

Effects of Y_2O_3 additions on the densification and thermal conductivity of spark plasma sintering AlN ceramics

Kyoung Hun Kim^{a,*}, Joo Seok Park^{a,b}, Jong Pil Ahn^a, Jae Hong Chae^a, Byung Ha Lee^b and K. B. Shim^c

^aKorea Institute of Ceramic Engineering and Technology, Seoul 153-801, Korea

^bDepartment of Materials Science and Engineering, Myongji University, Yongin 449-728, Korea

^cDivision of Advanced Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea

Spark plasma sintering (SPS) of AlN ceramics was carried out with Y_2O_3 as a sintering additive at sintering temperatures of 1,550 to 1,700 °C. The effects of Y_2O_3 additions on the sintering behavior and thermal conductivity of AlN ceramics were studied. Y_2O_3 added to AlN showed a noticeable higher densification rate than pure AlN, but the formation of yttrium aluminate phases by the solid-state reaction of Y_2O_3 and Al_2O_3 occurred on the AlN surface which could retard the densification during the sintering process. The thermal conductivity of AlN specimens was improved by the addition of Y_2O_3 up to 3 wt% in spite of the formation of a YAG secondary phase in the AlN grain boundaries because Y_2O_3 additions could reduce the oxygen content in the AlN lattice which is primary factor controlling the thermal conductivity. However, the thermal conductivity decreased at a 5 wt% addition because the extra formation of the YAG phase in grain boundaries could decrease the thermal conductivity by phonon scattering thus surpassing the helpful contributions of smaller Y_2O_3 additions.

Key words: Aluminum nitride, Ytria, Thermal conductivity, Sintering.

Introduction

Aluminum nitride (AlN) ceramics have attracted significant attention due to their excellent thermal and electric properties as substrates and packaging materials for high power integrated circuits [1-3]. The estimated theoretical thermal conductivity of a pure AlN single crystal has been calculated to be $320 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature [1]. The heat carrier in AlN is the phonon. The thermal conductivity of polycrystalline AlN is affected by many factors such as grain boundaries, pores, secondary phases, impurities and lattice defects. In particular, the most harmful impurity has been found to be oxygen. Dissolved oxygen ions in AlN occupy the nitrogen sites, and they generate aluminum vacancies to compensate the electric charge balance. These lattice defects induced by oxygen significantly reduce the thermal conductivity by phonon scattering [1].

Densification of pure AlN during sintering is difficult because of its high degree of covalent bonding character. For full densification, rare-earth and/or alkaline earth oxides are often added in the fabrication of AlN ceramics [4, 5]. These sintering aids have a double role during sintering. One is to help in the formation of liquid phase which can promote the densification by the process of liquid-phase sintering. The other is to improve the thermal

conductivity by decreasing the oxygen impurities in the AlN lattice [4-7]. The popular sintering aid is Y_2O_3 which reacts with the aluminum oxide layer on the AlN surface. The reaction generates yttrium aluminate liquid phases which are supposed to promote liquid phase sintering of AlN during sintering process. The yttrium aluminate phases remain as grain boundary phases such as $Y_3Al_5O_{12}$ (YAG), $Y_4Al_2O_9$ (YAM) and $YAlO_3$ (YAP). In this way, Y_2O_3 acts as an oxygen getter by fixing aluminum oxide in the grain boundary phases. The type of phases remaining depends on the ratio of the amount of oxygen content in the starting AlN powder and the amount of Y_2O_3 additions [6-8].

Recently, the spark plasma sintering (SPS) process has attracted significant interest for the fabrication of poorly-sinterable materials such as borides, carbides and nitrides. The SPS process is a type of pressure sintering method which uses a high-temperature spark plasma generated by discharging in the gaps between powder particles with an on-off electrical current [9]. The generation of the spark plasma in the initial stage of the SPS process accelerates the neck formation and thermal diffusion, and has a surface-activating and cleaning effect on the particles being sintered. Also, the electrical field formed by the DC current accelerates diffusion. Therefore, the SPS process has been applied to the densification of poorly-sinterable materials at lower temperatures and in shorter times than is impossible with conventional sintering processes [9, 10].

