

Sintering Behavior of Aluminum Nitride Doped with Y_2O_3

A.L. Molisani⁽¹⁾, H. Goldenstein⁽¹⁾, A.C. da Cruz⁽²⁾, A.H.A. Bressiani⁽³⁾, J.C. Dutra⁽⁴⁾,
J.L.A. Manholetti⁽²⁾, G.I. Horita⁽²⁾ e H.N. Yoshimura⁽²⁾

- (1) EPUSP – Escola Politécnica da Universidade de São Paulo
(2) IPT – Instituto de Pesquisas Tecnológicas do Estado de São Paulo
(3) IPEN – Instituto de Pesquisas Energéticas e Nucleares
(4) FEI – Faculdade de Engenharia Industrial

Keywords: AlN, sintering, Y_2O_3 , second phase, microstructure.

Abstract: The aim of this study was to investigate the sinterability of a commercial AlN powder doped with Y_2O_3 . It was done by sintering several samples with different compositions in a graphite furnace using a nitrogen atmosphere. The effect of the sintering temperature (between 1500 and 1700 °C) was studied by isochronal heat treatments whilst its kinetics was studied by isothermal sintering treatments at 1600 °C for different times. Sintered samples were characterised by density measurements, secondary electron image analysis and energy dispersive spectroscopy in SEM, to investigate their microstructural evolution. Pure AlN samples showed low sinterability in both series of experiments, reaching maximum relative densities of approximately 60%, when they were sintered at 1600 °C for 8 h and 1700 °C for 1 h. Additions of Y_2O_3 promoted the densification of AlN. However, the range of sintering temperatures utilised in this work was not enough to produce high density ceramics. The samples doped with Y_2O_3 presented lower weight loss than pure AlN samples.

Introduction

Aluminium nitride is an advanced ceramics constituted mainly of covalent bonds and presents an hexagonal crystalline structure 2H, similar to wurtzite. [1,2] It has several distinct physical properties, such as high thermal conductivity, low thermal expansion coefficient (closer to the silicon one), high resistivity, low dielectric constant, and high dielectric rupture resistance. These properties are remarkable, making its use possible on the manufacturing of electronic devices. [3] AlN may be used in the substrates for high power and high frequency devices, LSI and VLSI device packages, laser components, thyristor insulators, and structural parts resistant to corrosion and heating. AlN with high thermal conductivity has been produced by using sintering additives, such as CaO and Y_2O_3 . [4,5] This additive has a double role: to promote the densification of AlN and to capture the oxygen from the oxide layer present in the AlN powder surface, therefore prevent it from going into solution in the AlN crystalline cell, which causes a high decrease in thermal conductivity. [6]

This work investigates the influence of Y_2O_3 content on the sintering of AlN by conventional sintering in a graphite furnace, varying the temperature from 1500 to 1700 °C, and the sintering time from 0.3 to 8 h at 1600 °C.

Materials and Methods

AlN powders with and without addition of Y_2O_3 were prepared with the following compositions: 0.5, 2.0, and 4.0 wt.% Y_2O_3 . The amount of binder (polyethylene glycol) was

2.0 wt.% on the basis of the total mass quantity. Green samples were obtained by cold isostatic pressing (CIP) with 150 MPa after uniaxial pressing with 10 MPa.

The sintering treatment was performed in a graphite resistance furnace (Thermal Technology - 1000-560-FP20) under a nitrogen atmosphere with heating and cooling rates of 10 and 30 °C/min, respectively. The samples were sintered in a graphite crucible internally coated with BN and a pure AlN powder bed under them. A series of isochronal sintering treatments was performed at 1500, 1600, and 1700 °C for 1 h and another series of isothermal sintering treatments was done at 1600 °C for 0.33, 1, 3, and 8 h.

Both green and sintered densities were measured by the geometrical method. The relative densities were calculated on the basis of the theoretical density of AlN, 3.261 g/cm³. The sintered samples were characterised by secondary electron image analysis and energy dispersive spectroscopy in SEM (Jeol JSM-6300).

Results

The effect of sintering temperature upon the densification of AlN with or without addition of Y₂O₃ is shown in Fig. 1. It can be observed that the addition of Y₂O₃ enhances the sinterability of AlN.

