Properties of Aluminum Nitride Powders by Direct Nitridation

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ABSTRACT

AlN powder by direct nitridation is drawing more attention because of its lower production cost compared with that of carbothermal method AlN powder.

In this report, direct nitrided AlN powders produced by TOYO ALUMINIUM K.K. are compared with AlN powders produced by other companies.

The oxygen content and the specific surface area of these powders are equivalent to those of the powder by carbothermal reduction method.

AlN powders by direct nitridation were characterized by their high tapping density, and as a result, high green density or low shrinkage after sintering which is essential for accurate dimension control of I.C. packages and substrates.

The sinterability and chemical stability of AlN powders depend on their particle size distribution and specific surface area.

Furthermore, newly developed water resistant AlN powder, TOYALNITE WF grade, is introduced. This powder shows no reaction with water for 150 hours at 40 ℃ and for 480 hours at 20 ℃. The sintered bodies processed by aqueous slip casting from WF grade had thermal conductivities of 100-150W/mK.

Introduction

Aluminum nitride (AlN) ceramics are expected to become key materials of next generation in the microelectronics fields [1]. Their excellent thermal conductivity, electrical resistivity and suitable thermal expansion coefficient (similar to Si) make them ideal material for I.C. substrates and packages.

AlN powders synthesized from alumina by carbothermal reduction method [2] have been precedingly commercialized for electronic applications, however, this method needs high temperature, long reaction time and large amount of nitrogen to produce AlN. On the other hand, the direct nitridation method[3][4][5] has more advantages in terms of production cost because the energy of exothermic reaction between Al and N_2 can be effectively utilized in this method by controlling the reaction conditions precisely.

The qualities of powders by direct nitridation were proved to be comparable with those by carbothermal reduction method.

The aim of this report is to introduce the characteristics of these powders by direct nitridation.

Experimental

1. AlN powders

Four samples by direct nitridation and one sample by carbothermal reduction method were evaluated. The chemical composition and the caracteristics of these samples are shown in Table 1.

AlN powders by direct nitridation include UM, UF, R008 and AlN powder B. AlN powder B is a conventional direct nitrided powder produced by one of other manufacturers. AlN powder A is a typical AlN powder produced by carbothermal reduction method.

The analysis methods are as follows;

a. Oxygen and carbon contents: Measured by Horiba EMGA 2800 and EMIA 511

b. Metallic Al contents : Estimated from the amount of hydrogen gas evolved by reaction between Al in AlN and NaOH solution.

c. Cationic impurities :Measured by ICP(induced coupled plasma) analysis

The particle size distribution and specific surface area of the powders were measured by centrifugal method (Horiba CAPA700) and BET analysis, respectively.

The contents of large particles over 10 μm were determined by sieve analysis.

The stability against moisture of these powders were examined by measuring oxygen contents of the powders exposed in the humid atmosphere at 35℃(308K) in 70% relative humidity for certain periods.

2. Press forming and sintering

AlN powders listed above were blended with 10wt% of stearic acid in mixture of solvents consisting of toluene, MEK(methyl ethyl ketone) and ethanol. The mixtures were dried at 80℃ for 3 hours and granulated for press forming. The granulated specimen were press formed in 11mmϕ die, bisqued at 450 ℃(723K) for 1 hour in air and sintered at 1700-1900 ℃ (1973-2173K) for 3 hours in N_2.

The following parameters were measured to evaluate forming and sintering properties of the AlN powders.

a. Green density b. Shrinkage c. Oxygen contents in dewaxed bodies
c. Density of sintered bodies d. Thermal conductivity by laser flash method

3. Tape casting

Two different formulations, poly-vinyl butyral (PVB) resin system and acrylic resin system, were processed by the procedure shown in Fig. 1. Formed sheets were dried at room temperature for 1 day. Bisquing conditions of the green sheets were at 450 ℃ for 30 minutes for PVB system and at 400 ℃ for 30 min for acrylic resin system, respectively. Sintering tests were done at 1850℃ for 3 hours.

Properties of sintered substrates were evaluated.

4. Slip casting of AlN powder by aqueous binder system

AlN powders have not applied to the aqueous process such as slip casting, which is popular in the ceramics industry, because of their poor stability in water.

Water resistance of the powders were determined by dispersing them into water at 40 ℃ and estimating the duration time in which no pH value change of the dispersion due to the following reaction are observed.

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

Newly developed water resistant AlN powder [6)7)], TOYALNITE WF grade, showed excellent stability over 50 hours in water at 40℃ (in fact, this powder showed no change for 150hours), whereas conventional AlN powder reacts with water within 3 hours. At room temperature (20℃), WF grade never reacts with water for 480 hours.

