Fundamental Properties of AlN

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AlN is an important ceramic for electronic and fusion reactor material. In this presentation, the author summerize many kind of manufacturing method for AlN powder and coating. Further, characteristic properties such as high temperature strength, the modulus of elasticity, thermal conductivity, thermal expansion coefficient, thermal shock characteristic, electrical conductivity, optical properties and electronic structure. Also sintering behaviors of AlN and AlON properties are presented. Further, the wetting properties of AlN against Al, Cu, In, and AlIn and joining with Mo is discussed. On fusion reactor, rf radio frequency window material to heat plasma is necessary and AlN is a candidate for the use. One example of irradiated AlN with neutron is shown.

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1 Introduction

AlN ceramics have interesting properties :

1) a toughness ${\rm K}_{\rm Ic}$ as high as ${\rm 8MPa/m}^{1/2}$

2) a strength exceeds 1000MPa

3) low creep velocity at high temperatures

4) low thermal expansion coefficient

5) rather low elastic moduli

6) rather high thermal conductivity(k $\sim 50 \text{Wm}^{-1} \text{K}^{-1}$)

7) dielectric

8) low oxidation rate

All is currently of great interest in widely regions. Therefore, in this review, the author summarize every topics on crystallographic, physical and mechanical properties of AlN.

II Synthesis of AlN II-1 Direct reaction between Al and gas

Al + $N_2 \rightarrow AlN$

Because of the formation of viscous AlN on Al surface, continuous procession of chemical reaction between is hindered. $^{(1),2)}$ It is said that the viscous film on Al surface is able to brake by using 1 atmosphere of N₂ or by raising temperature above 1500 C^{.3)}

(1)

II-2 Powder production by using d.c.arc from Al electrode (4)-6)

In Fig.1 the schematic view of the apparatus and the relation between the AlN yield efficiency and N_2 pressure are

shown in Fig.2. The decreasing tendency of oxygen content in AlN with heattreatment is shown in Fig.3.⁶) Though lattice value of AlN obtained is compared with the one previous presented, it seems even if oxygen and carbon was contained in AlN that lattice parameter is independent to oxygen content.⁷⁾⁻¹² II-3 Chemical reaction at high temperature Zn-Al alloy in N₂ or NH₃ atmosphere. ¹³⁾⁻¹⁴)

II-4 Reaction of AlF_3 and NH_3

Near 1000 C synthesis of AlN becomes possible with the following reaction. 15)-17)

 $AlF_3(S) + NH_3(g) \rightarrow AlN(s) + 3HF(g)$ (2)

In this case, however, it is necessary to hold NH_3 pressure to be near 1 atm.. Also removal of adsorbed HF gas is necessitated. Further removal of residual AlF_3 must be done with blending of powder formed and with vaporization process above 1260 C in NH_3 atmosphere. As liquid NH_3 gas contains H_20 or oxygen below 10ppm, treatment with metallic Na becomes necessary.^{18),19)}

II-5 AlN from synthesized $(NH_4)_3AlF_6^{20}$

At the first place, by dipping 15g Al in 1700ml 15MHF during 7 days the following reaction proceeds.

Al(s) + 6HF(1)
$$\longrightarrow$$
 H₃AlF₆(1) + 3/2 H₂(g) (3)
excess HF

Precipitatation occurs by adding same quantities of distilled water and $6NNH_4OH$ to maintain pH-9. after filtration.

 $H_3AlF_6(s) + 3NH_4OH(1) \rightarrow (NH_4)_3AlF_3(s) + 3H_2O(1)$ (4) The precipitates are cleaned 3 times with 95% C₂H₅OH and dried

for 16 hr at $\gtrsim 125$ °C. They are sized to be 70 nm with pumping and heated for 30 min. at 600-650 °C under NH₃ atmosphere to proceed the following reaction

 $(NH_4)_3AlF_6(s) \xrightarrow{600^\circ C} AlF_3(g) + 3NH_3(g) + 3HF(g)$ (5) AlF₃ obtained changes to AlN through the reaction (2). II-6 AlN from organometallic precursor

Thermal decomposition to alkyl aluminum amido and imido occurs from the reaction of tri-alkylaluminum compound and NH₃

 $R_3A1 + NH_3 \rightarrow R_3A1 : NH_3 \rightarrow A1N + 3RH$ (6)

 $(R=CH_3, C_2H_5 \text{ or } C_4H_9 \dots)$

Powdered or coated AlN can be obtained with this method.^{21),22)} II-7 AlN from Alcl₃ and NH₃(CVD)

 $Alcl_3(g) + NH_3(g) \longrightarrow AlN(s) + 3HCl(g)$ (7)

With this reaction, AlN film is formed on Si substrate. As substrate temperature, 900-1250 $^{\rm O}{\rm C}$ was applied. $^{23)-27)}$

II-8 AlN film by sputtering method

All film can be formed with suitable conditions in gas pressure, substrate temperature and RF power by flowing $Ar+N_2$ mixed gas on Al target. ^{28),29)} Experimental conditions are given in Table 1. ²⁸⁾

II-9 AlN film with dual ion beam process

With dual ion beam deposition system as shown in Fig,4,AlN film is formed by ionizing Al target with Ar^{*} ion under the condition of $N_2=1.3 \times 10^{-2}$ Pa by low energy of 100-500eV.³⁰) II-10 AlN film with glow discharge method

AlN film was prepared by nitriding of freshly deposited Al

films in a nitrogen glow discharge with a spatial gradient in its intensity $^{31)}$

II-11 AlN from laser-chemical vapor deposition method

Using eximer laser, various metal films such as Al, Cd. Zn,Mo,W,Cr,Cu,Au.Pt,Ag and Pd, and composite film from Au and polymer have been carried out.³²⁾ By using prominent property to be able to absorb wave- length of 193 nm radiation of NH₃ and trimethylaluminum(TMAl), AlN film or powder can be obtained from their photodissociation.³³⁾ In Fig.5, schematic diagram of the apparatus is shown. Also experimental conditions are given in Table 2. The relation of the contents between AlN and Al_2O_3 is given in Fig.6. From this result, higher substrate temperature is recommended for getting higher efficiency of AlN formation.³³⁾ II-12 AlN from usual laser irradiation

Many reports were given to obtain ${\rm Si}_3{
m N}_4$ and SiC by using laser irradiation. Of course, it can consider that same procedure will apply on AlN formation .³⁴⁾

zII-13 AlN film by nitrogen ion implantation into aluminum

The formation of $Si_{3}N_{4}$ film using direct nitridation of silicon by low-energy ion implantation has been performed.³⁵⁾⁻⁴⁰ Likewise the formation of AlN film by using same procedure on Al has successed. In this case, 1 KeV acceleration voltage was applied. Afterwards 10 KeV was examined.⁴¹

According to the previous studies using ion implantation, the formation of hexagonal AlN with 6 x 10 16 and 6 x 10 17 N⁺ ions/cm² at an implantation energy of 40KeV³⁶ and with 5 x 10 15

to 5 x 10 ¹⁷ ions/cm² at 60 KeV became possible.³⁷⁾ In the contrary the formation of AlN was impossible after implantation of between 1 x 10¹⁵ and 1 x 10¹⁸N⁺ ions/cm² at 30 KeV and the substrate temperature of -100, +100 and +200 C.³⁸⁾One report detected a slight increase of mechanical properties with nitrogen implantation.³⁹⁾ When nitrogen doses from 1 x 10¹⁶ to 1 x 10^{18} N⁺ ions/cm² at room temperature with an energy of 50 KeV were implanted on aluminum films deposited onto a cleaved KCl crystal, the co-formation of AlN, Al and Al₂O₃ as observed with the temperature rise till 700 C.⁴⁰)

II-14 AlN from reduction and gas reaction from Al_2O_3

High purity AlN powder was synthesized by the reduction of alumina with the mixed carbon powder in flowing nitrogen at 1600 C for 5hr. In Table 3, elemental analysis value of AlN powder is shown. In Table 4, characteristics of the powder are given.⁴²⁾ II-15 AlN from autoclave pressure reaction

With the self-ignition reaction between aluminum powder and nitrogen at 1000 C and 7 x 10^6 Pa in autoclave as shown in Fig.7, AlN powder was obtained. Unreacted aluminum was solved with NaOH. In Table 5, optical properties are given.⁴³⁾

II-16 AlN from vapor-phase reaction

In the glass reactor assembly as shown in Fig.8,AlCl₃ heated at 180 C with a mantle heater has reacted with flowing NH₃ having velocity rate of 133 to 333 cm³/min added nitrogen of 150 cm³/min. at the temperature of 720-1190 C. In Fig 9., the relationship between particle size and reaction temperature is given⁴⁴⁾ Rapid growth of AlN film using particle precipitation aided chemical vapor deposition (PPCVD) was tried. With the comparison of aforementioned growth rate shown in Table 6, it could understand that the growth rate of PPVCD is extremely higher. $^{45)-51)}$ In Table 7, experimental conditions are given. In Fig.10,,experimental apparatus is shown. The structure of AlN obtained is compared in Fig.11. $^{45)}$

III Physical Properties of AlN

III-1 Crystal Structure

The comparison of lattice parameter values given by various investigators is summarized in Table 8.^{7)9)10)11)45)52)-55) III-2 Melting Temperature}

It is found that intense vaporization of AlN occurs at the temperature of $2000-2400^{\circ}$ C. It dose not show melting phenomenon.^{11),56)}

III-3 Hardness

The over-all hardness of AlN appears to be approximately $1200(K_{100})$.¹¹⁾

III-4 High Temperature Strength and Elasticity

In Table 9 modulus of rupture and elasticity of AlN ranging from room temperature to 1400° C is given.⁵⁵⁾Both values of AlN at 1400°C are higher than those of Al₂0₃.

III-5 Thermal Conductivity

In Table 10 , thermal conductivity values of dense SiC, hotpressed AlN and dense Al_2O_3 are compared.¹¹⁾More detailed measured values are given in Table 11.¹¹⁾ In Table 12⁵⁵⁾ the relation between oxygen content and thermal conductivity value is given. 57)

According to the presentation on thermal resistivity value of AlN containing Al_2O_3 , the incremental thermal resistivity caused by the oxygen is $\Delta W = W-W_0$ (8) ,at where W_0 is (1/3.2)cmK/W of pure AlN value in Fig. 12.the slope of the line becomes ($\Delta W/\Delta n$) = 0.90 x 10⁻²¹cm⁴K/W (9) at where n is the number of nitrogen atoms per cm³ in AlN as shown in Fig.12. ⁵⁵) The result concerning Al_2O_3 in AlN becomes

 $(\Delta Wn_p/n) = 43 \text{cmK/W}$ (10)

The decrement of thermal conductivity shown in Fig. 13 is due to the formation of 27R prototype when SiO_2 was added into AlN. 58)

The relation between the content of prototype and thermal diffusivity value is given in Fig.14. Likewise the increase of prototype content with increasing SiO_2 additive is shown in Fig. 15. In Fig.16, the change of reaction product with temperature is shown. In Fig 17., the relation among thermal diffusivity value, density and sintering temperature is given.