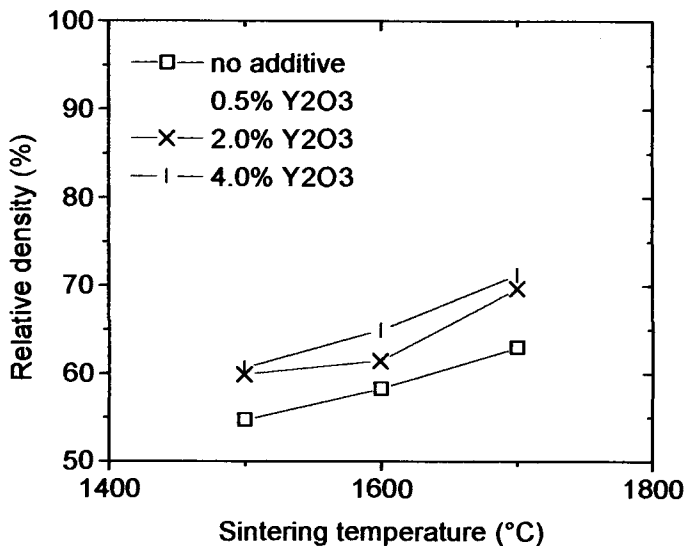


Fig. 1 – Relative densities of AlN samples doped with Y₂O₃ for different sintering temperatures (1h).

The increasing of the sintering temperature, between 1500 and 1700 °C, promotes an increase in density of all samples, i.e. with or without addition of Y₂O₃. Furthermore, the increase in the amount of Y₂O₃ content had a tendency to raise the density of AlN within the range studied (0.5 a 4.0 wt.%).

The effect of sintering time at 1600 °C upon the densification of all AlN samples may be seen in Fig. 2. It can also be observed that both the sintering time and the Y₂O₃ addition enhance the

densification of AlN. In general, the densities of the samples with different additive contents, for a given sintering time, were similar.

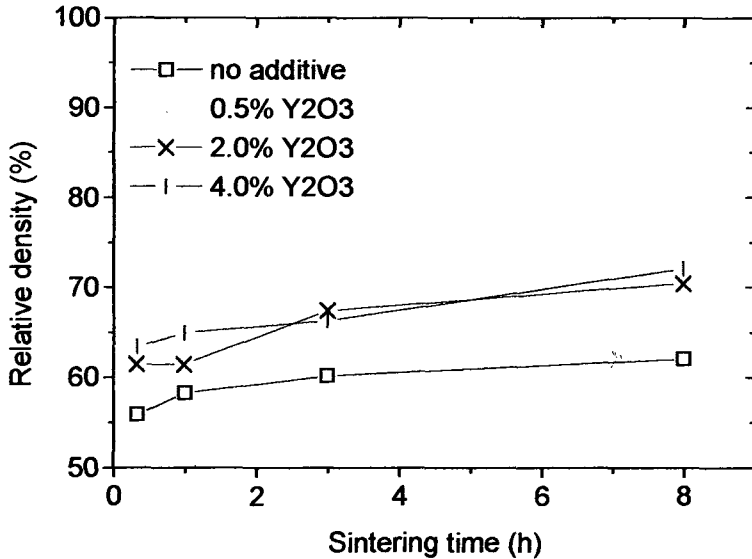


Fig. 2 - Relative densities of AlN samples doped with Y₂O₃ for different sintering times.

The average relative density of all AlN green samples was around 55%. The densities of sintered samples achieved around 70% for the doped samples with 4 wt.% Y₂O₃ and around 60% for pure AlN samples, when they were sintered at 1600 °C for 8 h or 1700 °C for 1 h.

The weight loss of the pure AlN samples of both series of isochronal and isothermal sintering treatments was around 1%, while the samples doped with Y₂O₃ had weight loss around 0.5%.

Fig. 3a shows a micrograph of a pure AlN sample sintered at 1500 °C for 1 h. In this condition, either densification nor grain growth was observed; the average grain size was similar to the average particle size of the initial AlN powder observed in SEM. The low sinterability of pure AlN is due to covalent nature of the Al-N bond, hence requiring the use of sintering additives, which promotes the sintering of this material in lower temperatures by the liquid phase formation. [4,7,8,9]

Fig. 3b shows a pure AlN sample micrograph sintered at 1700 °C for 1 h. This micrograph is different to the one showed in the Fig. 3a, where the primary particles were discernible. The microstructure of Fig. 3b suggests the presence of a second phase surrounding the grains. As no additive was used in this sample, the presence of a second phase could have been caused by the transformation of the oxide surface layer on the initial AlN powder into aluminium oxinitride (AlON) above 1650 °C, which promotes the densification process. [10] EDS analysis of pure AlN samples sintered at 1500 and 1700 °C for 1 h detected the presence of aluminium, oxygen and nitrogen.