In the present paper, rapid densification of Y_2O_3 -doped AlN was carried out using the SPS process at a relatively low temperature. We have studied the effect of Y_2O_3

*Corresponding author:
Tel : +82-2-3282-7870
Fax: +82-2-3282-2490
E-mail: khkim@kicet.re.kr

additions on the sintering behavior, microstructural evolution and thermal conductivity of AlN ceramics.

Experimental

Commercially available AlN powder (99.9%, Kojundo Chem., Japan) and Y_2O_3 powder (99.9%, Cerac, USA) were used as the starting materials. 1-5 wt% Y_2O_3 powder was added into the AlN powder as a sintering aid. The powder mixtures were ball-milled for 24 hours using Teflon-coated balls and ethanol as a mixing medium.

The dried mixtures were loaded into a graphite mold inside the SPS system (Dr. Sinter 515S, Sumitomo Coal and Mining Co., Japan). After applying an initial pressure of 40 MPa, the loaded mixtures were heated to the sintering temperature range from 1,550 to 1,700 for 5 minutes at a heating rate of 100 K/minute in a vacuum (< 10 Pa). After 5 minutes sintering at the temperature, the pressure was relaxed and the specimens were cooled in the chamber. The sintered bodies were typically 15 mm in diameter and 5 mm in thickness.

The bulk density was measured by the Archimedes method and an X-ray diffractometer (M03XHF22, MAC Science Co., Japan) was used to analyze the phases in the powders and sintered bodies. The thermal conductivity was calculated from the thermal diffusivity and specific heat measured by a laser flash technique (LFA 427, NETZSCH, Germany) and the bulk density. The microstructural characterization was carried out with a scanning electron microscope (SEM, 5900LV, JEOL, Japan).

Results and Discussion

Fig. 1 shows the effect of the variation of the sintering temperature and the amount of Y_2O_3 -added on the relative density of sintered AlN specimens. The density increased significantly with an increase of the sintering temperature for pure AlN specimens, with a relative density about

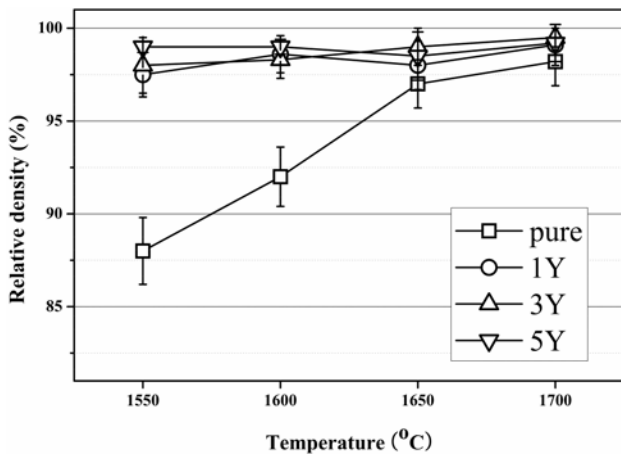


Fig. 1. Relative density of AlN specimens as a function of sintering temperature and amount of sintering aid (1Y $\equiv$ 1 wt% Y_2O_3 , 3Y $\equiv$ 3 wt% Y_2O_3 and 5Y $\equiv$ 5 wt% Y_2O_3).

97% theoretical achieved at 1,650 °C. Furthermore, the relative densities of the Y_2O_3 -added AlN specimens reach over 97% theoretical at 1,550 °C. It is hard to obtain high density AlN ceramics at such a low temperature using conventional sintering methods. It has been reported that the relative density of a pure AlN ceramic fabricated by a pressureless sintering method was 75% after sintering at 1,800 °C for 3 hours [11] and fully dense AlN ceramics could be obtained at above 1,700 °C for long soaking time with sintering aids using a hot-pressure sintering method [12, 13]. These comparisons clearly indicate that superior densification can be achieved through the SPS process.

Fig. 2 shows the XRD patterns of AlN powder and sintered specimens with and without Y_2O_3 addition after sintering at 1,700 °C. YAG phase was found to be a secondary phase in the Y_2O_3 -added AlN specimens.

