Lowering of The Sintering Temperature of High Thermal Conductive AlN Ceramics

Ichiro Hazeyama and Noboru Ichinose
Department of Materials Science and Engineering, School of Science and Engieering, Waseda University
3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169, Japan

Abstract

High thermal conductivity of aluminum nitride (AlN) was attained by using suitable amount of additives such as oxides and fluorides. Additives such as CaO, Y_2O_3, CaF_2, YF_3 and AlF_3 were investigated as AlN sintering aids, aiming at lowering the sintering temperature. AlN ceramics were sintered at 1600℃ using a mixture of CaO, CaF_2 and AlF_3 additives. The thermal conductivity of AlN with CaO-AlF_3, CaF_2-AlF_3, additives was found to be $160 W \cdot m^{-1} K^{-1}$.

Key-words: aluminum nitride, sintering, additives, thermal conductivity, oxides, fluorides

Introduction

Aluminum nitride (AlN) is known as a high thermal conductive ceramics. Its monocrystal conductivity is about $320 W \cdot m^{-1} K^{-1}$ [1]. However, it is difficult to process AlN ceramics and achieve high thermal conductivity. The thermal conductivity of AlN ceramics is reduced by the presence of impurities such as oxygen and transition metal ions[2] in the ceramics, and pressureless sintering is inefficient in producing pure AlN. Thus, AlN is usually sintered with a suitable amount of additives such as oxides[3] and fluorides[4,5], which promote liquid phase sintering. The liquid phase is produced by the reaction of Al_2O_3 that exists on the surface of AlN particles. For example, Y_2O_3 additive reacts with Al_2O_3 producing the Y-Al-O liquid phase which then promotes the sintering of AlN. CaO, YF_3 and CaF_2 additives also produce similar effects. This liquid phase migrates through grain boundaries and concentrates at grain boundary triple points, or migrates to the surface of the sintered AlN body[6]. This means that these additives can either trap or remove oxygen impurity at the grain boundary triple points. Moreover, it was reported that sintering in N_2 and reducing carbon gas atomosphere brought about good results in the removal of impurity phases. By using this method, the high thermal conductivity of AlN appears. Usually, AlN ceramics were sintered at more than 1800℃ in N_2 gas atmosphere including reducing carbon gas. But, from commercial points of view it is better to make the sintering temperature low for energy cost. Thus, we investigated the sintering of CaO, Y_2O_3, CaF_2, YF_3 and AlF_3 additives, for the purpose of lowering the sintering temperature of AlN ceramics. The effect of AlF_3 addition was investigated due to the fact that it decomposes at a low temperature (about 1300℃) and dose not become an impurity in AlN ceramics.

This paper reports the comparison of these additives and the effect of AlF_3 addition.

Experimental

1. Sample preparation

The samples were fabricated by means of the conventional procedure as follows; the starting materials are AlN (Tokuyama Soda Co.,Ltd., F grade; oxygen content ≦ 1.0%, average grain size 1.8 μm) Y_2O_3, YF_3, CaO, CaF_2

(Soekawa chemicals Co.,Ltd., purity 3N) and AlF_3 powders (High Purity Chemicals Co.,Ltd., purity 3N). These powders were weighed (Table 1) and mixed in ethanol with nylon ball for 4 hours. Slurry substances were obtained. These slurries were dried and acrylic binder was added. The mixture was again mixed in 1-1-1 tri-chloro-ethane. After drying, the mixed powders were pressed into 12mm diameter discs under the pressure of about $500kg/cm^2$. The samples were heated at 700℃ in flowing N_2 gas in order to burn out the binder. After this treatment, the samples were sintered at 1500, 1600, 1700 and 1800℃ for 2, 4, 8, 16 and 32 hours in N_2 atmosphere.

2. Evaluation

Dielectric constants of sintered samples were measured by the conventional method, and their densities were measured by the Archimedian method. Thermal conductivities were measured by the laser-flash method using a ruby laser (λ=0.6943mm) and liquid-nitrogen-cooled InSb infrared detector at room temperature. The sintered samples were identified by the X-ray powder diffraction method (XRD) after crushing in an agate mortar. The microstructures were observed by scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS) was applied to investigate the fluoride.