Fig. 4a shows a micrograph of an AlN sample doped with 4 wt.% Y₂O₃ sintered at 1500 °C for 1 h. There was not any evidence of densification or grain growth; the samples had a low relative density (~60%) and the grain size was also similar to the average particle size of the initial AlN

powder observed in SEM. Furthermore, was observed some grains bonded by necks, indicating that the sintering of AlN doped with Y_2O_3 could have occurred in the solid state at 1500 °C.

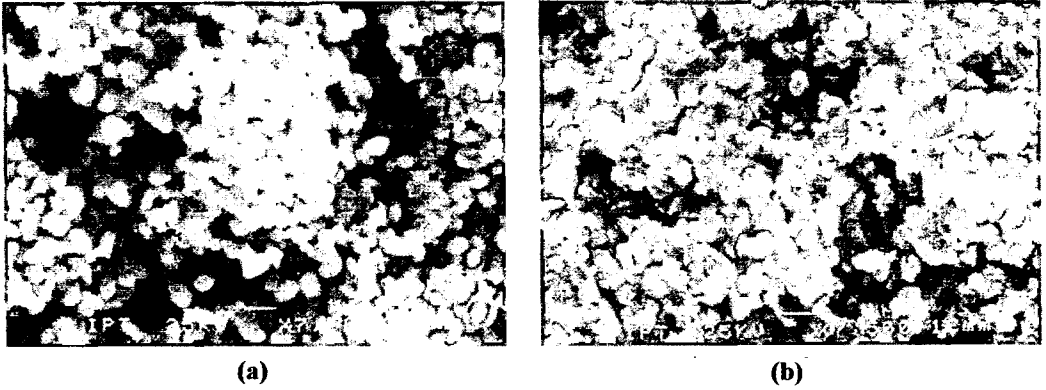


Fig. 3 – Secondary Electron Images of pure AlN samples sintered for 1h at: (a) 1500°C; (b) 1700°C.

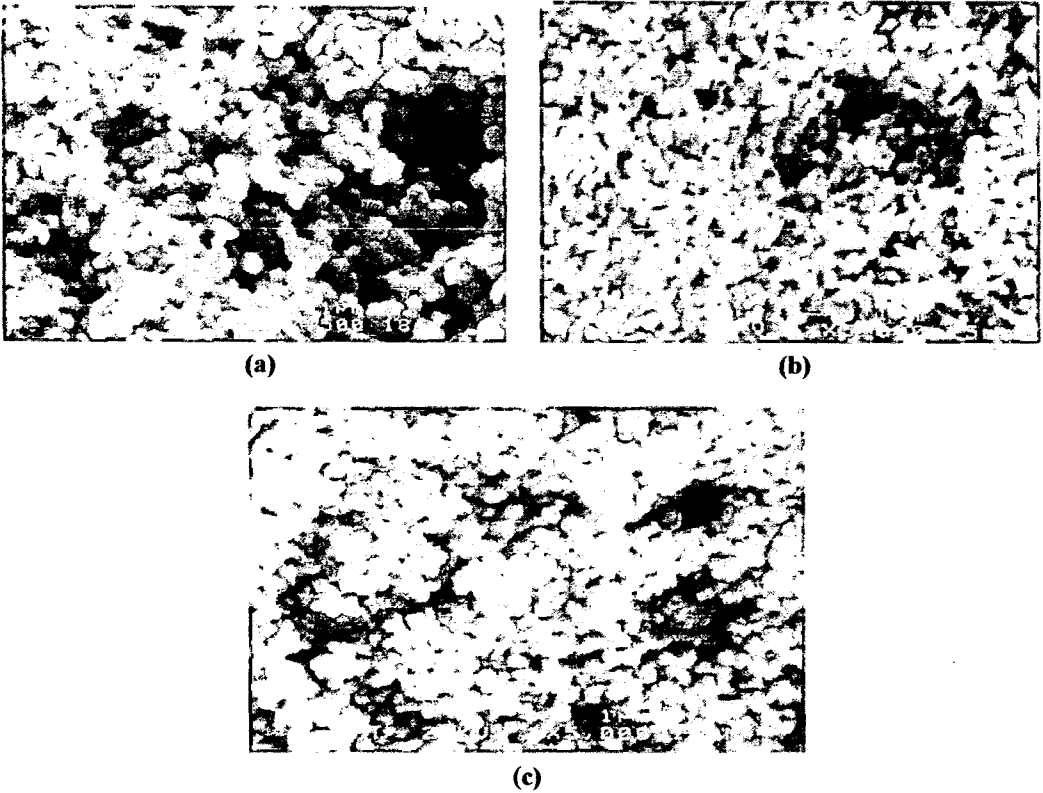


Fig. 4 – Secondary Electron Images of AlN samples doped with 4 wt.% Y_2O_3 sintered at: (a) 1500°C for 1 h, (b) 1600°C for 8 h, and (c) 1700°C for 1 h.