Fig. 3 shows the Z-axis displacement of the lower punch of the SPS system during the sintering process. The displacement directly reflects the initial sintering temperature and shrinkage behavior of powders during the sintering process in real time. At the beginning of the heating

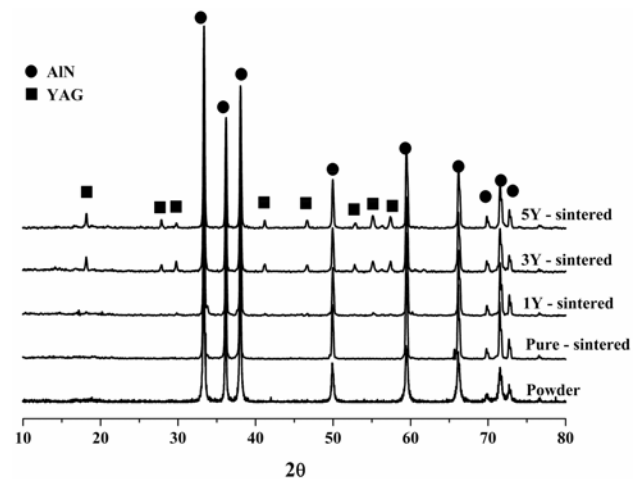


Fig. 2. XRD patterns of pure AlN powder and Y_2O_3 added AlN specimens sintered at 1,700 °C for 5 minutes.

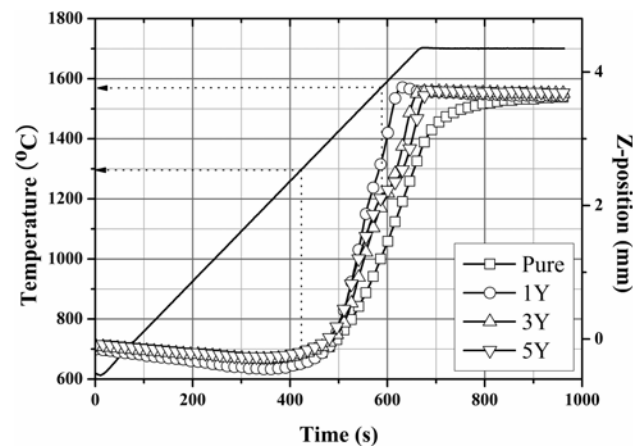


Fig. 3. Densification behavior of AlN powders during the spark plasma sintering process.

process, all samples expanded due to thermal expansion. Then, the samples began to shrink at a certain temperature. This temperature was the initial sintering temperature and for the pure AlN powder was about $1,380^\circ\text{C}$, while it was about $1,300^\circ\text{C}$ for the Y_2O_3 -added powders. Also, after reaching the sintering temperature, $1,700^\circ\text{C}$, pure AlN powder continued to shrink, while Y_2O_3 -added powders stopped shrinking. These results indicated that Y_2O_3 additions were beneficial in lowering the sintering temperature and promoting the densification of AlN ceramics.

In the case of Y_2O_3 additions, a retardation of densification was observed at about $1,580^\circ\text{C}$. This retardation was quite clear with an increase in the amount of Y_2O_3 addition. Qiao *et al.* reported that the formation of yttrium aluminate phases by solid state reactions could decrease the densification of AlN ceramics [14]. Referring to the XRD results shown in Fig. 2, the retardation of densification originated from the formation of the YAG phase through the solid state reaction between Y_2O_3 and Al_2O_3 .

Fig. 4 shows SEM images of fractured surfaces of AlN specimens sintered at $1,700^\circ\text{C}$. It has been reported that the Y_2O_3 -added AlN ceramics fabricated by a conventional sintering process showed a clear inter-granular fracture mode [11-13, 15]. However, the SPS-sintered AlN specimens showed mostly an intra-granular fracture mode. The YAG phase was found in the Y_2O_3 -

added specimens and their distribution increased with an increase in the amount of Y_2O_3 -added.