The water resistant powder was applied to aqueous slip casting process. The procedure of slip casting is shown in Fig 2. The properties of sintered bodies by this process were investigated.

Results and Discussion

1. Chracteristics of AlN powders

Chemical composition of AlN powders by direct nitridation are almost the same as that of AlN powder by carbothermal method. Since the oxygen contents of powders are closely related to their specific area, the oxygen content of AlN powder B is to be estimated high in spite of its low specific surface area. The powder B also contains a little amount of metallic free aluminum.

Fig. 4 shows particle size distribution of UF, R008 and powders A and B.

Powders by direct nitridation have wider particle size distribution than powder A, which results in their high apparent and tapping densities. The sieve analysis shown in table 1 indicates that R008 contains lower amount of large particles over 10 μm than UF.

The comparison of the stability of AlN powders against moisture shown in Fig. 5 indicates that AlN powder by carbothermal method is a little more stable than those by direct nitridation.

Fig. 6 shows the change of the ratio of O/BET. The amounts of oxygen per unit surface area of UF, R008 and powder A are in the same level. The result suggests that the thickness of oxide layer on UF and R008 is similar to that of powder A which is produced by carbothermal method. On the other hand, powder B had 1.5 times higher (O/BET) value at the end of the test.

2. Forming and sintering properties

Green densities of UF and powder A are shown in Fig 7.

AlN powders by direct nitridation have significantly higher green density than that by carbothermal method, and as a result, they are suitable for IC packages in which it is essensial to have low shrinkage after sintering in order to obtain

precisely controled dimensions.

The oxygen content data of bisqued bodies shown in Fig. 8, indicate that there is no difference among the AlN powders regardless of their production method.

These results seem to be contradictory to the results obtained by humidity test in which AlN powder A had better stability than other powders. As the increase of oxygen is mainly due to the blending process before bisquing, AlN powder A is supposed to be oxidized in this step.

The oxygen data in bisqued bodies were reflected to thermal conductivity data shown in Fig. 9 in which only small difference among the AlN powders was noticed. These data show that the thermal conductivity of sintered bodies from AlN powder by direct nitridation is now in the same level as that from carbothermal method AlN powders.

According to Fig. 10 and 11, AlN powder A was densified at lower temperature than AlN powders by direct nitridation. R008 showed the best sinterability among the powders by direct nitridation. This result suggests that sinterablity of AlN powder can be improved by removing large particles.

The 1 wt% Y_2O_3 system densified at lower temperature than 5 wt% Y_2O_3 system. On the other hand, thermal conductivities for 1 wt% Y_2O_3 system shown in Fig. 9 are only about 100W/mK while those for 5 wt% Y_2O_3 system are 150-170W/mK.

The sinterability and thermal conductivity seem to depend on the composition of second phase. In case of the 1 wt% Y_2O_3 system, the composition of second phase seems to correspond to the region near eutectic point of Al_2O_3 and YAG($Al_5Y_3O_{12}$) where the melting point of Al_2O_3-Y_2O_3 system is lowest. As the liquid phase is produced at low temperature, 1wt% Y_2O_3 system is densified at low temperature, but 1wt% Y_2O_3 is insufficient to trap oxygen which dissolves into lattice of AlN crystal and lower the thermal conductivity.

3. Properties of green sheets and substrates

The properties of green sheets from UF and powder A formed by PVB system are shown in Table 2.

Green sheet from UF showed much higher density and lower shrinkage than that from AlN powder A. Mechanical strength of the sheet from UF is also superior to that from AlN powder A, though the binder content for AlN powder A is higher than that for UF.

The properties of substrates from UF by PVB system are shown in Table 3. The green sheet was densified at 1800 ℃. The substrate fired at 1850 ℃ had thermal conductivity of 183W/mK.

The properties of green sheets and substrates from UF and R008 processed by acrylic resin system are shown in Tables 4 and 5.

R008 showed a little lower green density and higher shrinkage than UF.

The thermal conductivities of the substrates from UF and R008 were 200W/mK and 190W/mk, respectively.

Fig.12 shows the apparent densities of the substrates from UF and R008 as a function of sintering temperature. The green sheet from R008 was fully densed at 1790℃, while the green sheet from UF densified at 1815 ℃.

This result suggests that AlN powder with narrower particle size distribution will be densified at lower temperature.

4. Application of water resistant powder by aqueous process

The TOYALNITE WF powder examined here had the properties as follows;

Oxygen content : 1.5 wt%,
Specific surface area: 4.0 m^2/g
Mean particle size : 1.4 μm

Table 6 shows the results of aqueous slip casting test.