Results and discussion

The changes in the density and the thermal conductivity of the materials sintered at a temperature range of 1500-1800℃ for 4 hours are shown in Figs. 1 and 2. As shown in Fig.1, added materials such as Y_2O_3, YF_3, Y_2O_3-AlF_3 and YF_3-AlF_3 densified at $T > 1700$℃, and the thermal conductivity of these materials increases with increasing sintering temperature. The materials with additives, Y_2O_3-AlF_3 and YF_3-AlF_3, showed higher thermal conductivity than those materials without AlF_3 when sintered at T > 1700℃. This gives an information on the influence of the AlF_3 additive. Figure 2 shows the materials with additives, CaO, CaF_2, CaO-AlF_3 and CaF_2-AlF_3. As shown in this figure, there is a similar tendency on the density of these materials, however densification started at 1600℃. This temperature is lower than that of Fig.1. The thermal conductivity of the materials with AlF_3 is higher than those materials without AlF_3. From the above observations, additives such as CaO and CaF_2 may be useful for low temperature sintering, and the additive AlF_3 may give some good influence on the liquid-phase sintering. Higher thermal conductivity was obtained in the AlN-CaO-AlF_3 and AlN-CaF_2-AlF_3 systems.

Figure 3 summarizes the microstructural evalution of materials with CaO and CaO-AlF_3 addition. These materials were sintered at temperature 1500–1700℃ for 4 hours. The microstructures of the fractured surface of the samples with CaO addition are shown in Fig.3 a)–c), and those with CaO-AlF_3 addition are shown in Fig.3 d)–f). The materials shown in Fig.3 a) and d) were sintered at 1500℃. Fig.3 b) and e) show the materials sintered at 1600℃ and Fig.3 c) and f) at 1700℃. Both samples sintered at 1500℃ and the sample with CaO addition shown in Fig.3 b) were all porous. On the other hand, the sample with CaO-AlF_3 addition shown in Fig.3 e) and both of the samples sintered at 1700℃ showed no pores. It was found that the particle size of the sample with CaO-AlF_3 addition is larger than that of the sample with CaO addition sintered at same temperature, as shown in Fig.3 a)–f). Thus, the grain growth may be promoted in the AlN-CaO-AlF_3 system.

Crystallographic phases of sintered samples are listed in Table 2. The crystallographic phase of the samples with Y_2O_3 and Y_2O_3-AlF_3 addition were found to be similar to $Y_4Al_2O_9$. This phase is the liquid phase during sintering. This means that same sintering system may be promoted in the AlN body in spite of AlF_3 addition. A similar phase was observed in the samples with CaO and CaO-AlF_3 additive.

AlF_3 is known as a material that decomposes at approximately 1300℃. XPS measurements were carried out for three samples with CaO-AlF_3 addition, which were sintered at 1300, 1400 and 1600℃. The samples sintered at 1300 and 1400℃ were observed at the polished surface, and the sample sintered at 1600℃ was observed at the polished and fractured surface. Figure 4 shows the XPS analysis of the material sintered at 1400℃. Fluorine was detected at this temperature. The same result was observed in the sample sintered at 1300℃. This is the information that fluorine exists as the same state in the AlN body. But, it is found out that fluorine disappears at higher than 1400℃. Fluorine was not deteced on the polished and on the fractured surface of the sample sintered at 1600℃.

Figure 5 shows the relations between the thermal conductivity and holding time of the materials with CaO, CaF_2, CaO-AlF_3 and CaF_2-AlF_3 addition sintered at 1600℃. The thermal conductivity of each materials increased with increasing the holding time. However, at saturated value, they showed some difference between the samples with AlF_3 and without AlF_3. AlF_3 additive may be effective in the initial stage of sintering.

Dielectric constant of the materials with CaO-AlF_3 addition is shown in Table 3. It was measured in the following condition; 1MHz, at room temperature. The values obtained are close to the value of Al_2O_3 (8.5 at R.T. 1MHz).

Conclusion

CaO, CaF_2 are effective additives for the low temperature (1600℃) sintering of AlN ceramics. Doping AlF_3 with CaO or CaF_2 increases thermal conductivity. Thermal conductivity of $160 W \cdot m^{-1} K^{-1}$ has been obtained in sintering $AlN-CaO-AlF_3$ at 1600℃ for 32 hours.

Fluorine decomposes and may go out of the body by evaporation or some other way. Thus it may influence the liquid-phase sintering in the initial stage of the process.