Fig. 5 shows the thermal conductivities of AlN specimens. The thermal conductivity improved with an increase in the sintering temperature due to grain-growth and an increase in the density. In the case of Y_2O_3 additions, the thermal conductivity improved up to a 3 wt% addition, but it then decreased somewhat for a 5 wt% addition. Y_2O_3

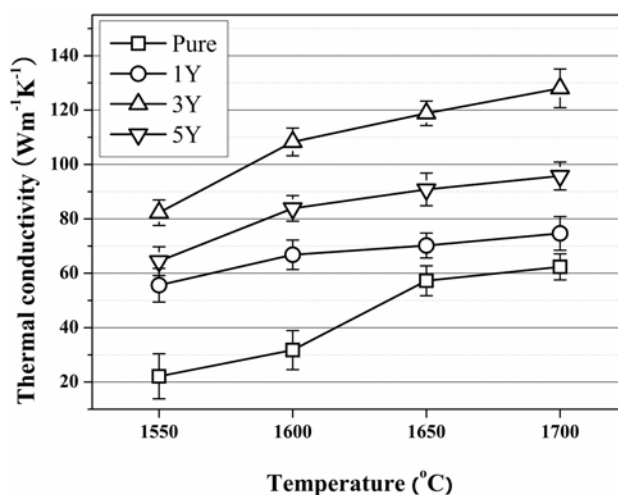


Fig. 5. Variation of the thermal conductivity of AlN specimens as a function of sintering temperature for 5 minute sintering.

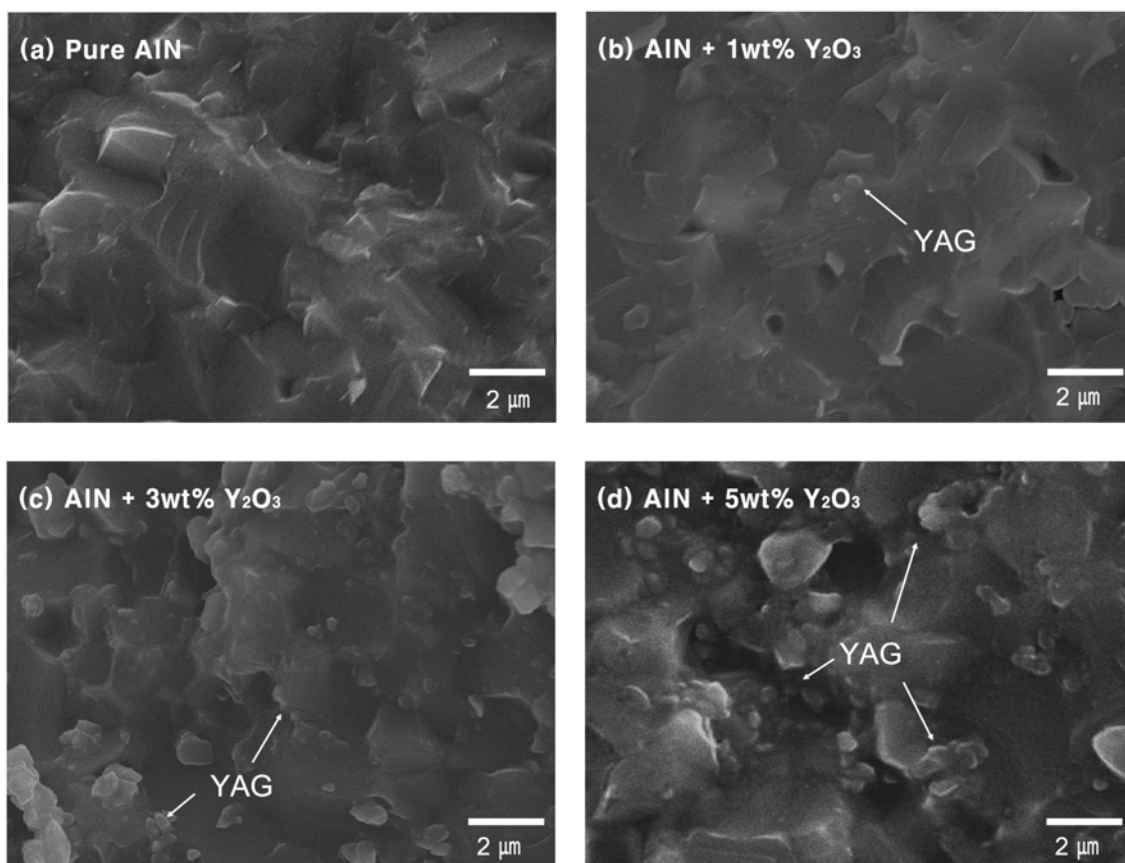


Fig. 4. SEM images of fractured surfaces of AlN specimens sintered at $1,700^\circ\text{C}$ for 5 minutes.

