Mechanical Strength and Thermal Conductivity of High Purity Al_2O_3 Ceramics using AKP-30 Powder

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Green specimens of as-purchased AKP-30 powder and AKP-30 powder with additives of either MgO (0.5 wt%) or ZrO_2 (1.5 and 3.0 wt%) were sintered in an electric furnace at a temperature ranging from 1450°C to 1650°C for 2 h. The relative densities of the sintered specimens of all compositions reached the maximum at 1600°C. The mechanical strength, measured by biaxial pressure mode, showed a value as high as 500 MPa. Thermal conductivity, measured by the Laser Flash Method, reached an average of 35 W/mK when the density was over 95%. AKP-30 specimens without additive consolidated to almost full density (98% of theoretical density) at very low temperature (1450°C) when sintered in a gas furnace with a prolonged firing of one day.

Key words: high purity Al_2O_3 ceramics, density, thermal conductivity and bending strength

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ความแข็งแรงเชิงกลและการนำความร้อนของอลูมินาที่มีความบริสุทธิ์สูงเกรด AKP-30

เปาว์ ณ นคร สุพัตรา จินาวัฒน์ และ ชิเกทากะ วาดะ (2548)
วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย **30(1)**

ชิ้นตัวอย่างทำจากผงอลูมินาเกรด AKP-30 ล้วน และผงอลูมินาเกรด AKP-30 เจือด้วยสารเติมแต่ง MgO 0.5%โดยน้ำหนัก หรือ ZrO_2 1.5 และ 3.0% โดยน้ำหนัก ถูกนำมาเผาซินเตอร์ในเตาไฟฟ้าที่อุณหภูมิตั้งแต่ 1450°C ถึง 1650°C เป็นเวลา 2 ชม. ความหนาแน่นบัลค์ของชิ้นตัวอย่างทุกสูตรเพิ่มขึ้นจนถึงค่าสูงสุดที่ 1600°C ความแข็งแรงเชิงกลเฉลี่ยวัดโดยการให้แรงดันสองทิศทาง มีค่าสูงถึง 500 MPa ค่าการนำความร้อนโดยเฉลี่ยของชิ้นตัวอย่างที่มีความหนาแน่นมากกว่า 95% ของความหนาแน่นทางทฤษฎี วัดโดยเทคนิคเลเซอร์แฟลชมีค่าประมาณ 35 W/mK ชิ้นตัวอย่างที่ทำมาจากผงอลูมินาเกรด AKP-30 ล้วน เมื่อนำมาเผาในเตาแก๊สโดยใช้เวลาในการเผานานขึ้นเป็นประมาณ 1 วัน ความหนาแน่นจะเพิ่มขึ้นจนเกือบถึงค่าสูงสุด (98% ของความหนาแน่นทางทฤษฎี) ที่อุณหภูมิต่ำมากคือ 1450°C

คำสำคัญ อลูมินาที่มีความบริสุทธิ์สูง ความหนาแน่น ค่าการนำความร้อน และความแข็งแรงเชิงกล

INTRODUCTION

Alumina is one of the most popular ceramics used in the electronic, mechanical and refractory industries. Use as a substrate for electronic circuits is one of the important applications of alumina ceramics. The essential properties for a substrate are mechanical strength and thermal conductivity, the higher property the better. Generally, commercial alumina substrates contain about 3-4 wt% of additives, sometimes called flux, such as SiO_2, CaO and MgO. These fluxes decrease the sintering temperature, but on the other hand, lower thermal conductivity. Consequently, the thermal conductivity of 96-97 wt% Al_2O_3 substrate, 20-24 W/mK, is much less than 42 W/mK of single crystal Al_2O_3.

The high cost of using high purity Al_2O_3 is due to the high price of commercial raw powder and the high sintering temperature, over 1700°C. Recently, powder technology has progressed very much and some high purity alumina powders with very fine grain size can be consolidated to almost full density at a temperature lower than 1700°C. AKP-30 is one of the high purity Al_2O_3 powders suitable for lower temperature sintering and commercially available.

The objective of this research is to measure the mechanical strength and thermal conductivity as a function of the sintering temperature of high purity alumina ceramics using AKP-30 as the raw powder.