References

1) G. A. Slack, Nonmetallic crystals with high thermal conductivity, J. Phys. Chem Solid 34, 321 (1973)

2) G. A. Slack et al., The intrinsic thermal conductivity of AlN, J. Phys. Chem Solid 48, 641 (1987)

3) K. Komeya et al., Effect of various additives on sintering of Aluminum Nitride, J. Ceram. Soc. Jpn. 89[6], 330 (1981) [in Japanese]

4) K. Shinozaki et al., 23rd Symposium of Basic Science of Ceramics 21 (1985) [in Japanese]

5) F. Ueno et al., 24th Symposium of Basic Science of Ceramics 176 (1986) [in Japanese]

6) T. Yagi et al., Migration of grain boundary phases in AlN ceramics by heating in reduced atmosphere, J. Ceram. Soc. Jpn. 97[11], 1372 (1989) [in Japanese]

Table 1 Additive content in AlN

Sample	Additives & Content (wt%)			
1	Y_2O_3	3wt%,		
2	YF_3	3wt%,		
3	CaO	1wt%,		
4	CaF_2	1wt%,		
5	Y_2O_3	3wt%,	AlF_3	1wt%
6	YF_3	3wt%,	AlF_3	1wt%
7	CaO	1wt%,	AlF_3	1wt%
8	CaF_2	1wt%,	AlF_3	1wt%

Table 2. Crystallographic phases of sintered samples

additives	Crystallographic phase		
Y_2O_3, AlF_3	AlN,	$Y_4Al_2O_9$,	YN
Y_2O_3	AlN,	$Y_4Al_2O_9$,	YN
CaO, AlF_3	AlN,	$CaAl_2O_4$,	$CaAl_4O_7$
CaO	AlN,	$CaAl_2O_4$,	$CaAl_4O_7$

Table 3. Dielectric Constant (1MHz)

Sintering condition	Dielectric constant
1600℃, 4 hours	9.4
1600℃, 8 hours	9.3
1600℃, 16 hours	9.1
1800℃, 4 hours	9.0