The thermal conductivity data in Table 6 seemed to be comparable with those shown in Fig.9 which were obtained by nonaqueous binder system.

These results show the water resistant powder works in aqueous binder systems, for instance, slip casting, aqueous spray drying, extrusion and so on.

Conclusions

1. AlN powders by direct nitridation are being improved to become comparable with those procuced of carbothermal reduction method in terms of their purity and thermal conductivity of sintered body.
2. High green density and low shrinkage are features of AlN powders by direct nitridation which is essential for precision of I.C. packages.
3. The sinterability of AlN powders by direct nitridation is improved by removing the large particles over 10 μm.
4. The substrates from AlN powders by direct nitridation were proved to have thermal conductivities of 180-200W/mK.
5. Our water resistant AlN powder, WF grade, withstood over 50 hours in 40℃ water. This powder is applicable to aqueous slip casting process.

References

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Table 1 Properties of Various Aluminum Nitride Powders

Manufacturers	TOYO ALUMINIUM K.K.			MANUFACTURER A	MANUFACTURER B
Grade	UM	UF	R008	A	B
Production Method	Direct Nitridation	Direct Nitridation	Direct Nitridation	Carbothermic Method	Direct Nitridation
Applications	Filler Structural Use	Bare Substrates IC Packages	Bare Substrates IC Packages	Bare Substrates IC Packages	Bare Substrates IC Packages
Mean Particle Size (μm) Specific Surface Area(m²/g) Contents of +10μm (wt%)	4.5 1.2 35	1.4 4.3 4.5	1.1 3.5 0.0	1.3 3.5 0.0	1.9 2.5 4.5
Apparent Density (g/cm³) Tapping Density (g/cm³)	0.90 1.48	0.85 1.45	0.75 1.37	0.26 0.51	– –
O (wt%) C (wt%) Metallic Al (wt%)	0.6 0.02 0.03	1.0 0.03 0.03	1.1 0.03 0.03	1.0 0.06 0.00	1.0 0.07 0.36
Fe (ppm) Si (ppm) Cu (ppm) Mg (ppm) Mn (ppm) Ti (ppm) Ca (ppm)	45 40 5 5 2 3 <5	50 60 10 5 5 3 <5	50 60 10 10 5 3 <5	15 36 tr 2 tr tr 75	52 62 6 8 6 4 –

Table 2 Properties of AlN Green Sheets

Binder System		PVB	
AlN Grade		UF	A
Production Method		(Direct Nitriding)	(Carbo-thermic Method)
Binder Content (per 100 parts of powder)	Resin	8	10
	Plasticizer	4	5
Green Density (g/cm³)		2.33	1.57
Tensile Strength (kg/cm²)		10	3
Elongation (%)		10	10
Shrinkage after Sintering(%)		14.5	24.1

Table 3 Properties of Sintered Substrates from TOYALNITE UF (PVB resin system)

Density (g/cm^3)	Fired at 1750°C	2.95
	Fired at 1800°C	3.27
	Fired at 1850°C	3.27
Thermal Conductivity (W/mK)		183
Oxygen Content (wt%) (Including Oxygen from Y_2O_3)		1.48
Second Phase (by XRD)		YAM、Y_2O_3
Bending Strength (kgf/mm^2)		30～35

Fired at 1850°C

Table 4 Properties of AlN Green Sheets from TOYALNITE

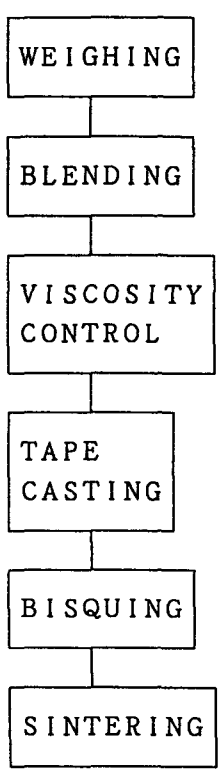
Binder System		Acrylic Resin	
AlN Grade		UF	R008
Binder Content (per 100 parts of powder)	Resin	13	13
	Plasticizer	3	3
Green Density (g/cm^3)		2.44	2.42
Shrinkage after Sintering (%)		14.5	15.0

Table 5 Properties of Sintered Substrates from TOYALNITE (Acrylic resin system)

Green Sheet		UF	R008
Density (g/cm^3)	Fired at 1750°C	2.95	3.16
	Fired at 1800°C	3.07	3.33
	Fired at 1850°C	3.30	3.30
Thermal Conductivity (W/mK)	Fired at 1800°C	—	190
	Fired at 1850°C	200	190

