JOURNAL OF MATERIALS SCIENCE **34** (1999) 1553–1556

The effect of carbon coating of AlN powder on sintering behavior and thermal conductivity

T. NAKAMATSU, F. POMAR*, K. ISHIZAKI
School of Mechanical Engineering, Nagaoka Gijutsu-Kagaku Daigaku (Nagaoka University of Technology), Niigata 940-2188, Japan
E-mail: tetsuya@ishizaki.nagaokaut.ac.jp

High thermal conductive AlN ceramics doped with Y_2O_3 were produced by sintering the powders obtained after applying a carbon coating to the surface of AlN powder grains. During sintering at 1800 °C for 1 hour, the carbon reacts with the surface of the AlN grains by carbothermal-reduction of Al_2O_3, and also with the $Al_2Y_4O_9$ intermediate phase to form AlN, Y_2O_3 and CO. By adding 0.56 mass% of carbon, almost all the $Al_2Y_4O_9$ is reacted and the thermal conductivity increases from 184 W/(m · K) to 224 W/(m · K). Further carbon addition decreases the thermal conductivity and also the final sintered density. © *1999 Kluwer Academic Publishers*

1. Introduction

Aluminum nitride (AlN) is a ceramic with high intrinsic thermal conductivity, electrical properties similar to those of alumina (Al_2O_3), but with a low thermal expansion coefficient similar to that of silicon crystal. Therefore AlN has been considered as an ideal substrate for semiconductors.

Many papers have been published about the effects of different additives and atmospheres on AlN sintering [1–9]. In this study, the authors have investigated the influence of a carbon (C) coating on AlN ceramic powder doped with yttria (Y_2O_3) using a carbon coating method developed by the author's group to achieve toughening of silicon nitride (Si_3N_4) [10–18]. A carbon coated AlN powder was produced by decomposition of methane gas on AlN powder, and this was then mixed with Y_2O_3.

Y_2O_3 has two roles. Firstly, it reacts with Al_2O_3 which is usually present on the surface of AlN powder, to promote densification by forming an Al_2O_3-Y_2O_3 liquid phase during sintering. Secondly, it reacts with surface alumina and the oxygen dissolved in the AlN grains [19].

The reduction of grain boundary oxides by C directly deposited on the surface of AlN grains was studied to obtain a high thermal conductivity AlN ceramic.

2. Experimental procedure

2.1. Carbon deposition process

Characteristics of the raw AlN powder supplied by Atochem are listed in Table I. A furnace specially built for C deposition on the AlN powder is shown in Fig. 1. Raw AlN powder was placed in a thimble type filter made of silica fibre. To prevent contamination from the filter (which tended to crumble), a perforated carbon foil was placed between the filter and the powder. The assembly was heated in 0.3 l/min of methane (CH_4) and 0.7 l/min of argon (Ar) gas flow. At 800 °C, CH_4 is thermally decomposed:

$$CH_4 = C + 2H_2 \tag{1}$$

By changing the treatment period at this temperature, AlN powders with different carbon contents were produced. The deposited carbon was in the form of a very uniform thin film, not detectable by X-ray diffraction. The carbon content was measured by combustion using a LECO analyzer.

2.2. Sample preparation and characterization

Carbon coated AlN powder is mixed with 5 mass% of Y_2O_3 (average particle size: 1.6 μm, specific surface area: 8.4 m^2/g, supplied by Shin-etsu Chemical) in a ceramic mortar for 25 min. Two grams of the mixture are pressed into cylinders (14 mm in diameter, 7 mm in height) using a hydraulic press with stainless steel dies. Powder compacts are CIPed at 400 MPa and sintered in a tungsten crucible for one hour at 1800 °C under one atmosphere of nitrogen gas, using a furnace equipped with tungsten heating elements.

The crystalline phases after sintering are identified by X-ray diffraction. The densities are measured by the Archimedean method in toluene. Thermal diffusivity at room temperature is measured by the laser flash method with samples ground to 3 mm in thickness. Thermal conductivity (K) is calculated using a published value of 7.201 cal/(mol · K), (0.734 J/(g · K)) for the heat capacity (C_p) of AlN at room temperature [20]:

$$K = C_p \lambda d \tag{2}$$

---

* *Present address*: Societe Europeenne Des Produits Refractaires, B. P. N25, 84131 Le Potet Cedex, France.