In Fig.18, it is shown that the density is independent on the SiO₂ content from the change of thermal diffusivity value. III-6 Thermal Expansion Coefficient

Thermal expansion coefficient of hot-pressed AlN is given in Table 13. 57 AlN powder produced from AlF₃ and NH₃ contained

oxygen content below 1wt.% and showed grain size of 5 x 10^{-4} cm. The lattice parameter is as follows :

 $a_0=3.1105 + 0.0005 \text{Å}$, $c_0 = 4.9788 + 0.0008 \text{Å}$ The value is slightly lower than that of AlN not containing oxygen. From this proof, it seems that oxygen content in AlN does not give an effect on the lattice parameter.⁵⁹⁾ In Table 14 , accurate thermal expansion coefficient is shown¹¹⁾, and in Table 15 the comparison with thermal expansion coefficient of Al₂O₃ and Si is given.⁶⁰⁾

III-7 Thermal Shock Characteristic

Because of the interesting properties such as high toughness, low creep velocity at high temperature , low thermal expansion coefficient, low elastic moduli and high thermal conductivity on AlN, it shows a good thermal shock resistance.⁶¹⁾ It has been said that the loss of 12% of the modulus of rupture 1400°C occurs after 30 cycles of heating in 2.5 min to and rapidly cooling to room temperature in an air blast.¹¹⁾ Although the thermal shock resistance characteristic of AlN is not so superior than those of Al_2O_3 and $Si_2N_2O_3$, AlN takes а intermediate value of ΔT between them as shown in Table 16.⁶¹⁾ III-8 Electrical Conductivity

Difference on electrical conductivity of AlN with or without oxygen has not been given. It was only shown that the electrical conductivity of oxygen containing AlN was observed to be independent of nitrogen partial pressure from 10^5 to 10^2 Pa in the temperature range from 800 to 1200° C.⁶²⁾ III-9 Optical Properties of AlN

Optical properties of single crystal AlN formed from sublimation at the temperature from 1780[°] to 1980[°] C using polycrystalline AlN, which was produced by an electrical discharge between aluminum electrodes in an atmosphere of nitrogen, was measured . As shown in Fig. 18, the following conclusions could be obtained :

(1) Fundamental absorption edge is at 5.9 + 0.2 eV.

- (2) In addition to this edge all the crystals showed a weak absorption centered around 2.8eV
- (3) Crystal plated with aluminum and heated at 1100°C for 2hr in Ar and removed aluminum showed a strong absorption centered around 2.8eV in additional to an apparent edge at 4.8eV
- (4) The authors have considered that the change of edge is associated with nitrogen vacancies and the 2.8eV absorption with interstitial aluminum.⁶³

The IR absorption characteristic of thin AlN films deposited by rf sputtering was studied . In Fig. 19, an absorption band at 675 cm $^{-1}$ is shown. 64)

Infrared reflection characteristic of single crystal AlN layers grown by vapor phase reaction of NH_3 with $AlCl_3$ is shown in Fig.20. The result showed the presence of an appreciable strain at the AlN -saphire substrate epitaxy interface. Optical absorption data shows that AlN is a direct band-gap material with a value of about 6.2eV(200m/4) at room temperature.⁶⁵⁾

III-10 Electroluminescence

Electroluminescence in the visible region is observed when AlN is excited by either ac or dc. AlN powder was prepared by the reaction of high-purity Al with N_2 at high pressure and temperature. After activated with Cu or Mn, it was sandwiched between two electrodes and either ac or dc was applied as shown in Fig.21 Electroluminescence behavior is illustrated.⁶⁶ III-11 Vaporization Behavior

The dissociation pressures of AlN were measured by the torsion-effusion method over the ranges 1780 to 1970 C.⁶⁷⁾ III-12 Surface-Acoustic -Wave Property

Surface-acoustic-wave of AlN films below the thickness of $2.5 \text{m}\mu$ has been reported.⁶⁸⁾⁻⁷⁰⁾It was measured by reflective impedance from aluminum interdigital transducers. The electromechanical coupling coefficient K²and propagation velocity V_s was measured against AlN thickness-to-transducers-wavelength ratio t/ λ as shown in Figs.22 and 23.⁷¹⁾The detailed interpretation has not been given till now.

III-13 Refractive Index

In Fig.24, spectral dependence of the refraction index of AlN is shown. The value expresses that AlN has the most ionic character. 72

III-14 Stability at Higher Temperature in a Various Atmosphere

It is shown how many percentage of AlN converts to Al_2O_3 or $AlCl_3$ when AlN was exposed to air, oxygen, dry steam, chlorine and hydrogen at elevated temperature as shown in Table 17.⁶²⁾ At

1700 C,it is understood that the rate of oxidation becomes rapid. In Table 18,the compatibility behavior of AlN in corrosive circumstances is shown.¹¹

Many papers have been presented on the oxidation behavior of AlN in air. $^{73)-76)}$ Using refection high-energy electron diffraction(RHEED) and X-ray diffraction, surface states of AlN powders and thin films in air at elevated temperature were given in Table 19.¹¹⁾ It can recognize that oxidation rate becomes higher at the temperature above 1200 C.

Also, AlN is stable up to 1000 C in air and remains stable up to 1400°C in vacuo. Furthermore it has been confirmed that AlN forms \check{J} -AlOOH when contacted with water at 100 C.⁷⁷) In Table 20, LHEED patterns of oxidized AlN are compared with that of Al₂0₃. It must consider the following reactions.

Aln + $3H_20 \rightarrow NH_3$ + $Al(OH)_3$ (11) 2AlN(s) + $3H_2O(g) \rightarrow NH_3(g) + (-Al_2O_3(g))$ (12) Aln + $2H_2O \rightarrow NH_3 + (AlOOH)$ (13)

Thermal stability of hot-pressed AlN was investigated at 1100 to 1400 C in dry air, wet air and wet N_2 atmosphere with 1.5 to 20kPa of water vapor pressure. In Fig.25, chemical free energy changes of AlN with oxygen and water vapor are given. It will be understood that AlN is easily oxidized to be Al_2O_3 and N_2 . Oxidation of AlN is accelerated with the existence of water vapor. At first, surface chemical reaction between AlN and the adsorbed water vapor proceeds at the temperature below 1250 C, and successibly diffusion of water vapor occurs through Al_20_3 films above $1350^{\circ}C.^{78}$

III-15 Compatibility Between AlN and Transition Metals

The stability behavior of AlN with group VII transition metals was studied.⁷⁹⁾With the coexistence of group III, rare earth. and group IV metals, binary aluminide, binary nitride and ternary phases were formed.⁸⁰⁾⁻⁸⁵⁾ Reaction with group V metals were sluggish, but AlN coexists with the respective transition metal or its solid solution with group V and VI metal aluminumnitrogen systems. In Table 21, coexistences with group VII metals are shown.⁷⁷ As shown in Fig.26, Ni₃Al will form at nitrogen partial pressures slightly below 1 atm., although the formation of CoAl and FeAl is impossible.⁷⁹⁾

IV Optical Properties

IV Lattice Vibration Spectra

The reflectivity and transmission spectra of AlN have been measured in the wavelength from 2 to 30 m/4 86 The object of the investigation was to make clear the dependency of the UV absorption edge on the nitrogen vacancy for the large range of values ranging from 3.8 to 6.0eV which corresponds to the band gap of AlN. $^{36}(67)(87)(88)(89)$

In Figs.27 and 28, absorption characteristic of AlN is shown at wide wavelength. In Table 23, the assignments are given for each absorption band.⁷⁹⁾ Nextly the reflectivity spectrum are given in Figs.29,30,and 31. From these results, no remarkable absorption in IR range has been given. The authors consider that specimens supplied from three sources were not crystallized matters. 86

In Fig.32, optical parameters calculated from the reflectivity data are shown. Good confidence can be confirmed in another paper as shown in Fig.33.²⁴⁾

As shown in Figs.34 and 35, small refractive index value, small absorption coefficient and high band absorption is caused by the formation of excess Al from sputtering method. The authors suggest that oxygen as impurity component deduces the decrement of density, intensity of absorption band and refractive index.27 The defect of nitrogen atom as well as absorbed Ar also affects on the results above-described. It is emphasized that the defect of nitrogen atom makes inner electrical field to be greater, so that the absorption edge is shifted to lower energy region. Likewises, the degree of inhomogeneity on sample structure influences on the decrease of refractive index value as well as another physical values. Although the relationship between optical reflection characteristic and specimen form, such as crystalline, thin films or powder, is detailed shown in Fig.36, Wide band reflection can be observed in each case.²⁾ Reflection at 7.8eV is coincided with the value presented band previously.⁹⁰⁾One report has given the transmission result as shown in Fig.37. 42

V Electronic Properties

Related to Si-oxide and Si-Nitride, chemical bonding state was studied at 1979. In 1981, first paper has been presented on AlN. Peak shifts on Al_{LVV} and Al_{KLL} line are shown in Fig.38, the result obtained are follows³⁵.

1) The valence band spectrum of AlN is completely different compared to that of Al or Al-oxide.

2) The main peak is at 61eV with three less intense peaks at 37,48,and 53eV.

3) With nitrogen ion implantation time to be longer, the chemical composition changes to $Al_{47}N_{53}$ through $Al_{58}N_{42}$. Though ELS(Energy Loss Spectroscopy)result is given in Fig.39, the conclusions are a follows :

- 1) The most intense energy loss peaks are due to surface and bulk plasmon excitations $(tw_S \text{ and} \hbar w_B)$. The loss peaks in the lower energy range near 3 and 5eV are due to single valence excitations.
- Al-oxide has an electron energy band gap of 5-6 eV depending on the degree of its structural disorder.