Table 6 Properties of Sintered Bodies from Water Resistant AlN Powder (TOYALNITE WF) Processed by Slip Casting (Sintered at 1850 °C for 3 hours)

Sintering Aid	Density (g/cm^3)	Thermal Conductivity (W/mK)
Y_2O_3 1%	3.23	97
Y_2O_3 3%	3.18	126
Y_2O_3 5%	3.20	157



Two formulations shown in the table below

24 hours

about 10000 cps

Clearance : 1.5mm
Casting Speed: 27 m/min
Drying:at R.T. for 1 day
Thickness: 0.6-0.8 mm

PVB system :450 ℃x 30 min in air
Acrilic system:450 ℃x 30 min in air

1850 ℃x 3hrs in N_2

FORMULATIONS

PVB RESIN SYSTWEM	AlN POWDER	190 g	DISPERSANT	2 g
	Y_2O_3	10 g	TOLUENE	50 g
	BINDER	16 g	M.E.K.	50 g
	PLASTICIZER	8 g	Et OH	50 g
ACRYLIC RESIN SYSTEM	AlN POWDER	190 g	DISPERSANT	2 g
	Y_2O_3	10 g	I.P.A.	4 g
	BINDER	52 g	TOLUENE	112 g
	PLASTICIZER	6 g		

FIG. 1 TAPE CASTING PROCEDURE

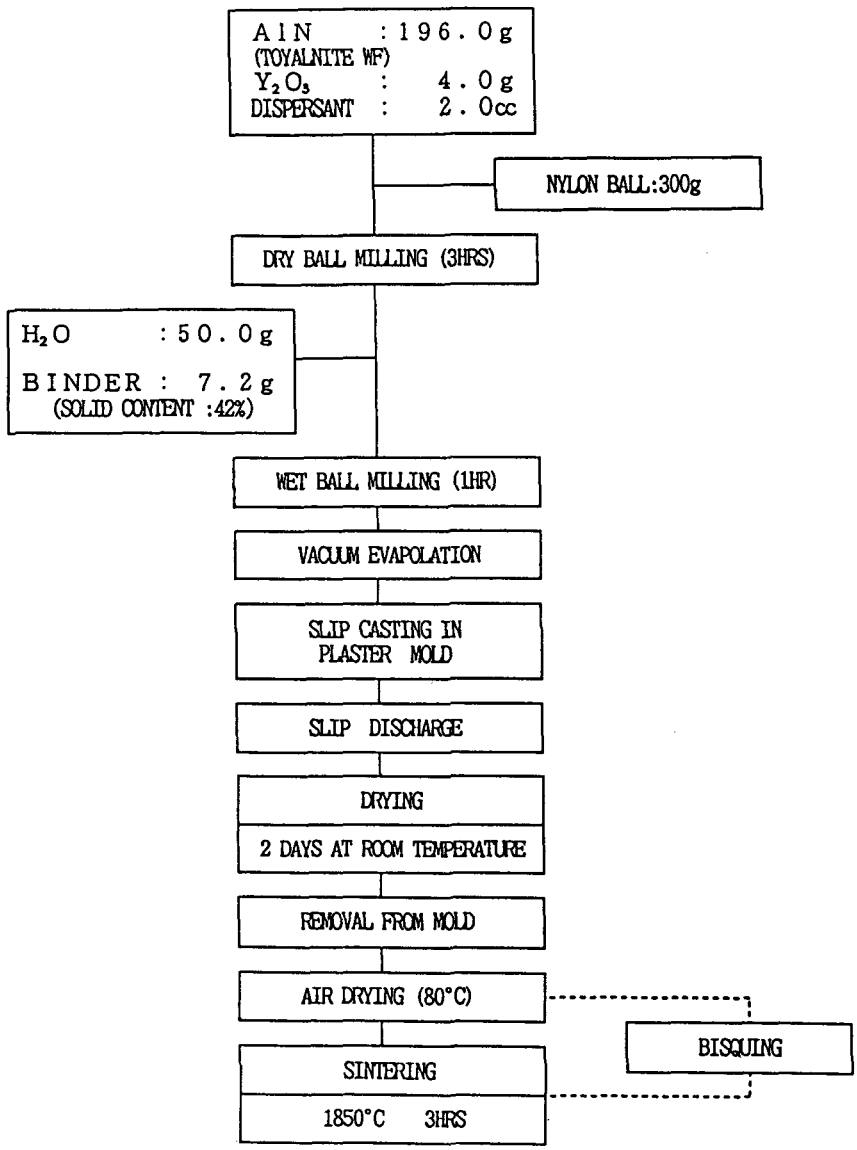


FIG. 2 AN EXAMPLE OF AQUEOUS SLIP CASTING PROCESS USING WATER RESISTANT ALN POWDER.

