Journal of the European Ceramic Society 20 (2000) 783–787

Synthesis of aluminum nitride sintered bodies using the direct nitridation of Al compacts

Takuya Okada[a,*], Motohiro Toriyama[b], Shuzo Kanzaki[b]

[a] *Synergy Ceramics Laboratory, Fine Ceramics Research Association, Hirate-cho, Kita-ku, Nagoya, 462-8510, Japan*
[b] *National Industrial Research Institute of Nagoya, Hirate-cho, Kita-ku, Nagoya, 462-8510, Japan*

Received 22 April 1999; received in revised form 2 July 1999; accepted 8 August 1999

Abstract

For the purpose of simplifying processes and low impurities, the synthesis of aluminum nitride sintered bodies was tried using direct nitridation of aluminum compacts with 5 wt% of yttria in near-net shape, followed by sintering at 1900°C. To prevent changes in the compact shape, nitridation was performed at nominal temperatures below the melting point of Al, and under nitrogen pressures 0.5 MPa. After nitridation, the generated AlN compacts reached 70% of the theoretical density. Densities of 94% of the theoretical density were achieved by pressureless sintering at 1900°C for 8 h in nitrogen atmosphere, and the thermal conductivity was 155 W/mK. The effects of the oxygen content of AlN sintered body and the structure of the AlN compact on the thermal conductivity are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: AlN; Impurities; Nitridation; Nitrides; Substrates; Thermal conductivity

1. Introduction

Aluminum nitride (AlN) has several unique properties, such as high thermal conductivity, high electronic resistivity, a moderately low dielectric constant, and a relatively low thermal expansion coefficient close to the one of silicon.[1,2] These properties make AlN ideal as substrate material for electronic devices, especially power integrated circuits. The advance of the electronic devices with a high chip density requires a material with excellent properties, especially thermal conductivity, so AlN is expected to become an alternative material to alumina (Al_2O_3), which is mainly in use for this purpose now. However, despite its excellent properties, AlN is still in minor position compared with Al_2O_3 because of its high price, which makes it unsuitable for mass use.[3]

AlN does not exist in nature, and now it is synthesized by direct nitridation of metal aluminum (Al) powder or carbothermal reduction of Al_2O_3 powder in commercial form.[4] Direct nitridation has the advantage of low costs due to its simple reaction system and reaction temperature lower than that of carbothermal reduction, whereas it still presents several drawbacks.[4] One is that the nitridation needs high reaction temperature up to 1500°C (it is still lower than the reaction temperature of carbothermal reduction) and long reaction time. The formation of AlN on the surface of Al metal particles inhibits the diffusion of reactant nitrogen gas to the unreacted Al. In addition, large heat generated by the reaction between Al and nitrogen causes the coalescence of fine reactant Al particles, so that the difficulty of nitrogen diffusion is magnified. Therefore, for complete nitridation, high reaction temperature and extended reaction time are required. On the top of it, a grinding process is also needed, as the coalescence of reactant Al and high reaction temperature result in agglomerated AlN powder, which inhibits densification in the sintering process. It is necessary for good sinterability to grind the AlN agglomerated powder to decrease the particle size.[5] This treatment also increases impurities, especially oxygen, and results in the degradation of the properties of AlN products including thermal conductivity. These processes also make AlN powder much more expensive compared with other materials.

As it concerns the production of AlN ceramics (sintered bodies), current methods consist of many processing

---

[*] Corresponding author at current address: Research Center, Denki Kagaku Kogyo K. K. 3-5-1, Asahi-machi, Machida, Tokyo, 194-0023, Japan.