The valence electron excitation at 7.4,9.2,12.5,19.0,19.5 and near 27eV should be due to interband transition from filled valence band states into empty conduction band states. The loss peaks at 3.0 and 4.6eV may be attributed to transitions from deep electron traps within the energy band gap. Corresponding excitations were detected in optical absorption spectra. $^{35)}$ It is shown that AlN reveals a quite similar VE spectrum. (1)20.0eV : bulk plasmon excitation.(2)7.2eV(electron the energy loss peak),near 10eV(band excitation), 17.5,225.5,28.5eV(loss peak) : energies at 4.6 and 7.2eV showed excellent The excitation agreement with optical absorption results of CVD AlN films 27) Reactive sputtered AlN films were characterized by X-ray

photoelectron spectroscopy and Auger electron spectroscopy. In Table 23,parameters used for sputter deposition of AlN films are given.⁸⁶⁾ Auger spectra showed Al_{VV} and Al_{KLL} transitions of AlN films are shown in Fig.40. The difference of crystallographic properties depending on the sputtering conditions strongly affected on the results of XPS and AES.²⁹⁾

Also, the electronic structure of thin AlN films produced by 10-keV N⁺ ion implantaion was studied with XPS.⁹²⁾ It did clear the transitions between occupied and unoccupied states, as well as localized levels in the band gap, due to the presence of structural defects.

VI Sintering

AlN exhibits a number of advantageous properties, and therefore to develop pressureless sintering techniques for the fabrication of dense and high strength material is necessary. AlN, however, cannot be sintered to high densities, analogous to the non-oxide ceramics. For this object, addition of sintering aids has been carried on. For an example, 1wt.% additions of Li_20 , CaO, MgO, MgO-SiO₂(talc), SiO₂, B_2O_3 , NiO, Cr_2O_3 And Y_2O_3 were performed.⁹³⁾ The sintering effect of metallic Ni(1wt%)was evident as having of bending strength of $300MN/m^2$.⁹⁴⁾ Ni was added as $Ni(NO_3)_2$ solution, and the relation between Ni content and density was shown in Fig. 41.⁹⁵⁾ The additional effects of $Y_{2}O_{3}^{96}$ Al-Mg-silicate⁹⁹⁾ and 1wt%(CaO or SrO)¹⁰⁰⁾ are shown to have high density.

The effect of impurity oxygen on thermal conductivity of AlN

was studied.¹⁰¹⁾ In Table 24, the purity of AlN powder is given.²⁹ Sintering conditions is given in Table 25.¹⁰¹⁾ The physical properties such as specific heat, thermal diffusivity and calculated thermal conductivity values are shown in Table 26.¹⁰¹⁾ As conclusions, the following results are summarized :

- 1) Thermal conductivity of AlN decreases remarkably with the increase of oxygen content.
- 2) Thermal conductivity depends on oxygen content as well as sintering temperature. This is due to the change of crystalline phases which precipitates at higher oxygen concentration sites by changing sintering temperature.
- 3) Though amorphous oxide coats on the surface of AlN with the thickness ranging from 40 to $120\mathring{A}$, it converts to \swarrow -Al₂O₃ above temperature of 1200°C and accerelates the sintering velocity by forming oxynitride of spinel type.
- 4) Above temperature of 1900° C, oxynitride reacts with AlN and forms 27R-pseudo-polytype. The reason why thermal conductivity decreases is due to the formation of 27R widely by solving oxynitride, which exists in grain boundaries.

Loehman suggested that a slight formation of AlN from characteristic FTIR absorption bands at 700 cm⁻¹ of standard AlN in glasses containing up to 7at% nitrogen. The result is shown in Fig. 42 102)

The increase of oxygen content of AlN by immersing in organic solvent which contains MgO is shown in Table 27^{101} , and the increase of density by adding MgO in AlN is shown in Fig.

 $43.^{103}$

In Table 28,the change of density when various additive was used to AlN is shown. $^{103)}$ The effect of $\rm Y_2O_3$ addition can be understood.

As ceramic nuclear fuel composite, mixture of AlN and UN, which shows no cracking behavior under thermal shock conditions and good oxidation resistance from protective layer's formation has been studied. 104

The effect of the oxygen impurity on the densification behavior of AlN was investigated.¹⁰⁵ As shown in Fig.44, it is anticipitated that oxygen accelerates densification.

As shown in Table 29, the effect of Y_2O_3 addition on AlN can be understood.⁹³⁾

The change of density and thermal conductivity value when various type of aid were added to AlN is shown in Table.30.¹⁰⁶⁾ From Fig.45¹⁰⁶, it will be seen that rapid increase of thermal conductivity value with the addition of Y_2O_3 above 0.5wt% at the temperature above 1800°C and gradual rise of the value with the addition more than 0.5wt% occurs¹⁰⁷⁾.

On the other hand, the relation between the thermal conductivity value of AlN and the impure components such as Mg, Fe and Si has been investigated.¹⁰⁷⁾In Fig.46, the decrease of thermal conductivity value with the increasing the oxygen content in AlN is shown. In Fig. 47, the results are given. The harmful effect of these elements can be understood.

The change of sintering density of AlN when additive such as

 CaC_2 , CaO, Y_2O_3 , and C was used is shown on Fig.48¹⁰⁸. It can be recognized that the addition of carbon is not effective to obtain good sintered AlN. The addition oc CaC_2 shows good thermal conductivity value against AlN as shown in Fig.49. Fig.50 also shows the sintering model for high thermal -conductivity AlN ceramics with CaC_2 additive, based on chemical and microstructural analysis.¹⁰⁸)

VII Others

VII-I AlON

Phase relation on the system Al_2O_3 and AlN was studied.¹⁰⁹⁾ Fused Al_2O_3 containing a small amount of nitrogen showed the formation of $\begin{pmatrix} -Al_2O_3 \\ -Al_2O_3 \end{pmatrix}$, but lithium $\zeta -Al_2O_3$ formed with 3.9% nitrogen.

As simple model of AlON, the following formula was given.¹¹⁰

Al240(72-3x)/2 N X (72-x)/2)-32

at where, \Box is cation vacancy amd x=8 is an ideal spinel, x<8 represents cation interstitials, and x >8 represents cation vacancies.

As shown in Fig.51, the following phase relations were derived 111) :

- Cubic AlON spinel melts incongruently at = 2050⁶C and is compositionally centered at = 35.7mol%AlN.
- 2) It is equivalent to the following stoichiometric composition : $Al_{23}O_{27}N_5$ or $5AlN9Al_2O_3$

3) Single-phase AlON material sintered to nearly full density

exhibits transparency in visible light.

More detailed phase diagram of $AlN-Al_2O_3$ was presented¹¹²) as shown in Fig.52. Each content of $AlN \, \mathcal{A}l_2O_3$, oxynitride and AlN polytypes are given in Fig.53.Also the changes on density and hardness of the system $AlN-Al_2O_3$ are shown in Figs.54 and 55. VII-2 Preparation of AlON

There are three methods to obtain AlON as follows $^{113)}$:

- 1) Clay/carbon=8.5/1(in nitrogen) \rightarrow reacted at 1700 C x 4hr.
- 2) Al₂O₃/carbon=16/1 \rightarrow reacted at 1750 C x 1hr.
- 3) Al₂O₃ 6H₂O + starch + NH₄OH = Al(OH)₃ppt \rightarrow soaked

at 180°C x 24hr \rightarrow reacted with coke at 800°C in nitrogen.

High temperature strength in Fig.56,oxidation behavior in Fig.57, dielectric constant in Fig.58(a),tan loss in Fig.58(b), and transmittance spectra in Fig.59 are shown respectively.¹¹⁴⁾ Thermal and mechanical properties of AlON is shown in Table $31.^{114}$

In Figs.60-63, hardness, high temperature bending strength, thermal expansion coefficient and thermal shock characteristic are summarized. Thermomechanical properties are given in Table 32.¹¹⁵) Lattice parameters in Table 33, electrical conductivity in Fig.64, and electrical conductivity as a function of aluminum vacancies in Fig.65 are shown.¹¹⁶)

The relation among porosity, elastic moduli and shearing strength are shown in Figs.66 and 67.¹¹⁷⁾ In Table 34^{117} , the comparison of elastic properties among Al_20_3 , AlON and $MgAl_20_4$ is presented.

VII-3 Metallization

Surface metallization is necessary for the application of electric circuit to ceramics substrate. Because the adhesion between metal and ceramic must be strong enough for the use, other methods such as the addition of glass intermediate layer and eutectic bonding by using copper have been applied. Since the wetting behavior is inferior to that of Al_2O_3 , direct metallization by electroless plating was tried.¹¹⁸,¹¹⁹ Table 35^{119} shows bath composition and working conditions for electroless Ni-P plating. In order to form anchoring bonding at the interface and to solve harmful element such as calcium, the appropriate etching by NaOH was developed.

Interaction between AlN and $74.7Pb0-9.4B_20_3-15.1Si0_2(wt%)$ glass was studied. The following inconvenient reaction to form gas bubble at the interface was found.

 $2Pb0 + 4/3 AlN \rightarrow 2/3Al_2O_3 + 2Pb + 2/3 N_2$ (14) From the thermodynamical consideration, glass composing from $20Li_2O-80B_2O_3(mol\%)$, which has low glass-transition temperature and surface tension values alike with those of the lead borosilicate glass, was derived. With application of the glass, it was determined that the interface is continuous and no evidence of any deleterious reaction can be seen even when the glass is fired at 900°C for 1hr.¹²⁰

VII-4 Wetting

Mo and AlN using the interlayer composition imposed of 60Mo and 40AlN(vol%) was joined at 1890K and 2.1GPa for 30 min, but

the joining was failed. 121

All showed the inertness at 2000 C in both Ar and carbon monoxide, and also it was very stable against not only liquid Ga, but also molten B_20_3 .⁵⁾

The wetting of AlN by liquid Ag and liquid Cu was measured in comparison with that of TiC. As shown in Fig.68, AlN is unwettable material. 122

The wetting of AlN by Nickel alloys containing Hf,Zr,Ti,V,Nb,Ta,Cr,MO and W was investigated. Adding Hf,Zr,or Ti in Ni caused to wet AlN as shown in Fig.69.¹²¹⁾

The wettability of AlN by liquid aluminum was compared with that of TiB_2 , TiN and TiC. AlN showed the worst wetting behavior as shown in Fig. 70.¹²⁴)

In Table 36¹²³, Gibbs free energies of formation at 1500°C of compounds in the system AlN-M are given. Table 37 shows the relative stability of MN and AlN phases.¹²³⁾ Fig.71¹²⁵⁾ exhibits a slight decrease of the wetting angle by adding In to Al. The addition of 2wt%CaO to AlN changed the fracture mode from transgranular to intergranular while concurrently decreasing strength, hardness, and toughness.¹²⁶⁾

In order to make clear poly-type formation mechanism in oxygen containing AlN,TEM observation was carried out. The steps of elemental structural rearrengements are as follows :

 Formation of substitutional solid slution of adsorbed oxygen in AlN lattice.