additions will improve the thermal conductivity of AlN ceramics through the reduction of oxygen content in the AlN lattice, but this could be accompanied by the formation of yttrium aluminate secondary phases, which can decrease the thermal conductivity because the secondary phases have very much lower thermal conductivities (YAG: $11 \text{ Wm}^{-1}\text{K}^{-1}$ [16]) than that of AlN and they can scatter the thermal conduction by phonon [1, 2]. In this study, the improvement of the thermal conductivity up to 3 wt% Y_2O_3 addition in spite of the presence of YAG secondary phases means that the dominant factor in the thermal conduction was the oxygen content in the AlN lattice. However, in case of a 5 wt% addition, the decrease of the thermal conduction compared with the 3 wt% Y_2O_3 -added specimen originated from the phonon scattering by the YAG phase.

Conclusions

Fully-densified AlN ceramics could be achieved by the SPS process at a lower temperature sintering and in a shorter time than by a conventional sintering process. The densification of AlN ceramics was accelerated significantly by Y_2O_3 additions. However, the densification could be retarded by the addition of Y_2O_3 due to the solid state reaction between Y_2O_3 and Al_2O_3 . A YAG phase was formed as a secondary phase by the addition of Y_2O_3 . The thermal conduction of AlN ceramics could be improved by Y_2O_3 additions due to the reduction of oxygen content in the AlN lattice. However, it could be reduced by the excess formation of yttrium aluminate secondary phases. In this study, the optimum amount was a 3 wt% Y_2O_3 addition and the highest thermal conductivity value was $127 \text{ Wm}^{-1}\text{K}^{-1}$ for a 3 wt% Y_2O_3 -added AlN specimen sintered at $1,700^\circ\text{C}$ for 5 minutes.

References

1. G.A. Slack, J. Phys. Chem. Solids 34 (1973) 321-335.
2. L.M. Sheppard, Am. Ceram. Soc. Bull. 69 (1990) 1801-1803.
3. Y. Baik and R.A. Drew, Key Eng. Mater. (1996) 122-124, 553-570.
4. K. Komeya, H. Inoue and A. Tsuge, Yogyo-Kyokaishi 93 (1985) 41-46.
5. K. Komeya, H. Inoue and A. Tsuge, J. Am. Ceram. Soc. 54 (1974) 411-412.
6. A.V. Virkar, T.B. Jackson and R.A. Cutler, J. Am. Ceram. Soc. 72 (1989) 2031-2042.
7. T.B. Jackson, A.V. Virkar, K.L. More, R.B. Dinwiddie and R.A. Cutler, J. Am. Ceram. Soc. 80 (1997) 1421-1435.
8. M. Kasori and F. Ueno, J. Euro. Ceram. Soc. 15 (1995) 435-443.
9. M. Tokita, J. Soc. Powder & Tech. Jpn. 30 (1993) 790-804.
10. M. Omori, Mater. Sci & Eng. A 287 (2000) 183-188.
11. S.F. Horvath, S.R. Witek and M.P. Harmer, in "Ceramic Substrates and Packages for Electronic Application, Advanced in Ceramics" (American Ceramic Society, 1989) 26 121-132.
12. G. Pezzotti, A. Nakahira and M. Tajika, J. Euro. Ceram. Soc. 20 (2000) 1319-1325.
13. J.Y. Qiu, Y. Hotta, K. Watari, K. Mitsuishi and M. Yamazaki, J. Euro. Ceram. Soc. 26 (2006) 385-390.
14. L. Qiao, H. Zhou, H. Xue and S. Wang, J. Euro. Ceram. Soc. 23 (2003) 61-67.
15. M. Medraj, Y. Baik, W.T. Thompson and R.A.L. Drew, J. Mater. Proc. Tech., 161 (2005) 415-422.
16. P.H. Klein and W.J. Croft, J. Appl. Phys. 38 (1967) 1603-1607.