EXPERIMENTAL PROCEDURE

AKP-30 (Sumitomo Chemical Co., Ltd.)(1) was used as the raw powder. The purity, the average particle size and the specific surface area of AKP-30 are >99.99 wt%, 0.3 μm and 5-10 m^2/g, respectively. Specimens of four compositions were prepared. They were AKP-30, AKP-30 with 0.5 wt% of MgO, 1.50 wt% of ZrO_2 and 3.0 wt% of ZrO_2 as additives. MgO and ZrO_2 are chemicals that have been shown as grain growth inhibitors. $Mg(NO_3)_2(6H_2O)$ (Fluka >99 wt%) and TZ-3Y (TOSOH) were used as the sources of MgO and ZrO_2, respectively. AKP-30 and the additives were wet mixed in a polypropylene bottle for 4 h to get a homogeneous mixture. After drying in an oven, binder (PVA) was added, and the powder was pulverized through a #100 sieve. The powder was pressed at 20 MPa into pellets of two sizes using dies of 12 and 35 mm in diameter. The 12 mm pellets were used for thermal conductivity and grain size testing, and the 35 mm ones were used for strength and density measurements. The specimens were sintered in an electric furnace at 1450, 1500, 1550, 1600 and 1650°C for 2 h with a heating rate of 5°C/min.

The bulk density was measured by Archimedes' method. Mechanical strength was measured in conformity with ASTM F-394.(2) Thermal conductivity was measured with the Laser Flash Method by ULVAC-RIKO Inc., Japan. The microstructure of the sintered ceramics was investigated by SEM (JEOL JSM-1670) at the Equipment Center of Chulalongkorn University. Particle size of the sintered ceramics was measured from SEM micrographs by the line intercepted method following ASTM standard E112-96. More details of the experimental procedure are written in the master's thesis of Pao Na Nakorn.(3)

RESULTS AND DISCUSSION

All the experimental data are shown in Table 1. The relationship between relative density (expressed as % of theoretical density) and sintering temperature is shown in Figure 1. As shown in the figure, all compositions reached about 98% of theoretical density at 1550°C and the maximum at 1600°C. The higher temperature of 1650°C is considered over firing for all compositions as evidenced by the decrease in density.

Table 1. Density, bending strength, average grain size and thermal conductivity data

Composition	Sintering temperature (°C)	% of theoretical density*	Bending strength** (MPa)	Average grain size (μm)	Thermal conductivity (W/mK)
AKP-30	1450	-	-	-	32.8(96.2)***
	1500	96.0	550-580(2)**	0.33	35.6(99.7)
	1550	97.8	380-510(5)	0.48	37.4(98.7)
	1600	99.0	290-465(4)	0.54	-
	1650	97.0	370-440(5)	1.25	-
AKP-30 +0.5 wt%MgO	1500	94.6	440-480(4)	0.80	24.2(93.2)
	1550	97.7	320-550(3)	0.87	34.2(97.7)
	1600	98.9	440-590(5)	1.71	35.9(98.0)
	1650	96.4	370-580(4)	1.85	36.4(99.4)
AKP-30 +1.5 wt%ZrO_2	1500	97.0	430-530(5)	1.03	-
	1550	98.0	540-650(3)	1.01	34.1(97.0)
	1600	98.0	420-520(5)	1.80	36.2(96.5)
	1650	97.0	430-540(4)	2.05	33.8(98.7)
AKP-30 +3.0 wt%ZrO_2	1500	95.8	460-680(5)	0.54	-
	1550	97.6	580-820(4)	0.92	34.2(95.3)
	1600	97.9	500-650(5)	1.56	30.0(97.0)
	1650	97.1	300-650(5)	1.33	33.9(98.5)

*The data is the average of five specimens.

**The data is the range of 2-5 specimens. Number in the parenthesis is the number of specimens. The reason for the difference in the specimen numbers comes from the difficulty of grinding and polishing.