TABLE I Specifications of raw AlN powder used

Particle size ϕ_{50} (μm)	2.4
Specific surface area (m^2/g)	2.4
Impurity	
O (mass%)	1.1
C (mass%)	0.069
Fe (ppm)	<50
Si (ppm)	50
Ca (ppm)	30

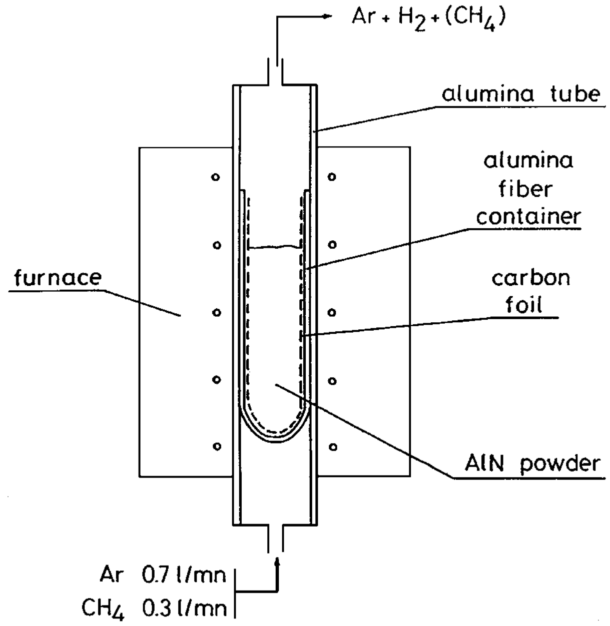

Figure 1 Schematic diagram of the furnace used for carbon coated powder production.

where λ and *d* are the thermal diffusivity and the density, respectively.

3. Results and discussion

3.1. X-ray diffraction analysis

Previous studies by Watari *et al.* [21] on the sintering of AlN with Y_2O_3 under a reducing carbon atmosphere confirmed the presence of CO and CO_2 gases in fractured AlN specimens by mass spectrometry. Watari *et al.* reported the following possible reactions (3)–(6) to reduce the $xAl_2O_3yY_2O_3$ phase at the grain boundary:

$$Al_2O_3 + N_2 + 3CO = 2AlN + 3CO_2 \quad (3)$$

$$Y_2O_3 + N_2 + 3CO = 2YN + 3CO_2 \quad (4)$$

$$Al_2Y_4O_9 + N_2 + 3CO = 2AlN + 2Y_2O_3 + 3CO_2 \quad (5)$$

and CO_2 gas could be reduced to CO gas by reaction with carbon in the furnace by:

$$CO_2 + C = 2CO \quad (6)$$

The usual carbothermally-reducing atmosphere cannot supply enough carbon inside a powder compact especially during densification. Therefore most of the Al_2O_3 on the AlN powder surface remains up to high temperatures and then reacts with the Y_2O_3 additive to form a liquid phase.

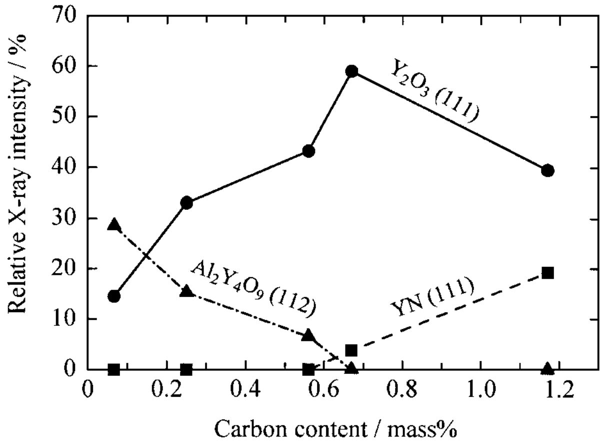

Figure 2 Relative intensities of intermediate phases ($Al_2Y_4O_9$, Y_2O_3 and YN) in AlN ceramics after 1 hour at 1800 °C as a function of carbon content in the starting AlN-Y_2O_3-C mixture.