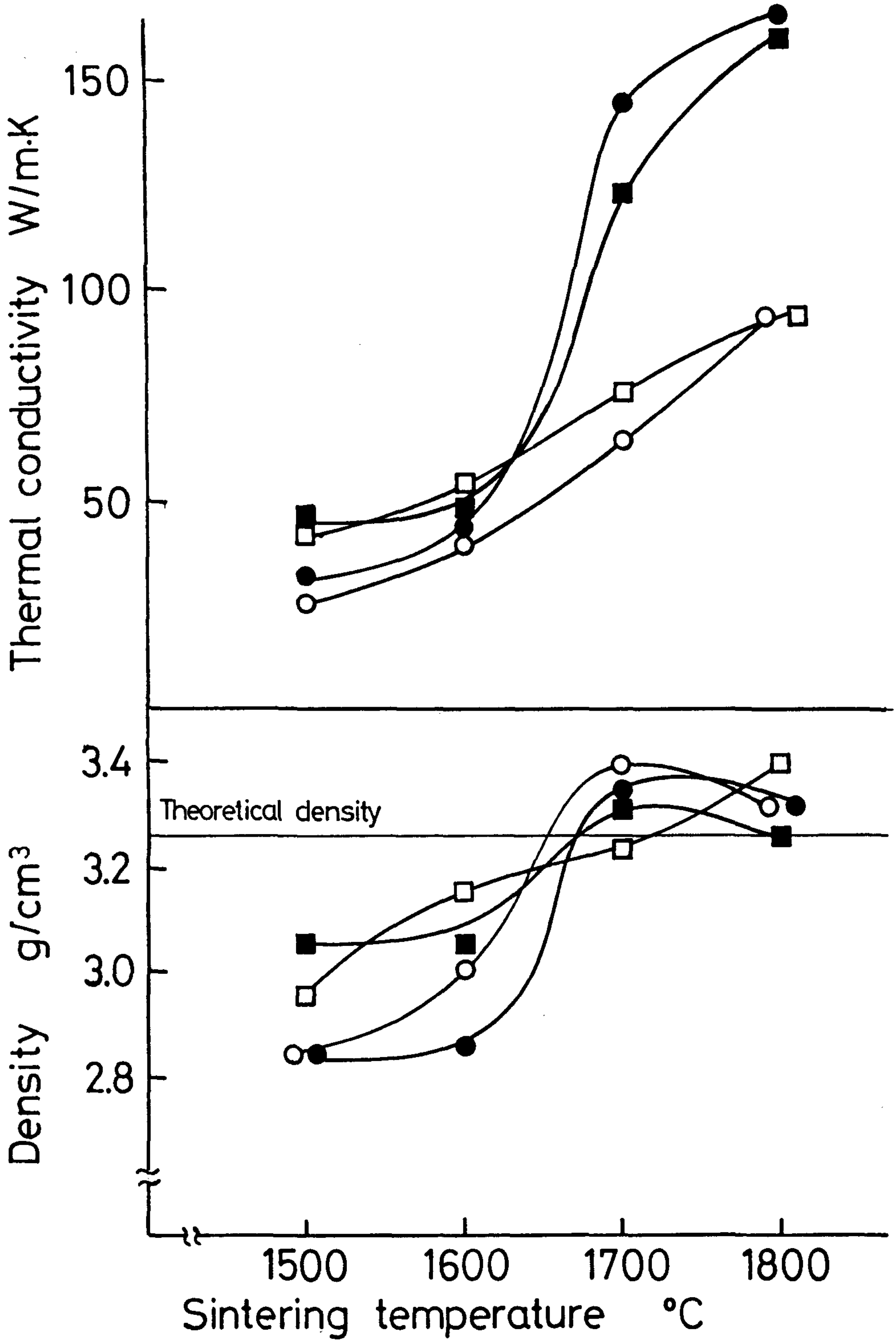

Figure 1 Thermal conductivity and density of AlN ceramics with Y_2O_3, YF_3 and AlF_3. ○:Y_2O_3, ●:Y_2O_3-AlF_3, □:YF_3, ■:YF_3-AlF_3