2) Through the formation of stacking fault stacks,

isostructural delamination of AlN-0 solid solution and oxygen-rich plate formations continue.

3) Finally polytype is formed through short-range ordering in oxygen-rich plates and its rearrangement¹²⁷).

Especially the additional effect of $\mathrm{Eu}_2\mathrm{O}_3$ to AlN was studied Raman and photolumiescence spectra. 128). The bv authors discussed the reason why the lattice parameter of wurtzite structure becomes minimum value with the addition of 4-5wt% Eu₂0₃, and deduced the substitutional effect of oxygen into nitorgen sites but it was impossible to consider the substitutional effect of europium into aluminum sites. The occurrence of large stress was discovered $^{129)}$.

The low-temperature(1600 C) sinterability of AlN was studied by doping with a mixed additive of Y_2O_3 , CaO,La₂O₃,CeO₂, and SiO₂.

It was concluded that the Y_20_3 -CaO-La $_20_3$ -CeO $_2$ SiO $_2$ sintering aid is attractive for this object.¹²⁹⁾

From the addition od SiO $_2$ and Y $_2$ O $_3$, the following reaction effects are considered : $^{130)}$

- 1) It induced good densification by liquid-phase sintering, and resulted in high thermal diffusivity.
- 2) It decreased 27R polytype and increased thermal diffusivity.

The effect of SrO additive(1mol%) on the electrical conductivity and dielectric behavior of AlN was studied. The addition of SrO to AlN increased the electrical conductivity and $\tan \zeta$, but reduced moisture effect on their properties because of

lower porosity. 131)

From a thermodynamic standpoint, the higher G_0 with, $G_0 < 0$, which is a standard free energy of aluminate formed from Al_2O_3 and the additive, the higher will be the thermal conductivity of sintered AlN. Further the presence of the second phase was expected to have a small effect on thermal conductivity.¹³²

By using TEM observation, AlN containing Y_2O_3 showed the formation of extended defects from dislocations and planar defects.¹³³⁾

Relation between surface tension and the wetting angle of liquid Pb on AlN is shown in Fig.72. It is confirmed that AlN is non-wettable material against liquid Pb. 123

Relation between partial oxygen pressure and wetting angle of liquid Si on CVDAlN is shown in Fig. 73^{134} . With the increase of partial oxygen pressure, it is shown that the wetting angle decreases.

The wetting behavior of AlN with various type of filler alloys, Sn, Cu and Al is shown in Fig.74. Filler alloys containing Ti have given good wetting on AlN.¹³⁵⁾ The wetting behavior of AlN for various braze alloys was studied. As shown in Fig.75, excellent wetting of AlN is obtained with the addition of titanium.¹³⁶⁾

VII-5 Interfacial reaction with metal and alloy

In Table 38, reaction product at the interface between liquid Ni alloy and AlN is shown.¹⁶¹⁾ The formation of AlN is found by adding Zr, Ti,Nb,Ta, Mo and W.¹³⁷⁾

For the joining between AlN and Cu or Cu alloy, the following filler alloy such as $Ti-Cu(28Ti-Cu,44Ti-Cu)^{138}$. $Ti-Ag-Cu(1Ti-27Cu-Ag)^{139}$ 140), $Zr-Cu(47Zr-Cu)^{141}$ was used. XPS studies between AlN and deposited Cu under ultrahigh vacuum conditions revealed that initial metallic bond forms between Cu and Al, and emphasized that the presence of surface oxygen on contaminated AlN powders may strongly affect the nature of the bonding associated with metallization.¹⁴²)

From the characterization of Au-AlN interface, it became clear that enhanced oxidation accompanies the diffusion of Au into AlN. 143

VII-6 Thermal stability of AlN

Weight change of AlN heated in a vacuum at 1150° C has shown the progressive decrease in the rate of weight gain due to thickening of the Al₂O₃ surface film in slowing reaction kinetics.¹⁴⁴⁾

VII-7 Composites

a) SiC-AlN-(Al₂OC)

1) Object

For the high-temperature structural ceramics, they must have oxidation and corrosion resistance, low bulk density, excellent creep and wear resistance and potential lower cost besides high temperature strength characteristic. Much attention was paid on high stress applications, so that SiC and Si_3N_4 was chosen. Although the addition of sialon has received its effectiveness for sintering of Si_3N_4 , wurtzite structured AlN, Al₂OC has become 2) Fabrication

The fabrication of SiC-AlN alloys is as follows :

- i) Carbothermal reduction of mixtures of Al_20_3 , $Si0_2$ and Carbon in a nitrogen atmosphere at 1625° C, and of montmorillonite- PAN intercalation compounds and sol-gelderived $Si0_2$ and Al_20_3 .¹⁴⁶⁾, 147)
- ii) Hot-pressing mixtures of β -SiC and AlN under vacuum at 35MPa and temperatures from 1700 to 2300 C.¹⁴⁸⁾⁻¹⁵³⁾
- iii) Sintering mixtures of Si_3N_4 and Al_4C_3 under 10MPa of argon.¹⁵⁴⁾
- iV) Preparation at temperature less than $1600^{\circ}C$ by rapid pyrolusis of mixtures of $[(Me_{3}Si)]_{0.80}(CH_{2}=CH)MeSi)_{11.0}$ $(MeHSI)_{0.35}]n(VSP)$ or $[MeHSiCH_{2}]_{n}(MPC)$ with $[R_{2}AlNH_{2}]_{3}$, where R=Et,i-Bu or simply by slow pyrolusis of the precursor mixture in the case of $[Et_{2}AlNH_{2}]_{3}^{155}$
- 3) Properties
- i) Lattice parameter

As shown in Fig.76. it is seen that parameter and unit cell volume increase gradually and the c parameter decrease gradually in going from SiC to AlN. Fig.77. gives only a slight negative deviation from Vegard's law.¹⁴⁸⁾

ii) Microhardness

Figs.78.79.80. show microhardness value vs AlN content, it is said that the existence of multiphase and porosity give the different value on microhardness.^{145),148),149)}

iii) Yound's Modulus

Fig.81 shows that the yound's elastic modulus was found to decrease approximately linear with increasing AlN content.¹⁴⁵⁾ Fig.82 shows near linear retaionship of the modulus with AlN content.¹⁴⁵⁾

iV) Thermal expansion coefficient

Fig.83, shows thermal expansion coefficient increases linearly with increasing AlN.¹⁵¹⁾

V) Fracture toughness

Fig.84 shows great scatter of fracture toughness value and the annealed specimens have a lower value than the hot-pressed specimens.¹⁴⁵⁾

Vi) Thermal conductivity

As shown in Fig.85 small additions of AlN to SiC or SiC to AlN cause a rapid decrease in thermal conductivity, and thermal conductivity value has a minimum near $50wt%AlN.^{145}$) Thermal conductivity value calculated from the results on thermal diffusivity in Fig.86 are shown in Fig.87¹⁵⁶) Good confidence with Fig.88 is found. Fig.89 shows temperature dependence of thermal diffusivity value of 50SiC-50AlN(wt%). The conclusion that the relative difference in thermal conductivity value decreases with increasing temperature., and further significant differences exist even at the higher temperature from two phases and solid solution matter.¹⁵⁶)

Vii) Creep behavior

Fig.90 shows the process of creep scems to be thermally activated, and the SiC-AlN specimens exhibit better creep resistance above about $1425^{\circ}C$.¹⁴⁵⁾ From the results of Fig.91 and 92, creep in SiC-AlN is thermally activated and the dominant mechanism is diffusional.¹⁵⁷⁾

b)AlN-Al₂O₃

1) Object

With combining superior properties of Al_2O_3 and AlN having excellent resistance to corrosion, light and tough ceramic fabric can be obtained.¹⁵⁸⁾

2) Fabrication

Vapor-phase infiltration of AlN through $AlCl_3$ -NH₃ reaction to Al_2O_3 .

3) Properties

The surface layer was AlN, so that they showed nonwettable against dental alloy melt.

$$c)Al_2O_3-Al_4C_3-AlN$$

1) Object

Compared with Al_2OC , the solid solution of Al_2OC -AlN had two major superiolities : it was easier to form by a solid state reaction, and it was easier to form by a solid state reaction, and it was more stable at high temperatures. Al_2OC -AlN ceramics seem hopeful candidate for the possible combinations of good mechanical properties(high hardness of Al_2OC with good functional properties(high thermal-low electrical conductivity of AlN.¹⁵⁹) d)AlN-BN

1) Object

The low strength, low toughness, and poor erosion resistance of BN could be improved by the incorporation of a hard phase such as AlN. Conversely, the performance of wear-resistant parts fabricated from AlN could be improved by adding BN.