In samples without a carbon coating, reaction (3) occurs in preference to reaction (4), and the grain boundary composition gradually changes from $xAl_2O_3yY_2O_3$ to Y_2O_3, which can be explained by the higher equilibrium oxygen partial pressure of Al_2O_3 compared with Y_2O_3, as evaluated by thermodynamic calculations (Ishizaki *et al.* [22, 23]), and experimentally shown by Yagi *et al.* [24].

Relative intensities of $Al_2Y_4O_9$ (112), Y_2O_3 (111) and YN (111) X-ray diffraction are shown in Fig. 2 for sintered samples with different carbon contents. The first point at 0.066 mass% of carbon corresponds to carbon impurity in the raw AlN powder. The peak intensities are normalized relative to the AlN (102) peak. In samples without carbon addition, $Al_2Y_4O_9$ and Y_2O_3 are present in the grain boundaries. Additions of small amounts of C may have two effects on the variation in relative intensity. One effect is the reduction of surface Al_2O_3 on the AlN powder during heating up and before the starting of densification, and the other is transformation of $Al_2Y_4O_9$ into AlN and Y_2O_3 by the following reactions:

$$Al_2O_3 + N_2 + 3C = 2AlN + 3CO \quad (7)$$

$$Al_2Y_4O_9 + N_2 + 3C = 2AlN + 2Y_2O_3 + 3CO \quad (8)$$

Reactions (7) and (8) have not been thoroughly considered, but Watari *et al.* [21] applied and reformulated the equations for the C coated AlN powder. The complete disappearance of $Al_2Y_4O_9$ is achieved for samples containg 0.67 mass% of C addition. For compositions sintered with more than 0.56 mass% of C, all the $Al_2Y_4O_9$ phase is transformed after sintering and a YN peak appears on X-ray diffraction patterns due to the nitridation of Y_2O_3 formed from transformation of $Al_2Y_4O_9$.

3.2. Carbon content in sintered bodies

The amounts of carbon in the AlN bodies after sintering relative to the carbon content present in the starting mix are plotted in Fig. 3.

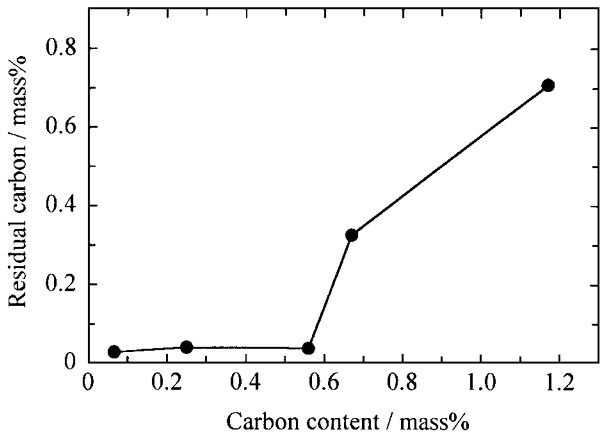

Figure 3 Amount of residual carbon in AlN ceramics after sintering at 1800 °C for 1 hour as a function of carbon content in the starting AlN-Y_2O_3-C mix. Addition of C more than 0.56 mass% produces residual C and its amount increases as C incorporation increases.

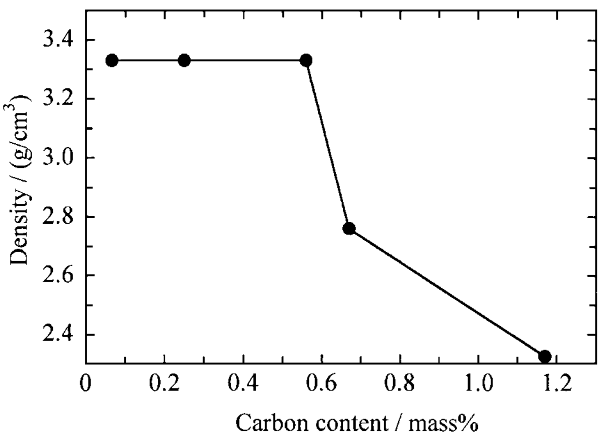

Figure 4 Change in density of AlN ceramics sintered at 1800 °C for 1 hour as a function of carbon content in the starting AlN-Y_2O_3-C mixture. The density decreases when more than 0.56 mass% of C is added.