***The value in parenthesis is the relative density of the specimen for which thermal conductivity was measured.

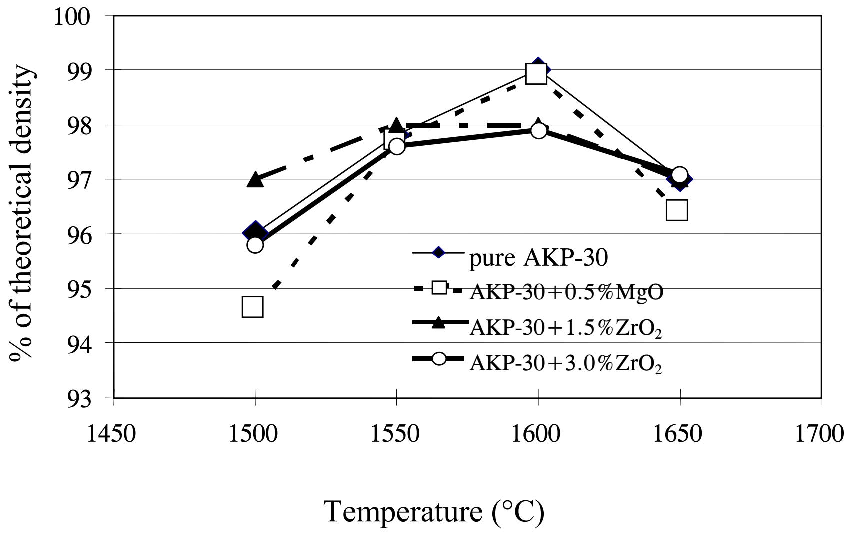
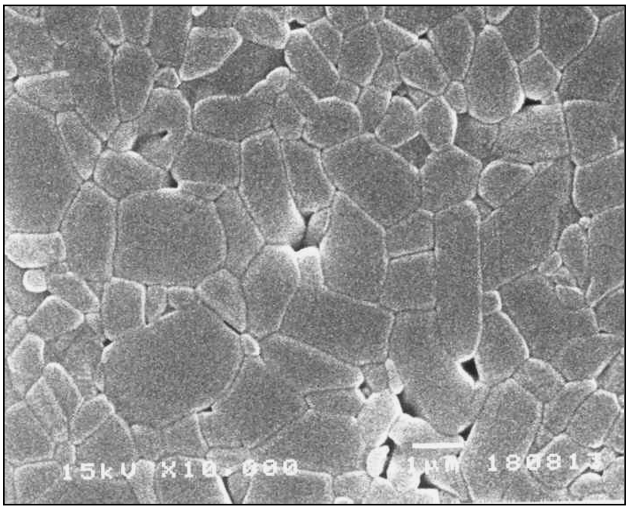


Figure 1. Relationship between sintering temperature and density.

Figure 2 (A) and (B) show the typical morphologies of AKP-30+ 0.5 wt% MgO and AKP-30 + 3 wt% ZrO_2. In (A), grain boundaries are clear and almost linear. This means that abnormal grain growth is suppressed by the addition of MgO. The white small grains in (B) are ZrO_2 particles. Small pores were observed at the triple point of grains in both specimens. The relationship between sintering temperature and average grain size is shown in Figure 3. The average grain size of all compositions is less than 2 μm even at 1650°C. The tendency of grain growth in AKP-30 is different from the other compositions. In the other three compositions, MgO and ZrO_2 worked as grain growth inhibitors. Grain size gradually increased with temperature, but the grains of AKP-30 (without grain growth inhibitor) were prone to grow abnormally over 1650°C.

(A) AKP-30+0.5 wt% MgO



(B) AKP-30+3.0 wt% ZrO_2

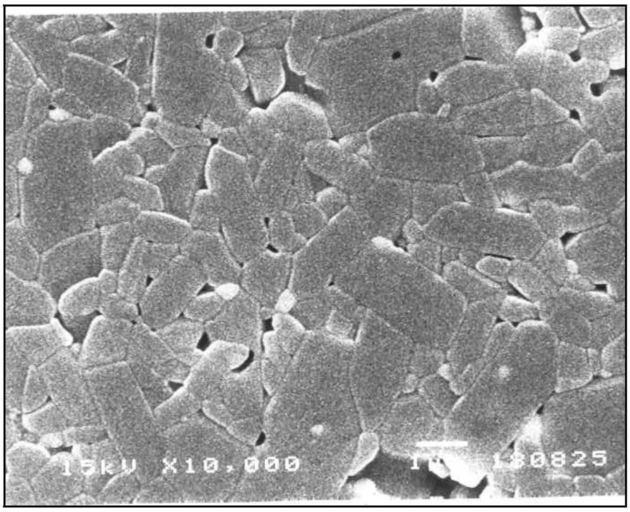


Figure 2. SEM micrographs of AKP-30 + 0.5 wt% of MgO and AKP-30 + 3.0 wt% of ZrO_2 sintered at 1550°C for 2 h in an electric furnace.