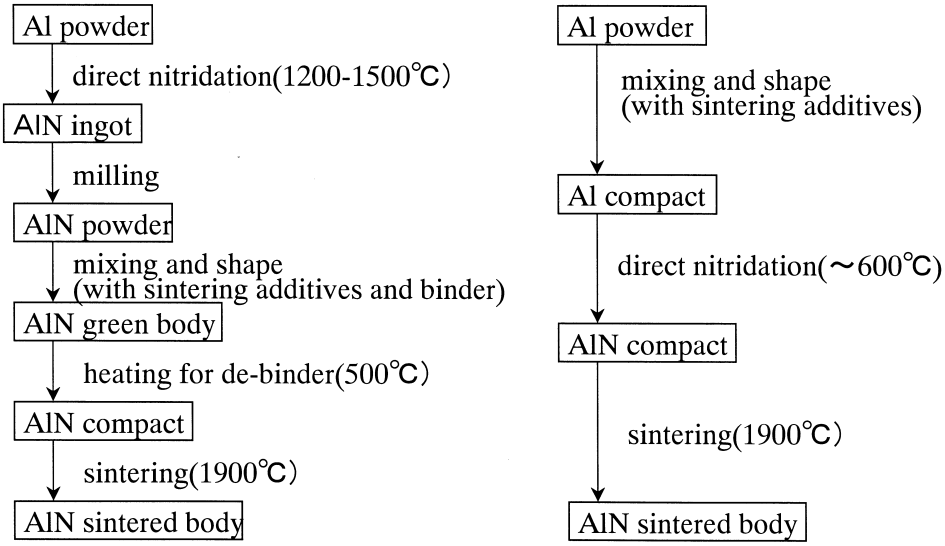
PII: S0955-2219(99)00204-6

steps: blending AlN powder with sintering additives, shaping green bodies using organic binder, drying up the binder, and sintering. The whole process of producing AlN ceramics is shown in Fig. 1(a). If it is possible to synthesize AlN compacts directly from Al metal compacts in near-net shape, the process can be drastically simplified, as shown in Fig. 1(b). In this simplified process, not only reduction of cost but also improvement of the properties of AlN could be expected, because of eliminating of the grinding procedure which increases impurities, as mentioned above. However, it is difficult to synthesize AlN compacts directly from Al compacts in near-net shape. The nitridation of Al compacts has been reported from various viewpoints. From the view of the self-propagating high temperature synthesis (SHS) method, several research works have been performed.[6–8] In these cases, over 100 MPa of nitrogen pressure are required for complete nitridation. In addition, the nitridation proceeds so explosively that the temperature of the reactant increases extremely, and as a result, the shape of the reactant entirely changed. It has also been reported that complete nitridation was achieved in atmospheric nitrogen at relatively low temperature by addition of little alkali or alkali-earth metal such as magnesium or calcium to Al metal,[9–11] but the required temperature for the nitridation is over 800°C, still higher than the melting point of Al. Reaction temperature must be reduced to at least below the melting point of Al for nitridation in near-net shape. There have been some reports of the complete nitridation of AlN–Al composite below of the melting point of Al as a kind of reaction sintering,[12] but major AlN content (over 50%) was required. In the case of the nitridation of Al compacts, the coalescence of the unreacted Al is more likely to take place than in the case of the nitridation of Al powder. Such coalescence makes the diffusion of enough nitrogen to complete nitridation more difficult.

In our group, direct nitridation of pure Al compacts (relative density 65%) in near-net shape have been tried, and complete nitridation could be achieved by pressure nitridation, under the reaction condition of low temperature, below the melting point of Al, and moderately pressured nitrogen atmosphere, a few MPa, without any reaction additives or diluents.[13,14] In the present study, the AlN sintered bodies were prepared by pressureless sintering of the AlN compacts synthesized directly from Al compacts by pressure nitridation. Several properties, including thermal conductivity, were also investigated.

2. Experimental procedure

Commercial Al atomized powder (ALCOA7123, with an average particle size of 24 μm by coulter-counter method and a BET surface area of 0.4 m^2/g) was mixed with 5 wt% of yttria (Y_2O_3), which results in 3.3 wt% after complete nitridation. The powder mixture was pressed to form disk pellets with a diameter of 12 mm and thickness of 2.5 mm. Their relative densities to theoretical were 65%. High purity nitrogen (99.999%) was used as a reaction gas. The schematic diagram is shown elsewhere.[14] The Al pellet, sustained by a graphite holder, was set in a reactor. A thermocouple was inserted to the pellet to record the temperature change during the nitridation. The reactor was put into the furnace and heated to 600°C with a constant rate of 10°C/min.



(a) (b)

Fig. 1. Processes flowchart for the preparation of AlN sintered body by (a) direct nitridation of Al powder (current process) and (b) direct nitridation of Al compacts in near-net shape.