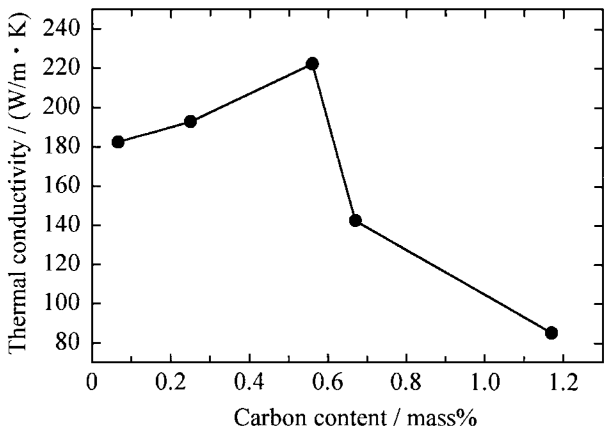

Figure 5 Change in thermal conductivity of AlN ceramics sintered at 1800 °C for 1 hour as a function of carbon content in the starting AlN-Y_2O_3-C mixture. The highest thermal conductivity 224 W/(m · K) was obtained for 0.56 mass% of C addition, and more C addition decreased thermal conductivity.

For samples sintered without C addition or with less than 0.56 mass% of C addition, the carbon contents after sintering are constant at around 0.04 mass%, which is negligible. The carbon incorporated is removed in gaseous form by reduction of the powder surface before densification and also in grain boundaries, perhaps by conversion to CO gas produced by the reactions (7) and (8).

However with further incorporation of C, elemental carbon remains in the sintered AlN bodies, and the carbon content after sintering tends to follow a line parallel to the dotted line. This residual carbon may consist of unreacted C in the AlN powder. According to the X-ray results in Fig. 2, for the samples with more than 0.56 mass% of carbon addition, the Y_2O_3 phase in transformed in situ to YN. Thus, there must be some production of CO gas, even if no more carbon is transformed. This phenomenon may be explained by the reduction of Y_2O_3 by CO and C (reactions (4) and (9)). Again, reaction (9) can be achieved with C coated powder:

$$Y_2O_3 + 3C + N_2 = 2YN + 3CO \qquad (9)$$

3.3. Effect of C content on density and thermal conductivity

Figs 4 and 5 show the effect of C content incorporated in the AlN-Y2O3-C starting mix on density and thermal conductivity. With up to 0.56 mass% of C additions, densified bodies were obtained; further additions of C reduced the density abruptly. Nevertheless, because complete densification was achieved with up to 0.56 mass% of C incorporation, and as the $Al_2Y_4O_9$ phase is transformed by reaction (5), the thermal conductivity of the resulting AlN ceramics was improved without needing to extend the sintering time. The thermal conductivity increased from 184 W/(m · K) without carbon to 224 W/(m · K) with 0.56 mass% of C incorporation.

With more than 0.56 mass% of C incorporation, the density was reduced and the thermal conductivity also decreased. The large amount of porosity (30% for samples sintered with 1.17 mass% of C) may be explained by two mechanisms, both suppressing densification. The first is the decrease of liquid phase by the reduction of surface Al_2O_3. Secondly excess C remaining on the AlN powder inhibits densification. Moreover the CO_2 gas coming from reaction (4) may not diffuse away as easily as CO gas coming out of the sample through the grain boundary, thus increasing the porosity.

It should be noted that optimum carbon amount is strongly related to the oxygen content of the starting mix, i.e., the surface oxygen content of AlN powder and Y_2O_3 as oxide additive. However, the carbon amount should be optimised for the required amount of liquid phase for densification and CO gas formation which suppress densification. The resulting 0.56 mass% C showing the highest thermal conductivity in this report is specific to the starting material used in this study.

4. Conclusions

High thermal conductivity AlN ceramics doped with Y_2O_3 were obtained by C coating on the AlN grains. First C reacts with the AlN powder surface, carbothermally-reducing Al_2O_3, and reacting with the $Al_2Y_4O_9$ intermediate phase to form a mixture of AlN,

Y_2O_3 and CO. The highest thermal conductivity of 224 W/(m · K) was obtained after complete removal of $Al_2Y_4O_9$, which occurs for 0.56 mass% of C addition. With further C incorporation, both the reduction of the powder surface and residual carbon suppress the densification and Y_2O_3 at the grain boundary is reduced by CO to form YN and CO_2. The CO_2 gas may cause an increase in porosity that reduces thermal conductivity.