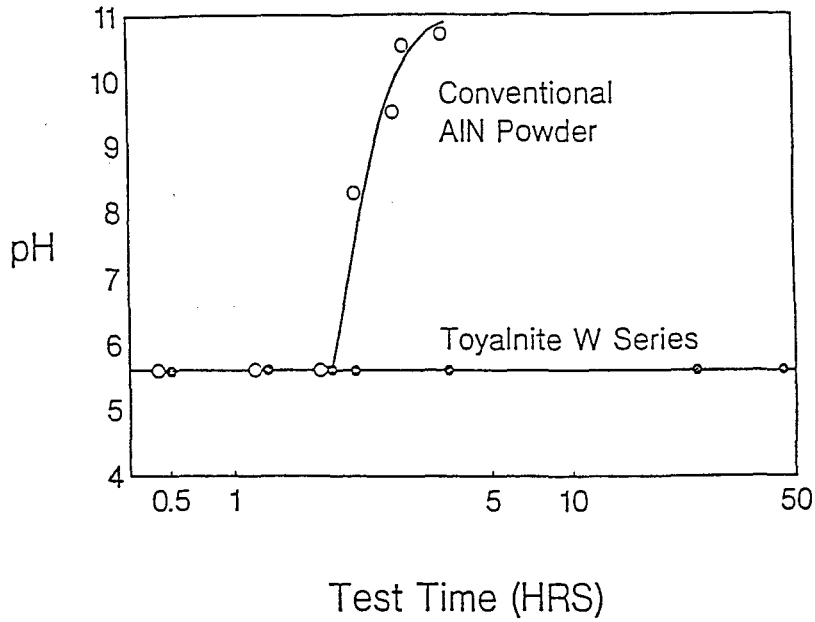


FIG. 3 WATER RESISTANCE OF THE WATER RESISTANT ALN POWDER.
(TEMPERATURE: 40 °C)

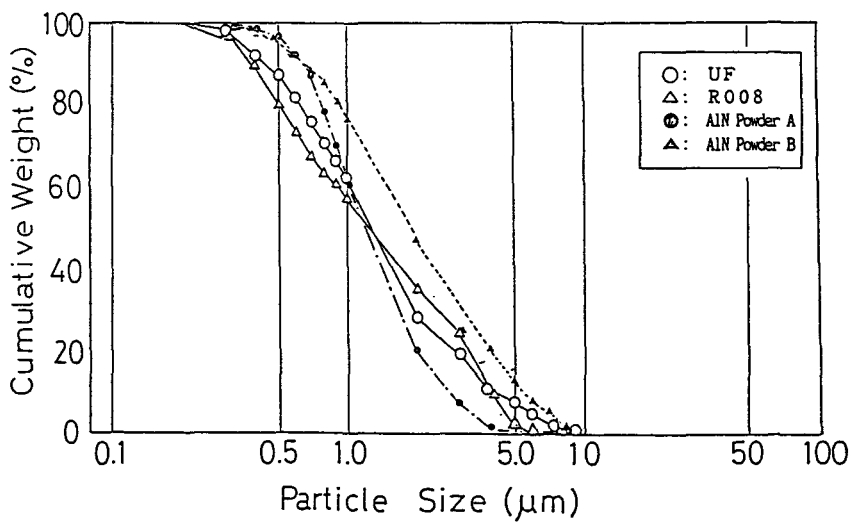


FIG. 4 PARTICLE SIZE DISTRIBUTION OF ALN POWDERS (MEASURED BY HORIBA CAPA 700)