Tajika et al. [11] studied the sinterability of many types of AlN powder doped with Y_2O_3 by dilatometry and observed that the sintering of these powders occurred in the solid state between 1300 and 1500 °C. There is also another report [12] showing that the sintering of AlN doped with Y_2O_3 occurred in the solid state between 1125 and 1500 °C.

Fig. 4b shows a micrograph of an AlN sample doped with 4 wt.% Y_2O_3 sintered at 1600 °C for 8 h. This micrograph also suggests the presence of a second phase surrounding the grains, indicating that liquid phase sintering took place at 1600 °C, although there is a report indicating that the lowest liquidus temperature for the system AlN-Al₂O₃-Y₂O₃ is 1686°C.[7] On the other hand, Koestler et al. [12] reported that sintering with liquid phase of Y_2O_3 -doped AlN starts above 1500 °C, although the samples only reached a full density after they had been sintered above 1800°C.

Fig. 4c shows a micrograph of an AlN sample doped with 4 wt.% Y_2O_3 sintered at 1700 °C for 1 h. On the one hand, its relative density was very close to the one from the same sample, but sintered at 1600 °C for 8 h; on the other hand, its volumetric fraction of second phase was much lower than the last one. EDS microanalysis of these samples showed the presence of aluminium and of yttrium in low percentage.

Summary

Pure AlN showed low sinterability when sintered between 1500 and 1700 °C, due to covalent nature of the Al-N bond, which difficulty its densification;

Pure AlN samples sintered at 1700 °C for 1 h seemed to have a second phase surrounding the grains, that could be resulted from the transformation of the oxide surface layer on the initial AlN powder into aluminium oxinitride (AlON) phase.

The presence of Y_2O_3 in AlN ceramics decreased the weight loss when compared to its value for pure AlN ceramic;

The samples with Y_2O_3 sintered at 1500 °C for 1 h had some grains bond by necks and very low density. The presence of a second phase surrounding the grains was observed at 1600°C, which increased its volumetric fraction with the increase sintering time in this temperature;

In general, the use of Y_2O_3 as sintering aid enhanced the AlN densification process between 1500 and 1700 °C, although the values of maximum relative density obtained in the range from temperature studied were low (~70 %).

Acknowledgements

The authors wish to thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the financial support of this work. Projects n° 99/14864-5 and 01/03968-9.

References

- [1] T.J. Morz, Jr., Am. Ceram. Soc. Bull., Vol. 72, n° 6, (1993), p. 78.
- [2] A.K. Knudsen, Am. Ceram. Soc. Bull., Vol. 74, n° 6, (1995), p. 97.
- [3] K. Watari, M.E. Brito, M. Yasuoka, M.C. Valecillos, S. Kanzaki, J. Am. Ceram. Soc., Vol. 103, n° 9 (1995), p. 891.
- [4] Y. Kurokawa, K. Utsumi, H. Takamizawa, J. Am. Ceram. Soc., Vol. 71, n° 7, (1988), p. 588.
- [5] P.S.D. Baranda, A.K. Knudsen, E. Ruh, J. Am. Ceram. Soc., Vol. 77, n° 7, (1994), p. 1846.
- [6] G.-C. Lai, Y. Nagai, J. Am. Ceram. Soc. Japan, Vol. 103, n° 1, (1995), p. 6.
- [7] K. Watari, H.J. Hwang, M. Motohiro, and S. Kanzaki, J. Mater. Res., Vol. 14, N° 4, (1999), p. 1409.

- [8] A. Bellosi, L. Esposito, E. Scafè, and L. Fabbri; *J. Mater. Sci.*, Vol. 29, (1994), p. 5014.
- [9] M.-C. Wang, C.-K. Hong, M.-S. Tsai, and N.-C. Wu; *J. Ceram. Soc. Japan*, Vol. 108, n° 10, (2000), p. 869.
- [10] Y.-W. park, S.-C. Choi, in *Proceedings of the Third European Ceramic Society Conference*, Ed. P. Duran and J.F. Fernandez, Faenza Editrice Iberica, Madrid in Spain, Vol. 1, (1993), p. 955.
- [11] M. Tajika, W. Rafaniello, K. Niihara, *Materials Letters*, Vol. 46, (2000), p. 98.
- [12] C. Koestler, H. Bestgen, A. Roosen, W. Boecker, in *Proceedings of the Third European Ceramic Society Conference*, Ed. P. Duran and J.F. Fernandez, Faenza Editrice Iberica, Madrid in Spain, Vol. 1, (1993), p. 955.