References

1. N. KURAMOTO, H. TANIGUCHI, Y. NUMATA and I. ASO, *J. Ceram. Soc. Jpn.* **93** (1985) 517.
2. T. YAGI, K. SHINOZAKI, N. ISHIZAWA, N. MIZUTANI and M. KATO, *J. Amer. Ceram. Soc.* **71**(7) (1988) C-334–C-338.
3. Y. KUROKAWA, K. UTSUMI and H. TAKAMIZAWA, *J. Amer. Ceram. Soc.* **71**(7) (1998) 588–594.
4. K. WATARI, K. ISHIZAKI, T. HAMASAKI and T. FUYUKI, *J. Ceram. Soc. Jpn.* **96** (1998) 1043–1048.
5. N. ICHINOSE, in "Sintering 87, IISS Symp., Tokyo, November 1987," edited by S. Somiya, M. Shimada, M. Yoshimura and R. Watanabe (Elsevier Applied Science, London and New York, 1987) p. 950.
6. M. FUJIMOTO and S. UEDA, *J. Ceram. Soc. Jpn.* **96**(2) (1988) 1210–1213.
7. A. V. VIRKAR, T. B. JACKSON and R. A. CUTLER, *J. Amer. Ceram. Soc.* **72**(11) (1989) 2031–2042.
8. K. WATARI, K. ISHIZAKI and T. FUJIKAWA, *J. Mater. Sci.* **27** (1992) 2627–2630.
9. K. WATARI, K. ISHIZAKI and F. TSUCHIYA, *ibid.* **28** (1993) 3709–3714.
10. T. YANAI and K. ISHIZAKI, *J. Ceram. Soc. Jpn.* **101**(7) (1993) 744–748.
11. K. ISHIZAKI, M. NANKO, Y. KONDO and A. YAMADA, in "Advances in Porous materials," Proceeding of Mat. Res. Soc. Symp., Boston, November 1994 (Mat. Res. Soc., Pennsylvania, 1995).
12. T. YANAI and K. ISHIZAKI, *J. Ceram. Soc. Jpn.* **103** (1995) 1004–1009.
13. *Idem.*, *ibid.* **103** (1995) 1177–1181.
14. *Idem.*, *Silicates Industriels* **60**(7/8) (1995) 215–222.
15. *Idem.*, *Mater. Trans.* **37**(12) (1996) 1802–1805.
16. K. WATARI, K. ISHIZAKI and M. KAWAMOTO, *J. Ceram. Soc. Jpn.* **96** (1988) 128–134.
17. K. WATARI and K. ISHIZAKI, *ibid.* **96** (1988) 551–555.
18. K. WATARI, K. ISHIZAKI and M. KAWAMOTO, *J. Ceram. Soc. Jpn.* **96** (1988) 874–884.
19. F. UENO and A. HORIGUCHI, in "EURO-CERAMICS Vol. 1, Proceedings of the First European Ceramic Society Conference, Maastricht, June 1989," edited by G. de With, R. A. Terpstra and R. Metselaar (Elsevier Applied Science, London and New York, 1989) p. 1383.
20. JANAF Thermochemical Tables, 2nd ed., US Department of Commerce, National Bureau of Standarts, Washington DC, 1971.
21. K. WATARI, M. KAWAMOTO and K. ISHIZAKI, *J. Mater. Sci.* **26** (1991) 4727–4732.
22. K. ISHIZAKI and K. WATARI, *J. Phys. Chem. Solids* **50**(10) (1989) 1009–1012.
23. K. ISHIZAKI, in "Hot isostatic pressing: Theory and applications," the second International HIP Conference, June 1989, Maryland, (ASM International, Ohio DC, 1991) pp. 129–138.
24. T. YAGI, K. SHINOZAKI, N. MIZUTANI, M. KATO and Y. SAWADA, *J. Ceram. Soc. Jpn. Int'l. Ed.* **97** (1989) 1374–1381.

Received 19 October 1997
and accepted 15 October 1998