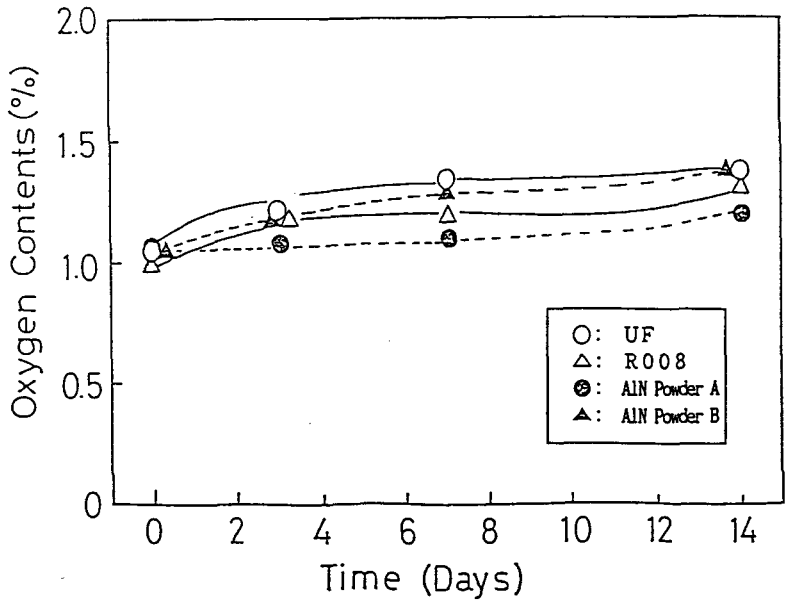


FIG. 5 STABILITY TO MOISTURE OF ALN POWDERS. (AT 35 ℃ 70% R.H.)

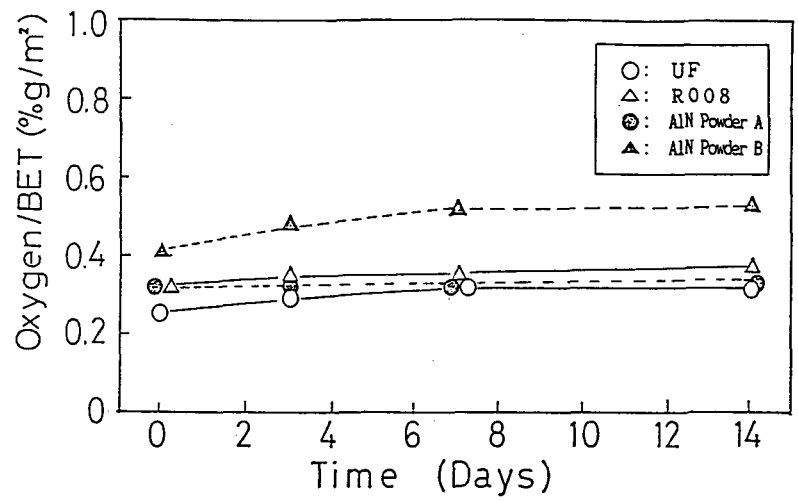


FIG. 6 THE CHANGE OF O/BET VALUE, REPLOTTED OF FIG. 5. (O/BET INDICATES THE RATIO OF OXYGEN CONTENT TO SPECIFIC SURFACE AREA)

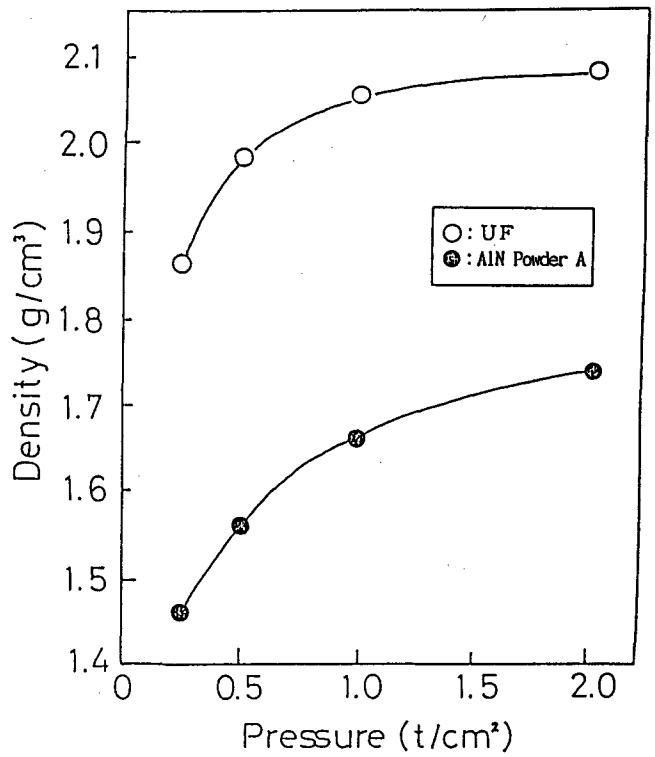


FIG. 7 GREEN DENSITY VS. PRESSURE OF UNIAXIAL PRESSING FOR ALN POWDERS OF DIRECT NITRIDATION AND CARBOTHERMIC REDUCTION.