2)Fabrication

From the good results that Si_3N_4 -BN particulate composites revealed a considerable improvement in thermal shock resistance and dielectric properties over monolithic Si_3N_4 and improvement of same property for SiC-BN particulate composites compared with monolithic SiC, the fabrication of AlN-BN particulate composites was tried.¹⁶¹⁾ Computerized thermodynamic analysis of the B-Al-N-Cl-H system indicated that BN-AlN composites can be prepared by codeposition using the commercially available, conventional reagents such as BCl₃ or B₂H₆, AlCl₃, and NH₃. The codeposition of AlN ranging from 0% to 100% was possible at wide temperature(1000 to 1400K) and pressures(0.1 to latm.).¹⁶⁰⁾AlN, AlN+5wt%CaH₂ and 5,10,15,20 and 30wt%BN mixed powders were inductive heated applying 11.5MPa and heating rapidly to 1700°C for 10min and then 1800° to 2000°C for 15 to 60min.¹⁶¹)

3) Properties

i) Thermal expansion coefficient

No significant differences in coefficient of thermal expansion were found for the composites compared with AlN.

ii) Room temperature flexural strength

BN additions decreased the room temperature flexural strength.

iii) High temperature strength

With increasing the BN content decreased the strength to a much larger degree than for AlN

iv) Young's modulus

Room temperature Yound's modulus revealed decreasing values with increasing amounts of BN.

e) AlN-TiB₂

1) Object

TiB₂ was widely used for aluminum electrosmelting from good high wear resistance. chemical inertness and electrical conductivity. TiB_2 , however, showed fracture in liquid Al through the penetration of Al along the grain boundaries. $^{161)}$ By making the of characteristics of AlN to increase use thermal conductivity, to decrease the interfacial energy of the system. and to induce limited micro-cracking from the magnitude of the thermoelastic mismatch between two phases, TiB₂-AlN composited was intended.^{161),162)}

2) Properties

In Table 39, phase characteristics of composite is compared with that of TiB_2 and AlN. Composite showed prominent character from inducing microcrack to have good resistance to subcritical crack growth and its strength in Al is not degrated with time.¹⁶¹⁾

f) AlN-ZrO₂

1) Object

For the development of composite ceramics exhibiting fine microstructures, superior properties(hardness, electrical and thermal conductivity, and potential applications for wearresisting objects, oxide-nitride systems are of interest.¹⁶³⁾ 2) Properties

From the sintering reaction between AlN and $2rO_2$ mixtures, the quaternary Zr-Al-O-N phase was identified.¹⁶³⁾ Further the effect of AlN addition to stabilize cubic $2rO_2$ phase was done, and it was found that the following displacement reaction above 20mol% AlN is completed at 50mol% AlN.¹⁶⁴⁾ VII-8 Use for r.f. Heating on Plasma in Fusion Reactor

Establishment of fusion reactor to produce clean energy, as reuirements for the construction, especially, materials design must be completed for long-aged operation. Some prominent review concerning materials selection have been presented.^{165),166)} Rf window acts as a vacuum boundary and separates the horn,which is open to the plasma chamber, from the waveguide, which contains a dielectric gas(SF₆). Al₂O₃ and BeO as candidate material for dielectric use has fundamentally investigated from the pointview of neutron irradiation.¹⁶⁶⁾ Necessiating subjects for rf window use has been summarized.¹⁶⁷⁾ No paper has been presented for AlN.

On the other hand, plan to stimulate transmutation gas effects in a neutron-irradiated ceramic has been designed, between Japan and Us. The author tried to manufacture $Al_{15}N$ from nitrogen isotope¹⁶⁸⁾.

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Gas pressure	1.1Pa	
Sputtering gases	Ar+N ₂ (20:80)	
Target to substrate distance	6 c m	
rf power	100-200W	
dc voltage	100V	
Substrate temperature	250°C	
Deposition rate	18Å/min	
Target	A1-99.999% pure;	8-in.diam.

Table 1 Typical deposition parameters²⁸⁾

_

Feedstock gases	Trimethylaluminum (TMAl) Ammonia (NH ₃)
Laser	Excimer laser operating at ArF [•] transition (193 nm) Avg. absorbed power in the gas is 0.5 W
Pressure	Background ~ 1. 3x10 ⁻⁴ Pa Working 400Pa
NH3/TMAI flow rate ratio	5Q/0.01
Beam-substrate distance	2 cm
Substrates	Fused quartz, Corning 7059 glass, and Si wafers
Top electrode for MIS devices	Thermally evaporated (~100-nm-thick) Al dots
Electrode area	0.002–0.2 cm ²
Substrate temperature (parameter)	~ 30–500 °C

Table 2. Typical deposition parameters for $(Al_2O_3)_{1-e}$ - $(AlN)_e$ L-CVD composite films.³³⁾

TABLE 3 Elemental analysis of synthesized AIN powder (cation content was measured by inductive coupled plasma atomic emission spectrometer) $\frac{92}{2}$

Element	Content (ppm)	tent (ppm)	
Mg	< 12		
Si	115		
Ca	25		
Ti	< 7		
Cr	10		
Mn	< 5		
Fe .	< 18		
Co	8		
Ni	25		
Cu	< 8		
Zn	7		
С	0.15 wt%		
0*	1.0 wt %		
N [†]	33.5 wt %		

*Neutron activation analysis.

[†]Chemical analysis.

Table 4 Some characteristics of the AlN powder⁴²⁾

X-ray diffraction pattern	Single phase AlN
Specific surface area	5. 0m ² g ⁻¹
Packing density (1500kgcm ⁻²)	1. 63x10 ³ kg. m ⁻³
Average particle size (agglomerated)	1. 23μm
Waximum particle size (agglomerated)	3. 8μm
Maximum particle size (agglomerated)	3.8μm
Colour	White

Activator	Major phase-type	F 1	3650A Hg Ph	253 F1	7A Hg Ph	El
Cl treated	α -Al ₂ O ₈ (phase 1)	no•	no	no•	no	blue (N ₁)
no dopant	δ-Al ₂ O ₂ (phase 2)	n0*	no	no • ···	blue	blue (N,)
	spinel (phase 3) spinel + new phase	no*	no	no*	blue	blue (N₂)
	(phase 3 and 4)	no*	no	no*	blue	blue (N,)
	AlN (phase 5)	no*	no	no*	blue	blue (N,)
Manganese	a-Al ₂ O ₂ (phase 1)	n0*	no	no*	no	blue (N _s)
-	δ-Al ₂ O ₂ (phase 2)	no*	no	pink	no	pink
	spinel (phase 3)	no*	no	yellow	green	green
	spinel + new phase			-	•	-
	(phase 4)	no•	no	red	no	pink
	AlN (Mn ²⁺) (phase 5)	no•	no	no*	blue	green
	AlN (Mn**) (phase 5)	no•	no	red	red	red
Europium	a-Al ₂ O ₂ (phase 1)	red	no	no•	no	red
	ð-Al ₂ O ₂ (phase 2)	no•	no	red	blue	red
	spinel (phase 3)	no*	no	pink	blue	red
	spinel + new phase			•		
	(phase 4)	no•	по	green	blue	red
	AlN (phase 5)	no•	no	no•	blue	red
Chromium	a-Al ₂ O ₂ (phase 1)	red	no	red	no	red
	δ-Al _s O _s (phase 2)	no•	no	pink	no	red
	spinel (phase 3)	no*	no	yellow	blue	red
	spinel + new phase					
	(phase 4)	no*	no	red	blue	red
	AlN (phase 5)	no*	no	no•	blue	blue (N ₁)

Table 5 Comparison of fluorescence, phosphorescence, and electroluminescence of phases in the Algo-AlN system *3)

* Fluorescence could not be observed because of insufficient filtering of visible light from the existing u.v. source.

Material	Growth rate (nm/s)
NH ₃ ,A1Cl ₃	1.1 - 3.3
NH3, ALCL3	0.17 - 16.7
NH3, A1Cl3	3.3 - 4.2
AlCH ₃ ·3NH ₃	0.15 - 0.27
NH3, AlBr3	- 0.56
CH ₃)Al·NH ₃	0.08 - 1.56

Table 6 Synthesis of AlN film by CVD⁴⁵⁾

	-			45}
Table	1	Experimental	conditions.	,

Gas flow Partial p	rate pressure of NH,	(m ³ /s) (Pa)	6.67×10^{-6} 2.46 × 10 ⁴	
Partial p	ressure of AlCl,	(Pa)	2.76×10^3	
run l	Gas temperature, T 1023	9 (K)	Substrate temperature, T _s 998	(K)
run 2	1073		1059	
run 3	1173		1161	
run 4	1073		1003	



Table 9 Lattice parameter of AlN⁵⁵

Lattice paran co	neter, 10^{-8} cm a_0	Author	Year	Ref.
4.991	3.119	Ott	1924	1
4.975 ± 0.008	3.110 ± 0.005	von Stakelberg and Spiess	1933	52
4.965 ± 0.01	3.10 ± 0.01	Kohn et al.	1956	9
4.978	3-111	Jeffrey et al.	1956	53
4-980	3-111	Taylor and Lenie	1960	1 1
4.982 ± 0.003	$3 \cdot 111 \pm 0 \cdot 003$	Drum	1965	5.4
4.9816 ± 0.0005	3.1127 ± 0.0003	Present work [a]	1971	55

[a]Calculated density is 3.255 g/cm³.

Table 10 Strength and elasticity properties of hot pressed aluminum nitride¹¹⁾

Temp. C	Modulus of rupture, (MPa)	Modulus of elasticity, (MPa)
25	265	3450
1000	186	3170
1400	125	2760

Table 11 Comparis values ¹¹	on of thermal	conductivity
Material	At 200°C	At 800°C
Dense SiC	100.8	42.0
Hot pressed AlN	30.2	20.2

22.7

7.14

Table 12 All samples for thermal conductivity studies⁵⁵⁾

Type [a]	Source	Color	Co[f] 1 10 ⁻⁸ cm	Fotaloxygen[g] 10 ²² atoms/cc	k at 300K ₩/m·k
SSC	Pechiney[b]	Blue-grey	4 • 9809	3±2	200
SSC	Pechiney[b]		4.9806	3±2	200
Hp	G.E.[c]	Blue-grey	4 • 9789	11 ± 2	28
Hp	G.E.[c]	Light-grey	4.9796	11 ± 2	65
CPS	NIRIM[d]	Chalk white	4.9810	≦12	14.5
HP	G.E.[c]	Steel grey	4.9788	43±2 [.]	41
HP	Cernc[e]	Grey	4 • 9780	22 ± 1	60
HP	G.E.[c]	Chalk grey	4 • 9801	47±4	44
HP	G.E.[c]	Grey	4.9793	11 ± 1	74

[a]SSC=synthetic single crystal

Dense AlpOs

HP=hot pressed polycrystalline ceramic CPS=cold pressedand sintered ceramic

[b]Grown by sublimation at about 2100°C in a commercial production furnace. Obtained from the Pechiney Compagnie de Produits Chimiques et Electromeiallurgiques. Grenoble France with thehelp of Dr. E. C. Lightowiers, University of London, see U.S. Patent 2.962.359(1960). The crysials were transparentwith a blue-grey cast and had several brown streaks running through them. For sample R162 the crystallogrnphic -axis was tilted 62 away from the axis of the rod. [c]Hot pressed in this laboratory at 19(x) C and 300 atomospheres. The density was greater than 97 percent of the theoretical density of 3.26gm/cm^2 . [d]Obtained from Dr. M. Iwata. National Institute for Researches in Inorganic Materials. Tokyo, Japan. The sample had been cold pressed and sintered, the density was 62 percent of theoretical. [c]Obtained from Cetac Hot Pressing inc., Menomonee Fulls. Wis. The density was 94 percent of theoretical. [f]Generally accurate to $\pm 5 \times 10^{-12}$ cm. [g]Measured using neutron activation techniques by Gulf Energy and Environmental Systems. San Diego, Culofornia.