During heating, the reactor was evacuated by a rotary pump. The vacuum pressure was about 100 Pa. After keeping the temperature for 30 min in vacuum, nitrogen gas was induced to the pressure of 0.5 MPa. Here, the temperature means the furnace temperature, but it was nearly equal to the sample temperature at the beginning of the nitridation. The nitridation time was 120 min. After nitridation, samples were picked up to check the nitridation ratio, and for some samples the microstructure was also investigated. The nitridation ratio was calculated from the weight gain of the pellet after nitridation. Then, AlN compacts were densificated by sintering in a graphite, resistance-heated furnace with a nitrogen flow rate of 2 l/min. The temperature was elevated to 1900°C with a rate of 5°C/min above 1000°C, and maintained for 8 h. The samples were contained in a boron nitride (BN) crucible with a BN cap to prevent decomposition and reduction reactions at the sample surface. The thermal diffusivity of the densified samples was evaluated by laser-flash method, and the thermal conductivity was calculated as a product of the thermal diffusivity, the thermal capacity and the density. Yttrium and oxygen content were determined using an inductively coupled plasma emission spectroscopy and an oxygen analyzer, respectively. Crystalline phases in the sample were identified by means of X-ray diffraction (XRD). The microstructure of the sample was observed by scanning electron microscopy (SEM), simultaneously energy dispersive spectroscopy (EDS) was used for elements distribution relative quantitative analysis. The densities of the samples were measured by Archimedean method using 2-propanol.

3. Results and discussion

Almost complete nitridation could be performed for powder compacts containing 5 wt% of Y_2O_3, as well as for Al compacts, by pressure nitridation below the melting point of Al, 600°C. The nitridation process and the structure of the generated AlN compact were investigated before sintering.

During the nitridation, the temperature of the pellet recorded by a thermocouple was only about 10°C higher than the furnace temperature. This indicates that the nitridation proceeded gradually, in contrast to an SHS process. The generated AlN compacts became a little thicker. The SEM image of the generated structure is shown in Fig. 2. The structure consisted of an inner part with lower density and an outer part with higher density. In the nitridation of aluminum molten alloy with a few % of alkali-earth metal, it is reported that nitridation product grows outward to the gas phase, perpendicular to the initial melt surface.[9] In the present case also, a similar process seems to take place. Inner unreact aluminum was partially melted by the heat of the reaction, and transported to the surface of the pellet by a kind of capillary rise phenomenon, so that the inner part resulted in a porous structure. The thickness of the inner part with lower density was about equal to that of the reactant Al compact, which also would suggest such a nitridation process. The reflection electron images of the fracture cross-section of the AlN compact is shown in Fig. 3. Bright points indicate the existence of yttrium in this image. Yttrium appears nonuniformly, mainly in the inner region. In EDS analysis, also, yttrium scarcely shows in the outer layer. It is considered that the outer layer is made from molten Al permeated from the inside. Y_2O_3, existing as solid, seems to be unable to follow the permeation, which results in its nonexistence in the outer layer. Overall relative density of the AlN compacts generated in 0.5 MPa was about 70%. Nitridation of Al results in 25% of density increasing. The density is lower than the expected value from the relative density of the starting reactant. This is attributed to the volume expansion that accompanies the nitridation.

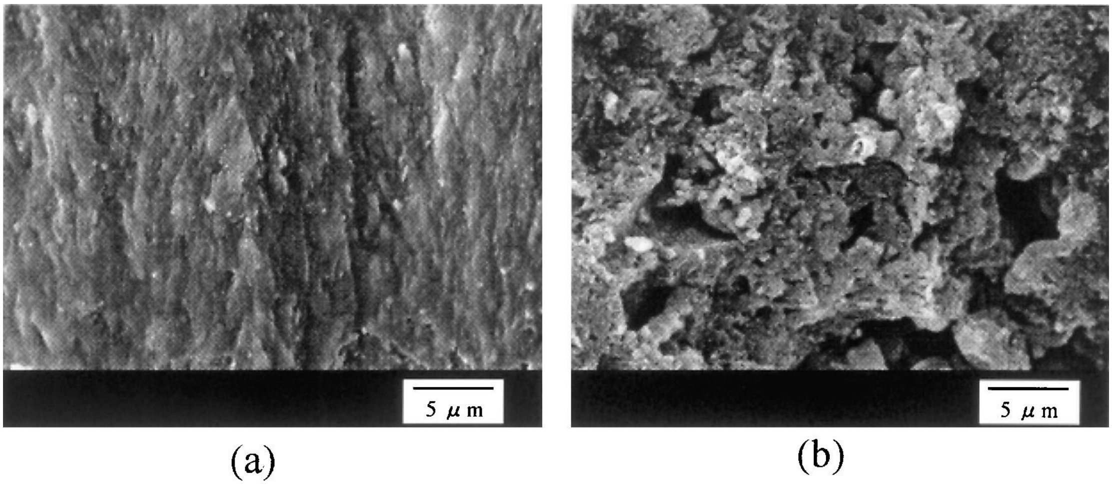


Fig. 2. SEM images of the fracture surface of the AlN compact: (a): outer part, (b): inner part.