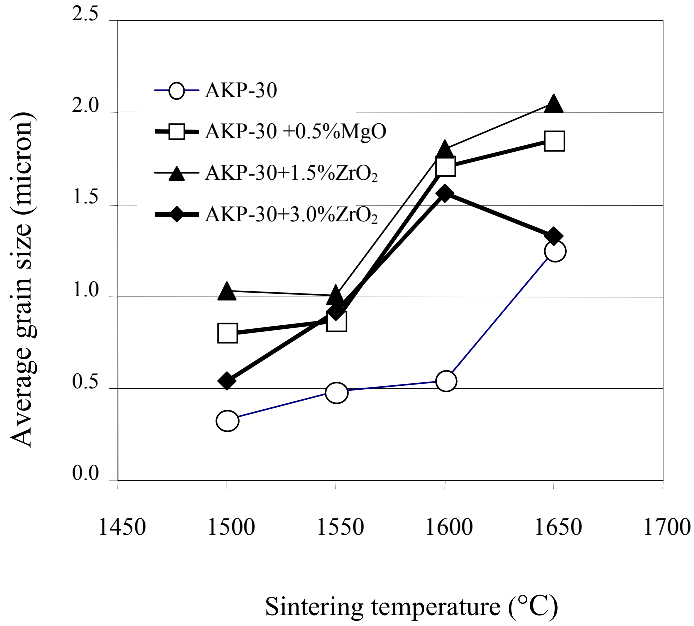


Figure 3. Relationship between the average grain size and sintering temperature for all compositions.

Figures 4 (A) to (D) show the mechanical strength measured by the bi-axial method.[2] Since the number of specimens for each condition was too small for the calculation of the average strength due to the difficulty in the preparation of specimens with high hardness, Al_2O_3 (Vickers hardness ~ 20 Gpa) and ZrO_2 (~ 12 Gpa), all data are graphically presented. The average strength of 500 MPa is high enough when compared with that of conventional alumina ceramics. It was found that the strength of AKP-30 + 3 wt% ZrO_2 was higher than the other three compositions. Although this could not be explained by the morphology and average grain size, we think that it is resulted from some effect of the composite, *i.e.*, an effective content of ZrO_2 is required in the inhibition of grain growth. The relationship between thermal conductivities and relative densities of selected sintered specimens (1450 - 1650°C) is shown in Figure 5. The thermal conductivity of the specimens was measured by ULVAC-RIKO Inc., Japan. Therefore, the amount of data is quite limited. The thermal conductivity of alumina ceramics, including 96 wt% of Al_2O_3, on the market is about 25 W/mK. Their low thermal conductivity is thought to come from the glassy phase between grain boundaries because some amount of SiO_2, CaO and other impurities have been added to decrease sintering temperature. Therefore, in this experiment, such impurities are unavoidable. When compared with commercial alumina ceramics, the thermal conductivities of these test specimens showed very good values, >30 W/mK, except for the one specimen having a bulk density of 3.70 g/cm^3 (93 % of theoretical density). The low thermal conductivity of this specimen suggests some amount of pores in the grain boundary. From Figure 5, when AKP-30 without additive and AKP-30 with small amounts of MgO or ZrO_2 are consolidated to over 95% of theoretical density, the thermal conductivity of the obtained Al_2O_3 ceramics is 35 W/mK on average. The thermal conductivity of single crystal Al_2O_3 was reported to be 42 W/mK.[4] The discussion on the relationship between the experimental results with single crystal Al_2O_3 is going to be reported elsewhere in the near future by the authors.