	Co Latttice	Thermal	conductivity
	parameter	Oxygen	at 300K
Specimen	(A+0.0005)	(wt%)*	(w/m·k)
A-1	4.9789	6.62±0.32	28
B-2	4.9796	0.90 ± 0.16	68
Single	4.9806	$\textbf{0.25} \pm \textbf{0.16}$	200
Crystal			

Table 13 Lattice Parameter, Oxygen Analysis, and Thermal Conductivity Data for Specimens⁵⁷⁾

"Neutron activation analysis performed by Gulf Energy and Environmental Systems, San Diego, Calif.

Table 14 Thermal expansion of hot pressed aluminum nitride 11

Temperature interval, *C	Linear expansion, cm/cm/*C	
25-200	4.03 × 10-*	
25-600	4.84×10^{-6}	
25-1000	5.64×10^{-6}	
25-1350	6.09×10^{-6}	

T(K)	$(\Delta a/a_0) \times 10^3$	$(\Delta c/c_0) \times 10^3$	
77	-0.31 ± 0.03	-0.27 ± 0.02	
120	-0.28 ± 0.03	-0.24 ± 0.02	
160	-0.26 ± 0.03	-0.22 ± 0.02	
200	-0.23 ± 0.03	-0.19 ± 0.02	
240	-0.17 ± 0.03	-0.13 ± 0.02	
270	-0.10 ± 0.03	-0.07 ± 0.02	
297	0.00 ±	0.00	
503	$+0.80 \pm 0.16$	$+0.64 \pm 0.16$	
628	$+1.38 \pm 0.16$	$+1.14 \pm 0.16$	
683	$+1.70 \pm 0.16$	$+1.53 \pm 0.16$	
901	$+3.02 \pm 0.16$	$+2.69 \pm 0.16$	
1099	$+4.37 \pm 0.16$	$+3.74 \pm 0.16$	
1269	$+5.56 \pm 0.16$	$+4.64 \pm 0.16$	

.

TABLE 15 Linear thermal expansion of AlN along the a and c axes.⁴⁰

Material	T	Measu	red lattice	parameter				
	(°C)		(Å)		Calculated temperature dependence of	rms	Me	an expansion
		Hexag	onal	Cubic	lattice parameters	deviation	coeffic	cient (x10 ⁻⁶ /*C)
		a	c ^b	a ^c		(×10-4 Å)		20—800 °C
							αı	α, α
AIN	18	3.1115	4.9798		$a_T = 3.1113 + 1.3130 \times 10^{-5}T + 4.147 \times 10^{-9}T^2$	0.36		
	154	3.1134	4.9811		•		5.27	4.15
	338	3.1162	4.9855		$c_{\tau} = 4.9793 + 1.4789 \times 10^{-5}T + 7.255 \times 10^{-5}T^2$	4.5		
	494	3.1187	4.9887					
	666	3.1219	4.9917					
	800	3.1244	4.9960					
$\alpha - Al_2O_3$	25	4.7576	12.9834		$a_T = 4.7569 + 3.3726 \times 10^{-5}T + 1.037 \times 10^{-9}T^2$	1.8		
	156	4.7623	13.0000				7.28	8.11
	350	4.7689	13.0205		$c_{\tau} = 12.9815 + 11.2939 \times 10^{-5}T - 9.321 \times 10^{-5}T^2$	13		
	496	4.7739	13.0356		1		7.71ª	8.56 ^d
	650	4.7789	13.0485					
	803	4.7848	13.0675					
							8.17 •	9.06*
Si	25			5.4309	$a_T = 5.4304 + 1.8138 \times 10^{-5}T + 1.542 \times 10^{-9}T^2$	0.53		
	157			5.4332	1			3.57
	356			5.4370				
	496			5.4398				3.90 f
	651			5.4429				
	813			5,4461				
								3.594

TABLE 16 Temperature variation of lattice parameters and mean expansion coefficients of AIN, sapphire, and silicon.

*Values shown here were calculated by using (205)-(220) lines

^dCalculated from data of Ref. 9.

•For the temperature range of 28-806 °C; as reported ir

Values shown here were calculated by using (205)-(220) lines for AlN and (054)-(330) lines for α -Al₂O₃. Values shown here were calculated by using (302 -(205) lines for AlN and 1,1,15)-(4,0,10) line; for α -Al₂O₃. Calculated by using $K\alpha_1$ and $K\alpha_2$ lines of (620), (-33), and

(444).

Ref. 10,

¹Calculated from di ta of Ref. 11.

"For the temperature range 25-800°C; as reported in R f. 13.

ΔT _c (°C)						
Sample size (mm)	A1203+	Si2N20++	AlN			
Prismatic beam 4 x 4 x 25	180					
Long cylinder 6(diam) x 80	180					
Short cylinder 20(diam) x 20 or 20 (diam) x 16 ⁺⁺	+ 105	230				
Thin disc 30(diam)x2.5+,++ or 30(diam) x 3	180	380	250			
Thick disc 30 (diam) x 4.5	165					

Table 17 Critical temperature difference for water quench 62)

Table 1 8 Stability of hot pressed aluminum nitride in various
atmospheres of elevated temperatures
(Test specimens, 0.25x0.5x0.5 in.) (1)

Atmosphere	Temp, *C	Time, hr	Conversion to other com- pounds, %
Air	1000	30	0.3 Al-O.
Air	1400	30	1.3 Al.O.
Air	1700	4	10.6 Al.O.
Oxygen	1400	30	0.9 Al-O.
Dry steam	1000	30	0.3 Al ₂ O
Chlorine	500	30	< 0.1 A1CI.
Chlorine	700	30	19.2 AICL
Hydrogen	1700	4	nil

Table 19. Corrosion of hot pressed aluminum nitride in wate	r
and mineral acids (0.25x0.5x0.5 in. specimens in 600 ml liquid, 72 hr) ⁽¹⁾	

Corrosive liquid	Témp, °C	Corrosion rate, mils/year
Water	100	14
Conc. HCl acid	72	320
1 Conc. HCl acid: 1 H ₂ O	110	570
Conc. H ₂ SO, acid	305	180
1 Conc. H ₂ SO, acid: 1 H ₂ O	145	550
Conc. HNO, acid	120	150
1 Conc. HNO, acid: 1 water	111	200
1 HF: 1 HNO, conc. acids	57	160
1 Conc. HF acid: 1 water	57	215

TABLE20Effect of heating AIN powder in air \bullet – bulk and surface \P

Temp	Phases present after heating for 3 h					
(°C)	XRD analysis (bulk)	RHEED analysis (surfaœ)				
600	AIN	AIN				
800	AIN	AIN				
1000	AIN	phase X				
1200	α-Al, O,	phase X + α -Al,O,				
1400	a-Al ₂ O ₃	α-Al ₂ O ₃				

*Annealing in vacuo showed no sign of oxidation even for samples heated to 1400°C for more than 24 h.

TABLE 21 Lattice &spacings (nm) from RHEED patterns from surface of oxidized AIN 77)

Standards			Results									
Standard RHEED Stan pattern of AIN, patter		Standard RH pattern α-Al ₂ (Standard RHEED pattern α -Al ₂ O ₃ ,		AlN heated to 1400° C in vacuo		AIN heated in air at 1000°C		AlN heated at 1200° C in air		AIN reacted with H ₂ O at 100° C	
room temp.		room temp.		d (nm)	I	d (nm)	1	d (nm)	1	d (nm)	1	
d (nm)	I•	<i>d</i> (nm)	Ι									
		0.346	s					0.346	s			
						0.290	s	0.288	s	0.317	\$	
0.272	vs			0.272	vs							
0.250	m	0.252	5	0.250	m	0.250	vs	0.250	s			
0.238	vs			0.238	vs					0.235	s	
		0.207	s			0.205	s	0.208	s			
0.183	s			0.184	s					0.188	vs	
		0.175	m					0.176	m			
		0.159	m					0.159	m	0.165	m	
0.155	s			0.155	s	0.155	w					
0.144	s	0.141	vs	0.141	Ş .	0.144	vs	0.140	5	0.144	vs	
0.131	s			0.131	s					0.132	vs	
						0.122	w	0.122	w			
811.0	m			811.0	m							
0.115	m			0.115	m							
										0.113	'n	
Comments												
In good		In good		Good		Unknown		Mainly		y-AlOOH		
agreement		agreement		agreement		phase X		α -Al ₂ O ₃ ,		bochmite		
with ASTM		with ASTM		with AlN		formed		some		formed		
data card		data card		at room				unknown				
no. 25-1133		no. 10-173		temperature								

*vs = very strong; s = strong; m = medium; w = weak.

Reactants	Products	Lattice parameter, a (nm)
AlN+Fe (25 at.%)* AlN+Co (25 at.%)* AlN+Ni (25 at.%)*	AlN+ α -Fe AlN+ β -Co AlN+ γ '-Ni ₃ Al	0.2867 0.3540 0.3556
AlN+Ru (30 at.%) [†] AlN+Rh (30 at.%) [†] AlN+Pd (30 at.%) [†]	AlN+RuAl AlN+RhAl AlN+Pd₂Al	

Table 22 Results of X-ray Analysis of Systems Group VIII Metal-Al-N ⁷⁹⁾

*Annealed at 1373 K for 150 h in evacuated quartz tubes. *Annealed at 1473 K for 140 h under Ar.

TABLE 2.3 Comparison of observed and assigned summation band energies using LO=91.4, $TO_1=82.5$, $TO_2=78.1$, LA=62.9, $TA_1=55.3$, and $TA_2=50.9$ meV.⁸⁶

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=

Ubserv	ed peak energy (meV)	Assignment	Assigned value (meV)
A	118.2±0.3	$LA+TA_1$	118.2
в	125.8±1.0	2LA	125.8
С	130.0±0.5	$TO_2 + TA_2$	129.0
D	133.3 ± 0.2	$TO_1 + TA_2$	133.4
		$TO_1 + TA_1$	133.4
E	137.9±0.3	$TO_1 + TA_1$	137.8
F	140.6±0.5	$TO_2 + LA$	141.0
G	145.5±0.2	$TO_1 + LA$	145.4
H	152.7 ± 0.3	3TA:	152.7
T	155.7 ± 0.2	LO+LA	154.4
-	-	2TO ₂	156.2
ĸ	160.6±0.5	$TO_1 + TO_2$	160.6
L	165.0±0.3	270	165.0
М	173.9 ± 0.2	$LO+TO_1$	173.9
N	245.0±0.5	3TO,	247.5

TABLE 24 Parameters used for sputter deposition of aluminum nitride on silicon.

