xO_yN_z$ films. The effect of oxygen on the sintering and hot pressing of AlN has been studied extensively (Sakai and Iwata 1977; Sakai et al. 1978). Besides McCauley and Corbin (1979), other investigators have studied the pressureless sintering of A1ON (Chen et al. 1991; Kollenberg and Rymon-Lipinska 1992). Several investigators have also studied the hot pressing



(a) AlN

(b) 21R +AlON+12H

(c) AlON

(d) Al_2O_3

Figure 3. Representative microstructures of AlN, AlON/polytypoid mixture, AlON, and Al_2O_3.

of Al_2O_3-AlN powder mixtures and determined the resulting properties; however, the formation of the various polytypoids makes the interpretation of their results difficult (Turpin-Launay et al. 1983; Shimpo et al. 1992; Sakai 1978a, 1978b, 1981a, 1981b). Figure 3(b) is an example of a mixed phase microstructure.

Sakai (1981a, 1981b) and Sakai et al. (1978) has reported on the room and high temperature flexural strength of AlN-Al_2O_3 materials in the 0–70 mole-percent Al_2O_3 region. The final products contained variable amounts of AlN poytypoids. Shimpo et al. (1992) investigated the properties of pure AlON as compared to AlON-BN composite materials. In a more comprehensive study, Turpin-Launay et al. (1983) and Launay et al. (1984) investigated the properties of materials in the AlN-Al_2O_3 system by both reactive hot pressing and reaction sintering; they have referred to these materials as ALUMINALON. Significant variations in hardness, flexure strength, and fracture toughness were observed. Kim et al. (1998) have also studied composites in this system. Djenkal et al. (2000) investigated the SiC-reinforcement of Al_2O_3 A1ON composites. The friction, wear resistance, and other mechanical properties of the ALUMINALON family of materials were systematically studied by Trabelsi et al. (1987) and Berriche et al. (2000).

4. Properties of AlN and AlON

AlN is a high band gap (about 6.2 eV) dielectric material with a very high thermal conductivity. The electronic band structure of Al_2O_3, AlON, and AlN is reviewed by French (1990). Slack (1973) estimated the thermal conductivity of a single crystal to be about 320 W/mK at 300 K. Since that time, there has been a great deal of effort in attempting to produce ceramics (Buhr et al. 1991; Iwamoto et al. 1992) that approach this value for a variety of high-performance substrate and packaging applications in microelectronics and high power devices (Ichinose 1988; Sheppard 1990). It also has excellent molten metal corrosion resistance and stability at high temperatures. Extensive high-temperature creep and compressive strength measurements have been carried out on AlN (e.g., Masson et al. [1994]). It is also very interesting to note that Heard and Cline (1980) have reported a brittle-ductile transformation in AlN at 0.55 GPa confining pressure; Al_2O_3 does not seem to exhibit this transformation up to a confining pressure of 1.25 GPa. AlON has not yet been studied in this way.

AlON has not been studied as extensively as AlN or α-Al_2O_3. The elastic properties have been worked out by Graham et al. (1988); the thermomechanical properties by Quinn et al. (1984) and Swab et al. (1999); dielectric properties by Westphal (1979) and Corbin and McCauley (1981); and the optical properties by Tropf and Thomas (1991). Kim and Richards (1985) investigated the electrical conductivity of AlON. Neutron irradiation studies are detailed by Jeanne et al. (1987). Goursat et al. (1976, 1981) have carried out extensive studies on the oxidation of AlON-based material at high temperature. The use of AlON-based materials has also been evaluated as refractory ceramics (Lepkova et al. 1996; Li et al. 2000). Table 2 summarizes a variety of representative properties for AlN, AlON, and α-Al_2O_3.

Table 2. Representative properties of polycrystalline AlN, AlON, and α-Al_2O_3.[a]

Property	AlN	AlON[b]	α-Al_2O_3
Density (g/cm^3)	3.26	3.711	3.98
Hardness (GPa)	12	13.8	15
Young's Modulus (GPa)	308	307–320	416
Flexure Strength (MPa)	400	228–307	380
Compressive Strength (GPa)	1.5–4.0	NA	1.3–4.0
Fracture Toughness (MPa $m^{1/2}$)	3.0–4.0	2.4–2.9	3.5
Bulk Modulus (GPa)	200	206–214	257
Shear Modulus (GPa)	127–130	123–128	150–169
Poisson's Ratio	0.23–0.24	0.25	0.23
Thermal Conductivity (W/m °C)	180–220	9.4–10.3	33
Coefficient of Expansion (/°C) ($X10^{-6}$/°C) (25–1000 °C)	5.6	7.6	8.1
Melting Temperature (°C)	Sublimes	2165	2050
Electrical Band Gap (eV)	6	6.2	9.9
Dielectric Constant (1 MHz)	8.9	8.56	9.9[c]
Dielectric Constant (7 GHz)	8.2	8.6	9.9
Dielectric Loss (1 MHz)	0.001	0.0005	0.002
Dielectric Loss (7 GHz)	0.002	0.0002	
Refractive Index (at 0.55 μm) n or n_o	2.23	1.785	1.768
Refractive Index n_e	2.17		1.76
IR Cut Off (μm)	6.3	5.2	6
Longitudinal Sound Velocity (km/s)	10.7–10.8	10.13–10.3	9.0–11.0
Hugoniot Elastic Limit (GPa)	7.0–9.4	10.5–10.9	5.0–14.0

[a]Munro 1997; Holmquist et al. 1989; Cazamias et al. 2000; Shafer and Mroz 1992; Hartnett et al. 1982.

[b]35.7 mole-percent AlN material.

[c]Sapphire dielectric constants: parallel to c axis = 9.39; perpendicular to c = 11.58 (Harris 1999).

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A brief review of aluminum nitride and AlON ceramics is presented in the context of the pseudobinary aluminum nitride-aluminum oxide phase equilibrium system. AlON is the name applied to the nitrogen stabilized cubic spinel in this system, with a composition centered at 35.7 mole-percent AlN. First, the phase equilibria and crystal chemistry of these phases are presented, focusing on a constant anion oxynitride spinel model and the various phases, including polytypoids, in this system. Then, a brief summary is given on the processing and microstructures of AlN and AlON, with comparisons to other microstructures in this system. Finally, selected properties of AlN and AlON are discussed and tabulated, with special reference to alumina. A comprehensive reference list is given.

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