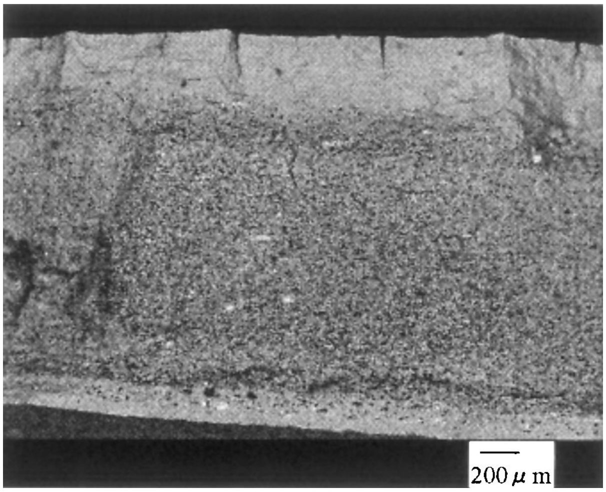


Fig. 3. A reflection electron image of the cross-section of the AlN compact.

The role of the pressured nitrogen on the nitridation is not clear, but we consider that N_2-overpressure have a large effect on full nitridation by maintaining the enough reaction rate.[14] In the case of nitridation of Al, it is important for full nitridation to break the surface nitride layer generated on metal Al particles, since the diffusion coefficient of nitrogen in the nitride layer is exclusively small. Heat is considered to have a good effect on cracking in nitride layer due to the difference of thermal expansion coefficient between AlN and metal Al. Nitridation of Al make a large heat, so the enough reaction rate could cause the cracking in the nitride layer. In this reaction condition, low temperature, the high N_2 pressure is considered to play an important role to maintain the enough reaction rate to make reaction heat for cracking the nitride layer.

Next, the AlN compacts synthesized by pressure nitridation were densified at 1900°C for 8 h in pressureless sintering. The relative densities, thermal conductivity and content of yttrium and oxygen in the AlN sintered body are shown in Table 1 (as Sample A). The thermal conductivity of the AlN was 155 W/mK, which is comparable with the commercial AlN sintered body. The result shows that this new process including pressure nitridation of Al compacts is a good candidate as a method for producing AlN sintered bodies with high thermal conductivity. This good thermal property is attributed to the low oxygen content of the AlN sintered body.

Table 1
Properties of the AlN sintered bodies

Sample	Relative density (%)	Thermal conductivity (W/mK)	Content (wt%)		
			Y	O	O* (except Y_2O_3)
A	94	155	2.4	1.1	0.4
B	94	170	0.8	0.4	0.2

Oxygen impurity in AlN is present in the AlN lattice as Al_2O_3 in the bulk. Oxygen dissolved in the AlN lattice has a detrimental effect on the thermal conductivity of AlN due to oxygen-related defects in the AlN lattice caused by the formation of Al vacancies.[15] The scattering cross-section of phonons is increased by the vacant Al site, which leads to low thermal conductivity. It has been shown that the thermal conductivity of AlN is linear to the inverse of the oxygen content of AlN.[16] Lowering the oxygen content, therefore, is the most important factor for the enhancement of the thermal conductivity.

In the AlN sintered body prepared by the process using pressure nitridation, the content of oxygen impurity, except for Y_2O_3, was only 0.4 wt%. This value is lower than the one in the AlN sintered body prepared by conventional processes. In conventional processes to produce AlN sintered body, AlN powder is used as raw material. AlN powder usually contains about 1 wt% of oxygen impurity,[1] so that the AlN sintered body also has 1 wt% of oxygen impurity except for Y_2O_3, at least, if the sintering atmosphere is not reductive. In this study, on the other hand, the Al atomized powder used as raw material contained only 0.4 wt% of oxygen impurity, and it is unlikely that oxygen entered into the sample throughout the process due to the elimination of the grinding step. As a result, low oxygen content is attained.

Incidentally, the AlN sintered body with 155 W/mK was heated at 1900°C for 4 h in carbon crucible. The properties of this sample are also shown in Table 1 (as Sample B). The thermal conductivity increased up to 170 W/mK. Yttrium and oxygen content was reduced to 0.8 and 0.4 wt%, respectively. The reduction of yttrium and oxygen is considered to be due to the reductive atmosphere in the furnace. During heating in a carbon crucible at high temperature, Y_2O_3 and Al_2O_3 react with carbon and result in each nitride and carbon monooxide (CO) gas.[17] In our case also, yttrium nitride (YN) was detected in the sample by XRD. It is considered that Yttrium and oxygen are removed as YN and CO, respectively, since YN is relatively volatile. Although, due to the existence of YN, the oxygen content except for Y_2O_3 remains undeterminated, it is clear that the oxygen content was reduced, which would lead to the improvement of the thermal conductivity.