	Base	Ar	
Sample	pressure (Pa)	presputter (min)	Sputtering gas
1	7x10 ⁻⁵	120	70%Ar/30%N ₂ *
2	7x10 ⁻⁵	120	50%Ar/50%N ₂
3	3x10 ⁻⁴	30	100%2

-

*All gases are nominally 99.999% pure.

No.	Mean particle diameter (µm)	Ca	Mg	Cr	Mn	Cu	Fe	Si	Oxygen content (wt%)
R-16	0.2	++	+	tr	tr	tr	++	++	4.4
R-17	0.4	+	+	tr	tr	tr	÷÷	++	7.2
R-18	0.7	tr	tr	tr	-	tr	tr	++	6.7
R-20	2.5	tr	tr		_	tr	tr	+	1.6

Table 25Particle size, emission spectrographic analysisand oxygen contents of AlN powders. 1010

++: weak, +: very weak, tr: faint trace, -: not detected.

Fe and Si in R-16 are both 100~200 ppm.

1 Conditio	ons of l	hot-pressi	ng Density O	xygen Content after
er (MPa)	(°C)	(min)	(10 ³ kg/m ³)	hot-pressing (wt%)
5 15	1900	60	3.23	3.9
3 20	1800	120	3.25	4.5
) 35	2000	120	2.54	0.8
20	1800	120	3.19	2.9
45	1900	120	3.24	2.6
	1 Conditio er (MPa) 5 15 3 20 3 35 7 20 7 45	d Conditions of l er (MPa) (*C) 5 15 1900 8 20 1800 0 35 2000 7 20 1800 7 45 1900	d Conditions of hot-pressi er (MPa) (°C) (min) 5 15 1900 60 8 20 1800 120 0 35 2000 120 7 20 1800 120 7 45 1900 120	1 Conditions of hot-pressing Density Officer Par (MPa) (°C) (min) (10 ³ kg/m ³) 5 15 1900 60 3.23 6 15 1900 120 3.25 7 35 2000 120 2.54 7 20 1800 120 3.19 7 45 1900 120 3.24

Table 26 Characteristics of hot-pressed AlN.¹⁰¹⁾

Table 27 Specific heat, thermal diffusivity and calculated thermal conductivity of hot-pressed AlN, 27R and 21R-pseudo-polytypes of AlN, oxynitride in spinel structure and $\alpha - Al_2O_3$.¹⁰¹¹

	Oxygen		T.	hermal	Thermal		
Crystal.	content	Specif	ic heat	diffusi	vity	conduct	ivity
phase	in powder	at 300	K at 450K	at 300K	at 450K	at 300K	at 450K
of sample	(wt%)	(J/(Ky.K))	(cm	² /s)	(\\/1	n•K)
AIN	1.76			0.234	0.148	53.76	45.78
AlN	2.59			0.198	0.130	47.46	41.58
27R	12.3	774	854	0.024	0.020	6.30	5.46
21 R	15.6	728	883	0.022	0.018	5.46	5.46
oxynitrid	e 39.1	707	1055	0.043	0.027	10.92	10.50
α -Al ₂ 0 ₃	47.1			0.118	0.056	36.12	22.68

milling liquids	AIN	AIN + I w/o Mg	ý ,
	1.6	1.8	as received
lso-propanol	 3.1	5.1	after 5h milling
	3.6	4.8	after sintering
Ethanol	5.2	*	after 5h milling
	5.4	*	after sintering
n-hexane	43	*	after 5h milling
	41	*	after sintering

Table 28 Increase of oxygen content during powder processing. Data given in weight percent $(\pm 5\%)$.⁽⁰³⁾

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★ not : ivestigat∈d

AlN powder	Oxide added	Sintering ^u temp.(°C)	Density (g/cm)	Linear shrinkage	3-pt. bend strength(MPa)
	••			Δ L/L	
FST	-	1800	3.00	0.155	293
		1700	2.59	0.104	163
		1600	2.28	0,091	129
RWK	-	1800	3.34	0.179	291
		1700	3.39	0.176	298
		1600	3.00	0.123	180
FSt	1% Ca0	1800	3.28	0.164	285
	•	1700	3.32	0.190	485
		1600	2.85	0.155	185
FSt	1% Y203	1800	3.30	0.192	310
		1700	3.30	0.200	300
		1600	3.20	0.176	190
FSt	1% NiO	1800	3. 21	0.164	320
		1700	3.15	0.150	310
		1600	2.56	0.114	160
FSt	1% B ₂ O ₃	1800	3.14	0.172	321
		1700	3.09	0.178	228
		1600	2. 47	0.134	152
FSt	1% Li20	1800	3. 24	0.152	272
		1700	3.05	0.129	160
FSt	1% talc	1800	3.11	0.175	355
		1700	3.07	0.153	239
FSt	1% MgO	1800	3.07	0.168	303
		1700	2.99	0.151	196
FSt	1% SiO2	1800	3.16	0.164	351
		1700	3.06	0.144	287
FSt	1% Y203+	+ 1800	3.37	0.187	287
	5% SiO ₂	1700	3.38	0.196	461
FSt	1% Cr ₂ 03	1800	3. 37	0.168	369
		1700	3.21	0.158	341

Table 29 Summary of sintering experiments and results on the AlN(0) compounds.⁹³⁾

ⁿ60 mins hold, nitrogen atmosphere.

	Additive	Density (10 ³ kg/m ³)	Thermal conductivity (W/mK)	
	CaCO3	3. 21	75	
	SrC03	3.26	55	
	BaCO3	3.10	60	
	$CaC_3O_4 \cdot H_2O$	3.12	63	
	SrC ₂ O ₄ • H ₂ O	3.19	41	
	$BaC_2O_4 \cdot H_2O$	3.26	58	
	Y203	3.29	72	
I	La203	3.33	62	
	CeO ₂	3.29	53	
	PreOil	3.29	56	
	Nd203	3.29	53	
	Sm203	3.29	51	
	Gd203	3.28	50	
	Dy203	3.28	50	
	NiO	3.07	42	
	$Ce_2(C_2O_4)_3 \cdot 9H_2$	0 3.30	59	
	Ti02	2.64	18	
I	Zr0 ₂	2.84	23	
	Hf02	2.80	22	
	MnCO3	2.77	21	
	Li ₂ CO ₃	2.18	5.9	
П	MgCO ₃	2.31	6.0	
	MgC204 • 2H20	2.13	5.1	

Table 30 The effect fo additive on the densification and thermal conductivity of AlN.¹⁰⁶⁾

I Effective froup for densifying and increase of thermal conductivity

II Non effective group

III Group to hinder sintering and to decrease thermal conductivity

Table 31 Thermal/Mechanical Properties of ALON 114)

	ALON	ALON	AD-99
Composition	Al, 0, N,	Al, 0, N,	Al ₂ O ₃
Grain size	25 µm	100 µm	25 µm
Density (g/cc)	3.639	3.648	3.798
MOR (σ_i)			
RT, MPa (psi)	306 (44.4×10 ³)	256 (37.1×10 ³)	262 (38.0×10 ³)
1000°C, MPa (psi)	267 (38.73×10 ³)		
1200°C, MPa (psi)	$190(27.57 \times 10^{3})$		
Elastic modulus (E)			
MPa (psi)	3.3×10 ^s (47.29×10 ^s)	3.2×10 ^s (46.68×10 ⁶)	3.5×10 ⁵ (51.1×10 ⁶)
Poisson's ratio (γ)	0.249	0.263	0.238
Thermal expansion	5.23×10 ⁻⁶ /°C	5.23×10-°/°C	7.1×10⁻⁰/°C
Ccefficient (a)	(25°C→200°C)	(25°C→200°C)	(25°C→200°C)

	ALON R-35.7	ALON R-30.0	A1.0, AD-99	MgAl-O.*
Strength, σ (MPa)	307	305	262	172
Poisson's ratio, ν	0.25	0.25	0.24	0.26
Elastic modulus, E (MPa)	3.3×10 ⁵	3.2×10 ⁵	3.5×10 st	2.7×10 ⁵
Density, $\rho (g/cm^3)$	3.65*	3.61*	3.83	3.58
Coeff. of expansion, α (/°C), 0°-200°C	5.6×10 ⁻⁶	5.6×10 ⁻⁶	6.3×10 ^{-6†}	5.6×10-
Thermal diffusivity, a		210 10		
$(cm^2/s)^{5}$	0.040	0.037	0.087*	0.050
Specific heat, c (J/kg.°C)	707*	707	880*.**	837
Thermal conductivity, k				
(W/m.°C)	10.3	9.4 ^t	29.4*	14.9
Experimental ΔT_{-} (°C)	175	180	225	
Calculated R (°C) ^{††}	- 124	128	-90	84
Calculated $R' (W/m)^{**}$	1280	1200	2650	1250
	br 1000 10	· · · · · · · · · · · · · · · · · · ·		

Table 32 Room-Temperature Thermomechanical Properties of Aluminum Oxynitride Spinel, Alumina, and Magnesium Aluminate $^{\rm (15)}$

*Hot-pressed, all data from Coors product literature, May 1982. 'Coors product literature. 'Theoretical density 3.71 g/cm³. 'Ref. 15. 'For AMMRC 25- μ m material, a=0.035 cm²/s. 'Calculated from thermal diffusivity, a. **Value determined at 100°C. " $R = [\sigma(1-\nu)]/Ea$. ' $R' = [k\sigma(1-\nu)]/Ea$.

Table 33 X-Ray Diffraction Results 116)

<i>d</i> (nm)	θ	hk!	a (nm)
	Sample No. 1 (2	30 mol & AIN)	
0.2809	7.27	220	0.7946
0.2397	8.53	311	0.7949
0.1986	10.31	400	0.7945
0.15295	13.44	511	0.79475
0.1405	14.66	440	0.7946
Average lattice p	arameter		0.7947
	Sample No. 2 (2)	8.7 mol% AIN)	
0.2805	7.28	220	0.7935
0.2394	8.56	311	0.7939
0.1984	10.32	400	0.7938
0.1527	13.46	511	0.7934
0.1404	14.67	440	0.7941
Average lattice p	arameter		0.7937

Table 34 Elastic Properties of Pore-Free ALON Relative to Corundum and Spinel 117)

	Spinel (MgAl ₂ O4)		AL	.ON	Corundum (Al ₂ O ₃)	
Property	Ref. 12	Ref. 17	30 0% AIN	35.7% AIN	Ref 18	Ref. 19
ĸ	197.3	198.0	226.3	229.8	251.2	254.4
G (GPa)	108.4	108.1	132.0	135.5	163.4	163.2
$(\partial K/\partial P)_T$ (unitless)	4.9	4.3	4.5'	4.2 ¹	4.3	4.3
$(\partial G/\partial P)_T$ (unitless)	0.5	•	0.85	0.95	1.7	1.8
$(\partial K/\partial T)_{p}$ (GPa/°C)	-0.015	-0.015	-0.017	-0.017	-0.017	•
$(\partial G/\partial T)_{p}$ (GPa/°C)	-0.009	•	-0.012	-0.012	-0.020	*

*Not evaluated by the indicated reference. 'Derivative values from specimen ON-130; not corrected for porosity. 'Derivative values from specimen 29821-13; not corrected for porosity.