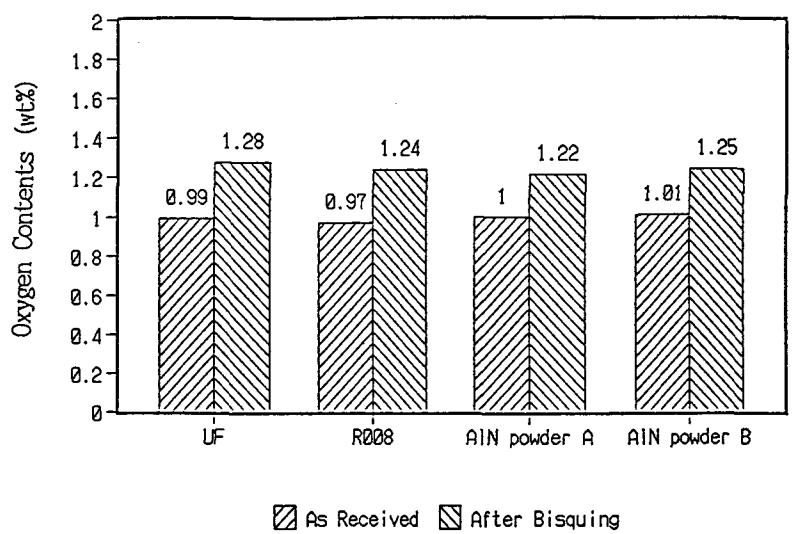


FIG. 8 OXYGEN CONTENT OF ALN POWDERS BEFORE AND AFTER DEWAXING. DEWAXING CONDITION: 450 °C FOR 1 HOUR IN DRY AIR.

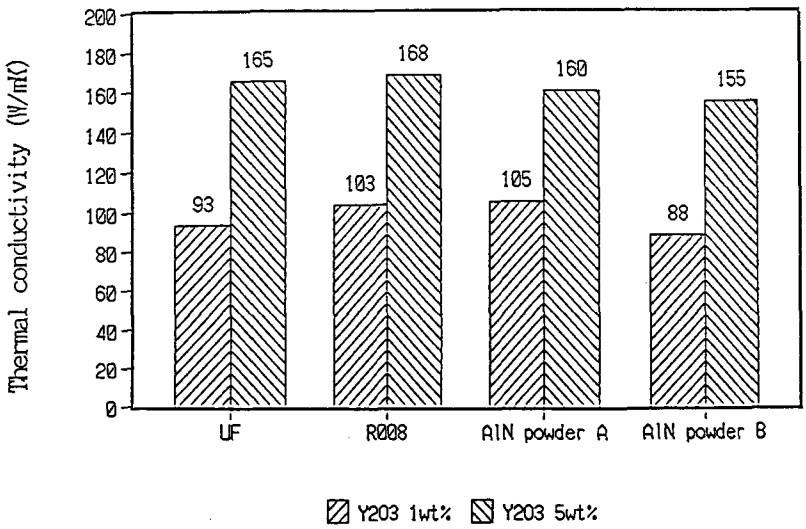


FIG. 9 THERMAL CONDUCTIVITY DATA OF SINTERED ALN. SINTERED AT 1850 °C FOR 3 HOURS WITH 1WT% AND 5WT% Y_2O_3.

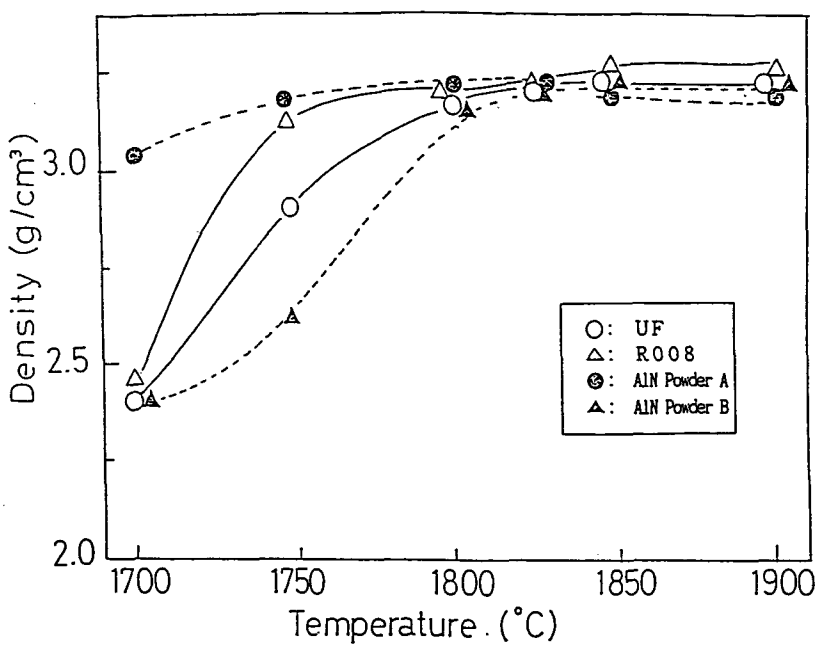


FIG. 10 DENSITY VS. SINTERING TEMPERATURE FOR VARIOUS ALN POWDERS (PRESS FORMED AND SINTERED WITH 1WT% Y_2O_3).