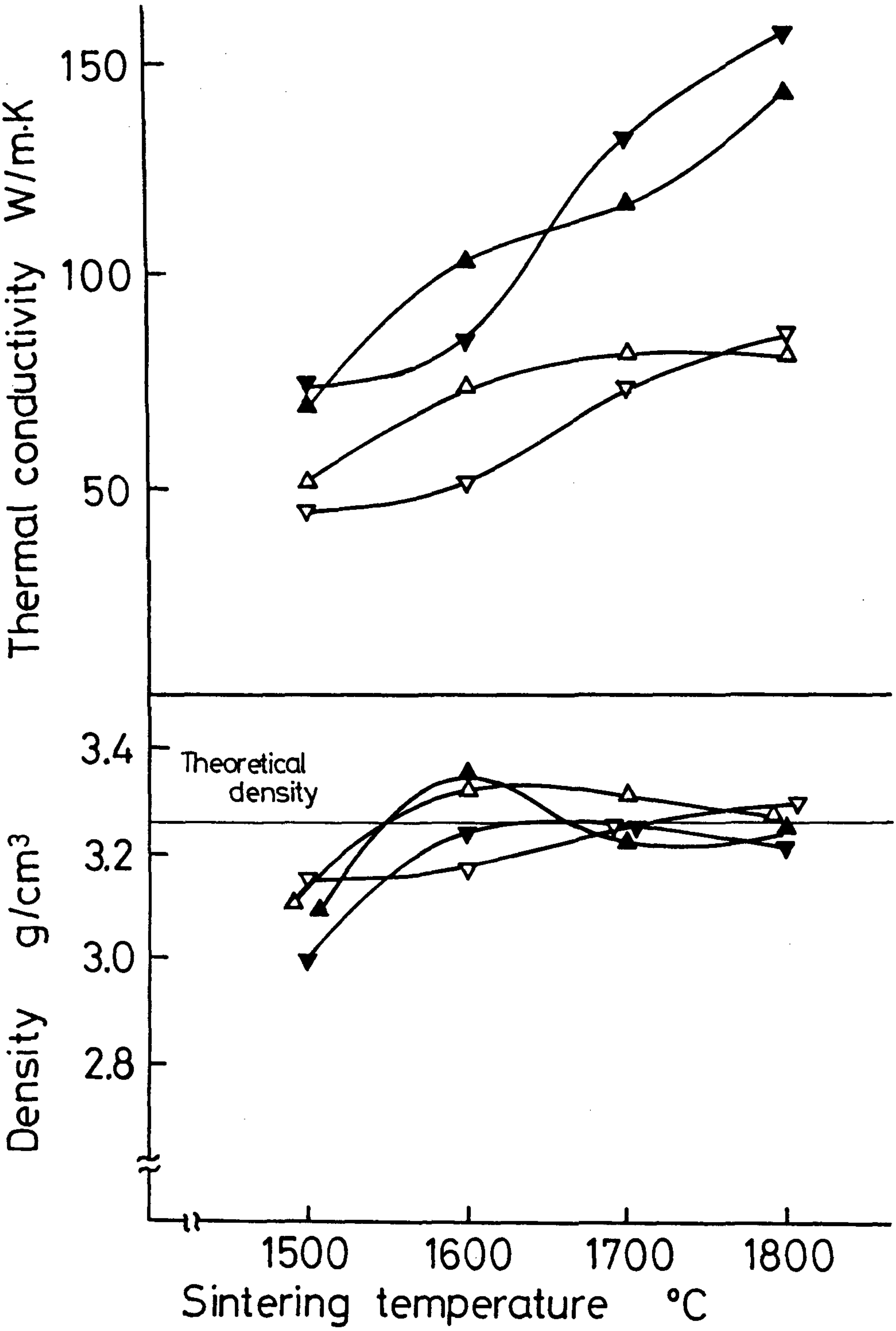

Figure 2 Thermal conductivity and density of AlN ceramics with CaO, CaF_2 and AlF_3. △:CaO, ▲:CaO-AlF_3, ▽:CaF_2, ▼:CaF_2-AlF_3

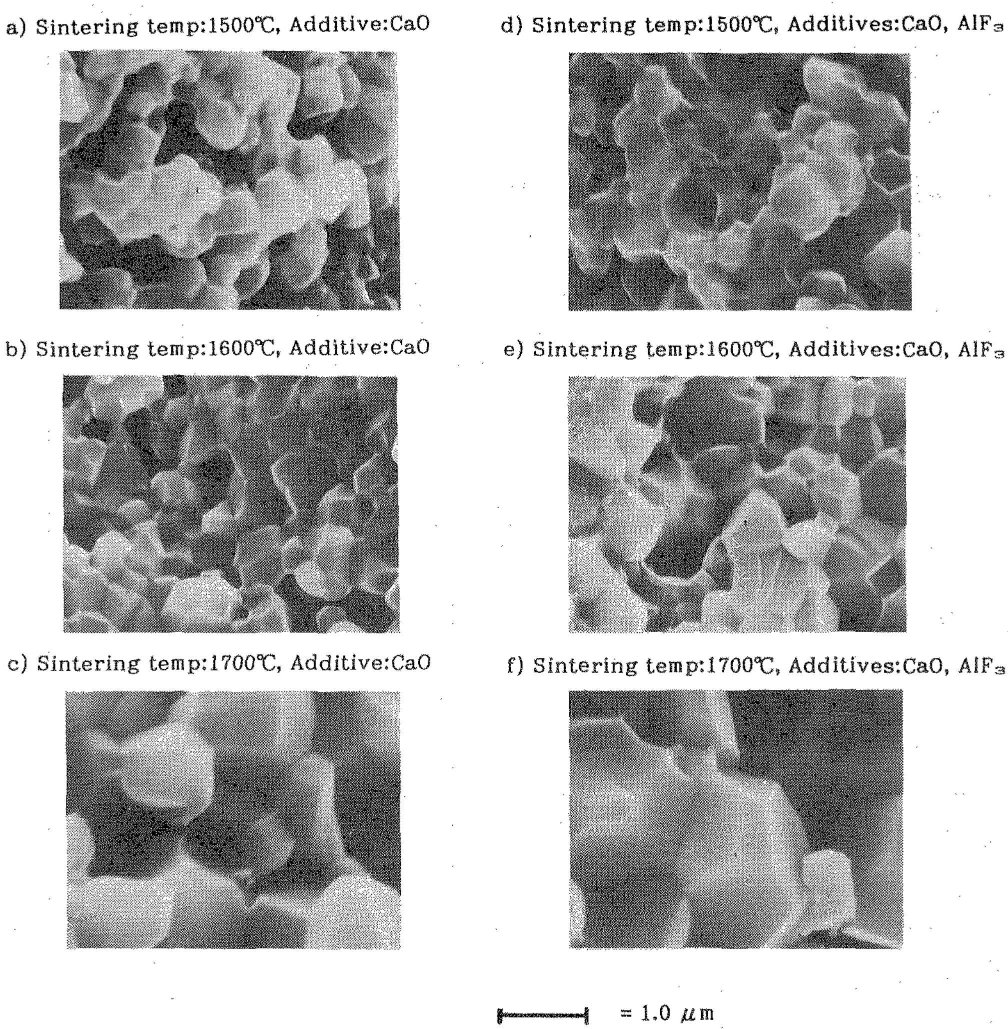

Figure 3 Microstructure of sintered AlN.