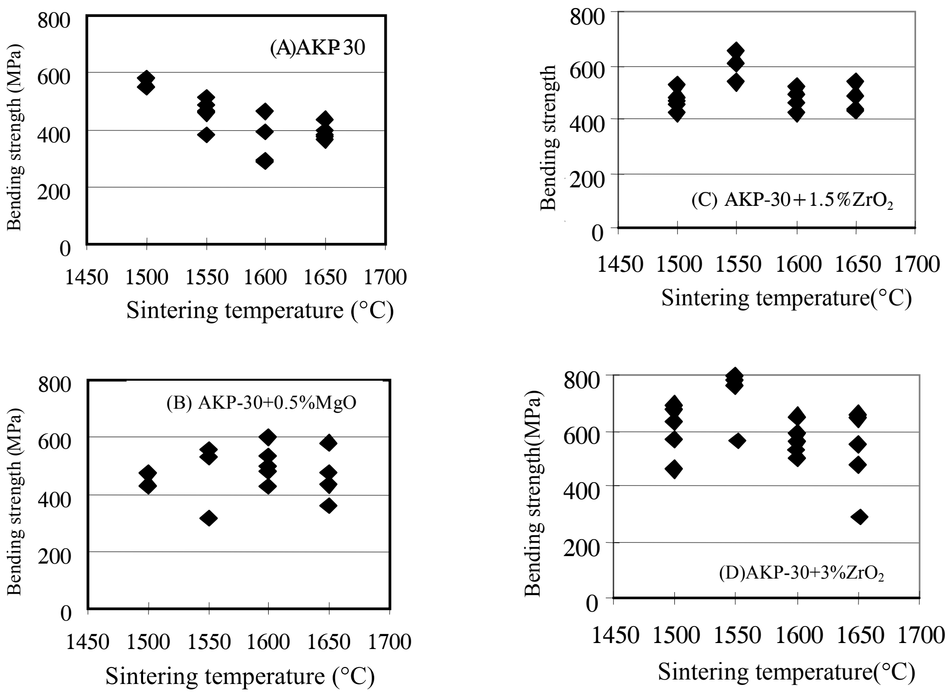


Figure 4. Mechanical strength of 4 compositions as a function of temperature.

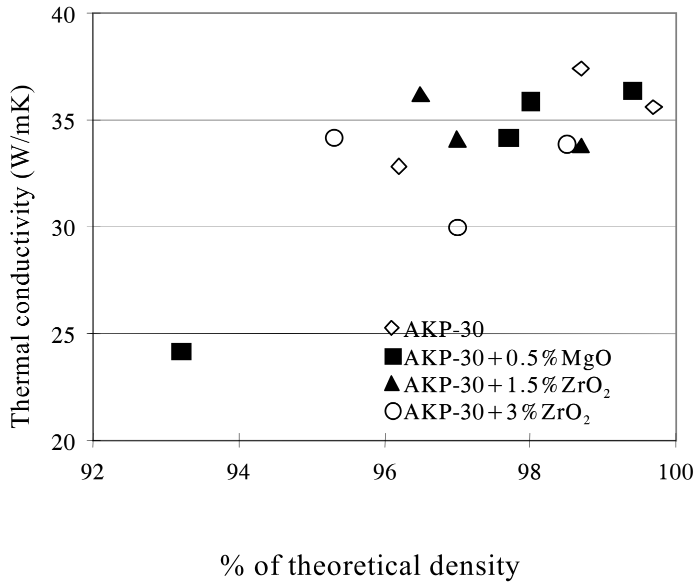


Figure 5. Thermal conductivities of sintered Al_2O_3 ceramics (1450-1650°C) as a function of relative density.

To investigate the effect of heating on the thermal conductivity, specimens of AKP-30 without additive were sintered in a gas furnace in Japan at 1450, 1500 and 1550°C for 2 h. The heating rate was 30°C/h from R.T to 400°C followed by 80°C/h till soaking temperature. Therefore the total sintering time was about one day. The results are shown in Table 2. The relative densities of the specimens are from 98.0-99.5%. which are higher than those of the specimens sintered in the electric furnace (Table 1 and Figure 1). The density difference comes from the difference in heating schedule and atmosphere. In the electric furnace, total sintering time was about 7 h. In the gas furnace, hydrogen included in the fuel changed to H_2O, hence the moisture pressure in the atmosphere increased. The moisture might accelerate the sintering of Al_2O_3. It was found that the thermal conductivities of the specimens were in the same range with those shown in Figure 5.

Table 2. Densities and thermal conductivities of AKP-30 specimens sintered in a gas furnace for 1 day.

Sintering temperature (°C)	% of theoretical density	Thermal conductivity (W/mK)
1450	98.0 98.2	31.5 30.0
1500	98.5 98.2	31.6 31.8
1550	99.2 99.5	33.1 33.4

CONCLUSIONS

AKP-30 powder and AKP-30 powder with 0.5 wt% of MgO; 1.5 and 3.0 wt% of ZrO_2 were sintered nearly to full density at 1550°C for 2 h. The density reached the maximum at 1600°C for all compositions. The mechanical strength measured by the bi-axial pressure mode showed strength as high as 500 MPa. Thermal conductivity measured by the Laser Flash Method reached 35 W/mK on average when the relative density was over 95%. AKP-30 consolidated to almost full density (98% of theoretical density) at very low temperature (1450°C) when it was sintered in a gas furnace with a long time firing of about one day.

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