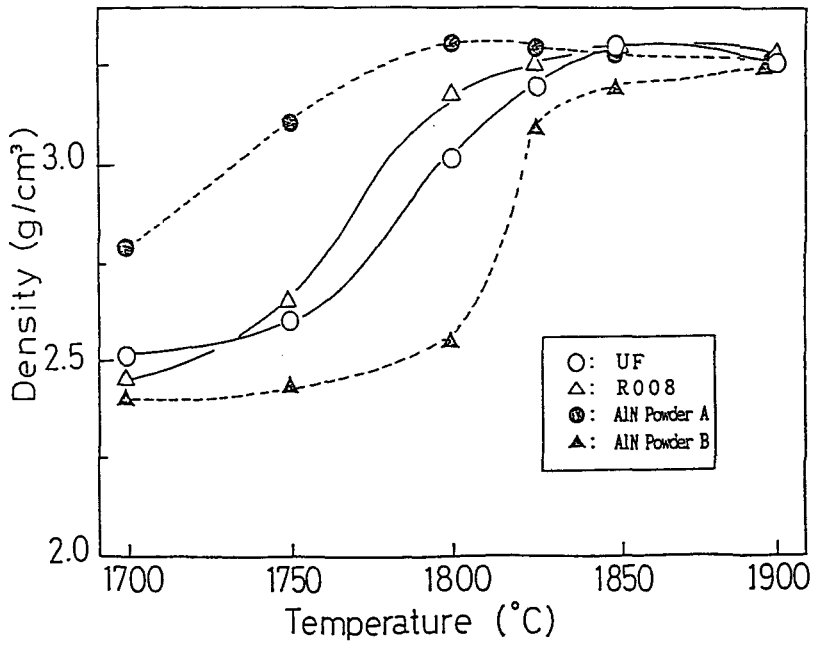


FIG. 11 DENSITY VS. SINTERING TEMPERATURE FOR VARIOUS ALN POWDERS.
(PRESS FORMED AND SINTERED WITH 5WT% Y_2O_3)

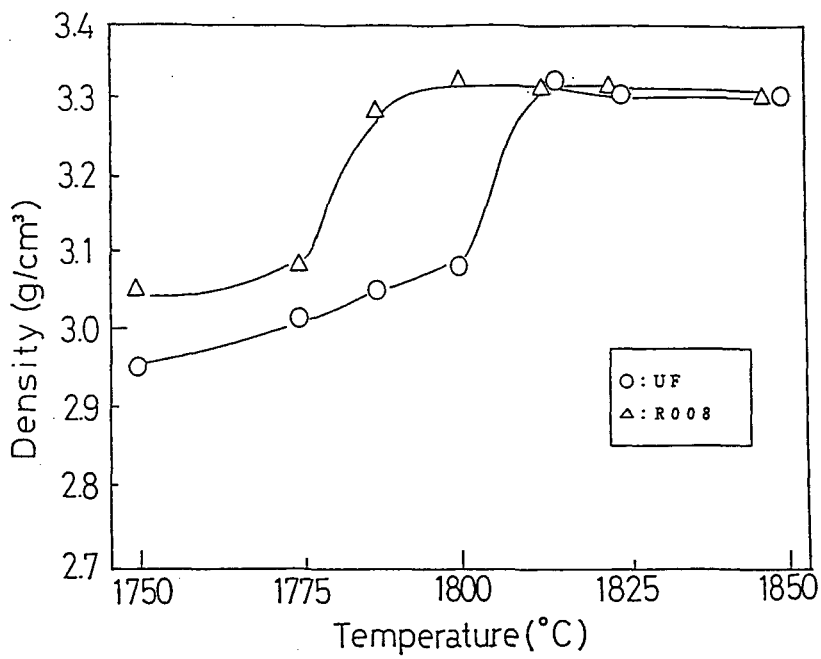


FIG. 12 SINTERBILITY OF ACIYLIC SYSTEM GREEN SHEETS WITH 5WT% Y_2O_3. ALN: UF AND R008