Chemicals	Concentration/mol dm 3		
NaH ₂ PO ₂ · H ₂ O	0.15		
(NH ₄) ₂ SO ₄	0.50		
C ₁ H ₄ (OH)(COONa) ₃ · 2H ₂ O	0.20		
NiSO ₄ 6H ₂ O	0.10		

 Table 35. Basic bath composition and operating conditions for electroless Ni-P plating 119)

Bath temperature is 90℃. pH adjusted with H₂SO4 is 6.0.

Table.36 Gibbs Free Energies of Formation at 1551℃ of Compound in the Systems AlN-M¹²¹

∆ G (kJ/mol)
- 2 3 0
- 2 1 8
- 1 9 3
- 1 3 0
- 1 1 3
- 1 0 5
- 13
+ 42
- 1 1 3
- 1 4 2

fable.37 Relative Stability of MN and Phases¹³⁷,

Metals		∆ G _{nn} -∆ G _{elm} (KJ/mol)	
	Nitride Stable		
Ηf		- 88	
Zr		- 75	
Тi		- 50	
	AlM Stable		
Та		+ 13	
NЪ		+ 29	
v		+ 38	
Cr		+ 1 3 4	
Мо		+176	

11, Cr, HI, ND, Y, Ia, Cr, MO, W)					
Mixture	Phases detected*				
AlN, Ni, Zr	AlN, ZrN, AlNi, Ni				
AlN, Ni, Ti	AIN, TIN, AINI, NI				
AlN, Ni, Hf	AIN, HfN, Ni				
AlN, Ni, Nb	AIN, NDN, AINI, NI				
AlN, Ni, V	AlN, AlNi, Ni, AleV				
AlN, Ni, Ta	AIN, Ta, AINi, Ta ₂ AI, Ta ₃ AI,				
AlN, Ni, Cr	AlN, Cr, AlNi, Ni				
AlN, Ni, Mo	AlN, Mo, AlNi				
AIN; Ni, W	AIN, W, AINi				

Table 38 X-Ray Analysis of Reacted Systems AlN-Ni-M (M = Ti Cr. Hf Nb. V. To. Cr. Mo. W) 1617

*After firing at 1500°C for 4 h in Ar.

Table 3.9 Phase characteristics in composite 161)

Phase	Young's modulus 298 K (GPa)	Critical stress intensity 298, 1071 K (MPa m ^{1/2})	Coefficient thermal expansion 298–1273 K (10 ⁻⁶ K ⁻¹)	Hardness 298 K (GPa)	<i>K</i> 1098 K (MPa m ^{1/2})
Composite	405	5.07, 3.49	5.64	17	10.9
TiB,	450-550	\$ 6	7.65	20	_
AIN	280-320	2.7 ^d	2.7*-6.2*	12*	—

⁴Keihn and Keplin, Ref. [13]. ^bDavies and Evans, Ref. [14].

'Gerlich, Dole and Slack, Ref. [15].

^dDe Witt and Hattu, Ref. [16].



Fig. 1 Apparatus for preparation of AlN 6)

A: Aluminum electrode, B: Cooling pipe, C: Holder, D: "O" ring, E: Plastics board, F: Vessel, G: Quartz window, H: Tray, P: Nitrogen purifier, Q: Rectifier, R: Resistor, S: Alarm, T: Recorder, W: Water, N: Nitrogen











Fig. 4. Diagram of dual ion beam deposition system. 30)



Fig. 5. Schematic diagram of the L-CVD apparatus. 33)



Fig. 6. T_s vs c plot of L-CVD (Al₂O₃)_{1-c}-(AlN)_c samples.³³⁾

Fig. 7. Autoclave pressure reactor 43)



Fig. 8. Schematic illustration of the reactor assembly. (a) glass vessel, (b) mantle heater, (c) ribbon heater, (d) reactor, (e) electric furnace, (f) chromel-alumel thermocouple. 44



Fig. 9. Change of mean diameter with reaction temperature. NH_3 flow rate $180 \text{ cm}^3 \text{ min}^{-1}$, N_2 flow rate $150 \text{ cm}^3 \text{ min}^{-1}$. *44*)



Fig. 10. Experimental apparatus for PPCVD "5)



Fig. 11. X-ray diffraction spectra of the AlN films a) powder b) Fig. 5. c) Fig. 6. d) Fig. 7.45)



Fig. 12. The thermal conductivity at 300K of AIN samples as a function of the oxygen concentration. The heavy, sol d line extrapolates to $\kappa = 3.2$ W/cmK for pure AIN. 35)









Fig. 16. Effect of sintering temperature on thermal d ffusivity and density of AIN ceramics at room temperature. Disted line indicates the theoretical density of AIN (3.26 g/cm³). ⁵⁰



Fig. 17. Effect of SiO₂ content on thermal diffusivity and density of HP-AIN ceramics at room temperature. Dotted line indicates the theoretical density of AIN (3.26 g/cm^3) .⁵⁸⁾



Fig. 18. Optical absorbance vs. wavelength for an AlN single crystal at 20°. Curve 1: as grown crystal. Curve 2: crystal heated at 1100° for 2 hr in argon. Curve 3: crystal plated with aluminium and heated at 1100° for 2 hr in argon. Aluminium then removed. ⁶⁴



Fig. 19. IR-transmittance of AlN on Si. $d_{AlN} = 270 nm^{65}$



Fig. 20. Infrared reflection spectra at room temperature of (0001) AlN-(0001) sapphire and (0001) sapphire. 66)



F i g. 21. Schematic diagram showing the change of electroluminescence intensity and current with time as a function of the electric field applied to AIN crystals. These crystals are placed between conducting glass (electrode 1) and a metal plate (electrode 2). Electrode 1 is placed next to the photomultipler. During the "forward period" electrode 1 and 2 are anode and cathode, respectively; they change accordingly in the next—"reverse"—period to cathode and anode, respectively. Note that the light flash immedit tely following the first application of a ield is not observed. The flash appears only up n field reversal. The scale for the light intensity values (given in photomultiplir current) is broken. A schematic view of the experimental arraigement is shown at the top. 67)



Fig.22 Electromechanical coupling coefficient K^2 vs AlNthickness-to-iDT-wavelength ratio t/λ . Propagation along AlN [0001] axis, lowest-order mode. Samples A. B. and C using 10- μ -wavelength iDT, sample D using 15- μ -wavelength iDT, 7/)



Fig. 23 Propagation velocity V_0 vs AlN-thickness-to-IDTwavelength ratio t/λ . Propagation along AlN [0001] axis, lowest-order mode. Samples A, B, and C using 10- μ -wavelength IDT, sample D using 15- μ -wavelength IDT. ?/)







Fig. 25. Chemical free energy changes of possible oxidation reaction for A N b ℓ oxygen and water vapour. 72)



Fig. 26. Equilibrium nitrogen partial pressure vs temperature for reactions of AlN with Fe, Co, and Ni.79)



Fig. 27. Absorption bands in the two-phonon combination region. The assignment of the peaks is discussed in Sec. IV. P6)











Fig. 34. Spectral dependence of the refraction index 27)

Fig. 35. Optical absorption vs. photon energy. (a) without consideration of surface roughness, (b) with consideration of surface roughness²⁷⁾



Fig. 36. Comparison of the reflection spectrum of AIN epitaxial thin film $(d + 3\mu)$ with those of sintered powder and single-crystal assembly. The ordinate is scaled in an arbitrary unit. 2)



Fig. 37. The transmittance against wavelength curve for specimen (b) (0.50 mm thickness). 42)



Fig. 38.Auger spectra for pure aluminum, aluminum oxide (native oxide on Al surface), and aluminum nitride produced by low energy nitrogen implantation at $E_{ye}^{low} = 1$ keV up to the nitrogen saturation concentration. AES parameters: E_{ye}^{o} = 2 keV/3 keV for Auger energies <1000 eV/>1000 eV, f_{ye}^{o} = 5 μ A, modulation frequency 17 kHz, modulation amplitude 2 V/5 V pp for Auger energies <1000 eV/>1000 eV, and scan rate 100 eV/min. ³⁵⁾



Fig. 39. Valence electron excitation spectra for pure aluminum, aluminum oxide, and aluminum nitride (sampled surfaces as in Fig. 1) measured by ELS. ELS parameters: $E_{\rm her}^{*}$ = 100 eV, $t_{\rm her}^{*}$ = 1 μ A, modulation f equency 17 kHz, modulation amplitude 1 V pp, and scan rate 10 eV/min. ³⁵)



Fig. 40. AES spectra obtained from sputter deposited aluminum nitride showing the Al_{LVV} and Al_{KLL} transitions. 2%)

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Fig. 41. Densities of AIN with Ni additions sintered 2000°C for h. Ni was added as Ni(NO₃)₂ solution





Fig. 42. Fourier transform ir spectra of oxynitride glasses and powders used to make them. 192)


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Fig. 45. Effect of Y_8O_9 content on the density and thermal conductivity of AIN ¹⁰⁶



Fig. 46. Relationship between impure oxygen content and thermal conductivity of AIN ¹⁰⁶)



Fig. 47. Effect of lapure metal content on therma conductivity of AIN 107)







Fig. 49. Effect of additive on thermal conductivity for HP-AIN. 108)



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Fig. 52. Phase diagram for the Al_2O_3-AlN composition join in one atmosphere of flowing nitrogen (ref. 7). $^{\prime\prime2}$)



Fig. 53. Relative intensities of the most important peaks of the different phases after hot-pressing (1850°C, 30 mn). //2)



Fig. 54. Densities of mixtures $AlN-\alpha Al_{203}$ Fig. 55. Vickers microhardness of mixtures $AlN-\alpha Al_{203}$ after hot-pressing II_{203} after hot-pressing II_{203}



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