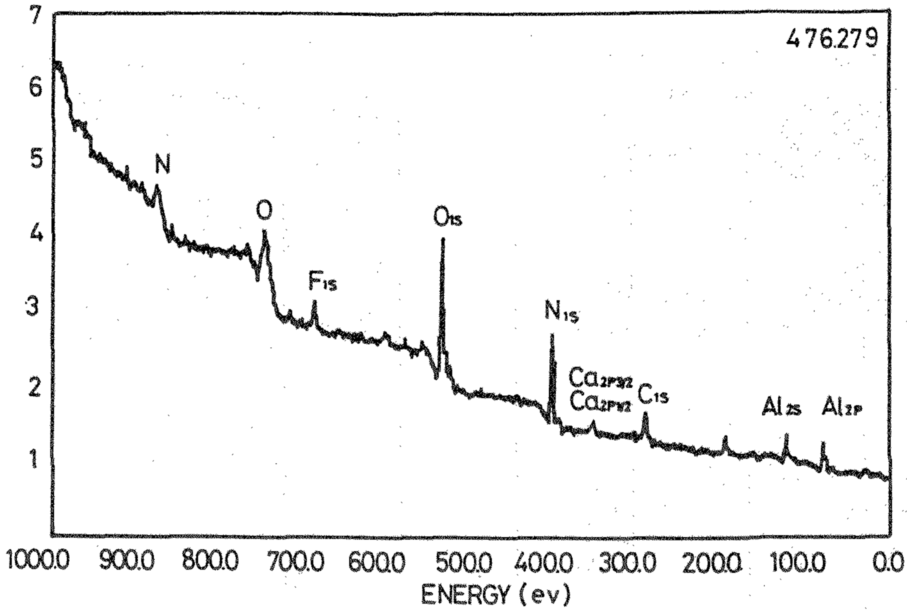

Figure 4 X-ray photoelectron spectroscopy of AlN ceramics sintered at 1400 ℃.

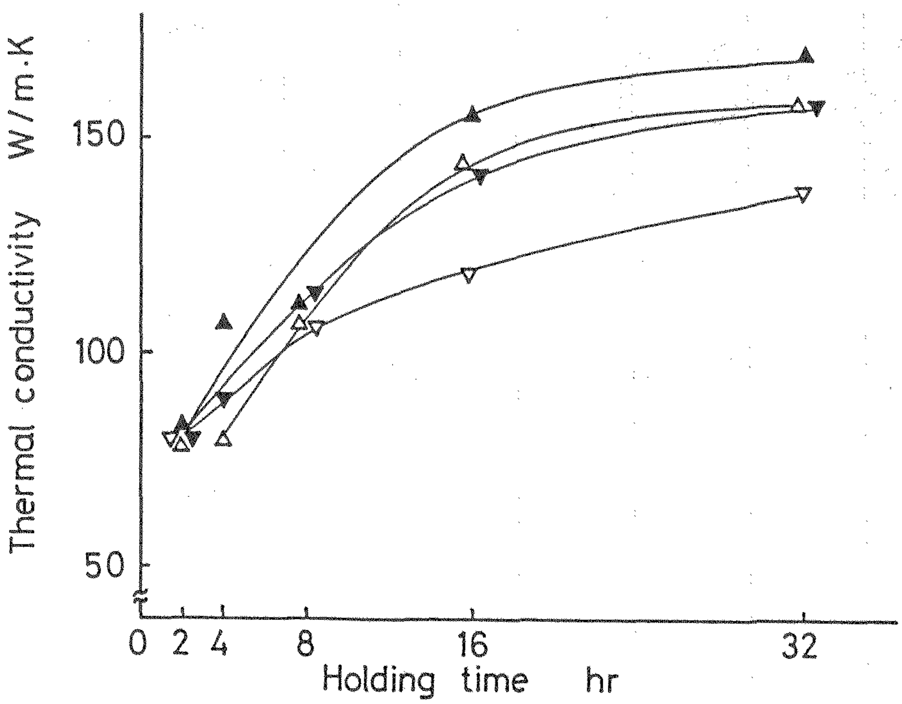

Figure 5 Thermal conductivity of AlN ceramics sintered at 1600℃. △:CaO, ▲: CaO-AlF_3, ▽:CaF_2, ▼:CaF_2-AlF_3