There are some problems to solve in the AlN sintered body prepared by this new process. First, the density does not reach the theoretical value. The relative density was no more than 94% to theoretical, as shown in Table 1. The SEM image of the structure of the sample is shown in Fig. 4. Some pores were found inside of the

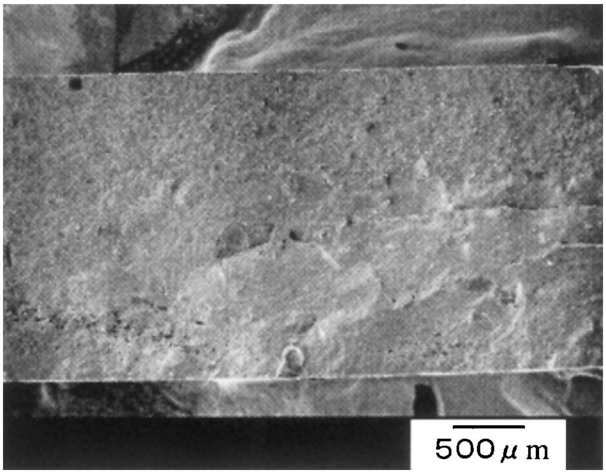


Fig. 4. A SEM image of the fracture cross-section of the AlN sintered body.

sample. It is considered that they are formed due to the nonuniformity of AlN compacts as described above. AlN compacts generated by pressure nitridation consist of an inner part with relatively low density and an outer part with relatively high density, as shown in Fig. 2. The outer part seems to be densified earlier and closed pores are likely to remain inside, precluding density from reaching the theoretical value. There were little Y_2O_3 in the outer part, as shown in Fig. 3, but the AlN compact consists of particles with nano-size, which also would help to sinter with little Y_2O_3. Second, the thermal conductivity is not the expected from the low oxygen content. This is considered to be also due to the non-uniformity of AlN compact, especially regarding the Y_2O_3 distribution. Y_2O_3 serves as not only a sintering additive but also an oxygen getter by reacting with Al_2O_3 to form yttrium aluminate. It lowers the oxygen vacancies in the AlN lattice and leads to the high thermal conductivity. Such nonuniformity of the distribution of Y_2O_3 could generate a region with low thermal conductivity, which would have a large effect on the thermal conductivity of the whole sample. In both cases, it is most important to synthesize the AlN compacts with uniform structure and composition. As it was discussed, the nonunformity of the distribution of Y_2O_3 may be caused by melting of unreacted Al taking place during the nitridation. Optimization of the reaction conditions during the pressure nitridation should be pursued in the future.

4. Conclusions

AlN sintered bodies with high thermal conductivity were prepared by sintering AlN compacts synthesized by pressure nitridation of Al powder compacts. The AlN sintered body generated in this study contained low oxygen impurity, which would contribute to its good thermal property. The use of pressure nitridation of Al compacts simplifies the whole production process. With the advantage of low cost, this procedure becomes a strong candidate to be included in a new production process AlN ceramics with high thermal conductivity. For improvement of the properties, synthesis of AlN compacts with uniform structure is important, therefore, the optimization of the reaction conditions in the pressure nitridation is required.

Acknowledgements

This work has been carried out as part of the Synergy Ceramics Project under the Industrial Science and Technology Frontier (ISTF) Program promoted by AIST, MITI, Japan. Under this program part of the work has been funded through NEDO. The authors are members of the Joint Research Consortium of Synergy Ceramics.

References

1. Jackson, T. B., Virkar, A. V., More, K. L., Dinwiddie, R. B. Jr and Cutler, R. A., *J. Am. Ceram. Soc.*, 1997, **80**, 1421–1435.
2. Watari, K., Hwang, H. J., Toriyama, M. and Kanzaki, S., *J. Am. Ceram. Soc.*, 1996, **79**, 1979–1981.
3. Hashimoto, N., Yoden, H. and Shigehito, S., *J. Am. Ceram. Soc.*, 1992, **75**, 2098–2106.
4. Selvaduray, G. and Sheet, L., *Mater. Sci. Tech.*, 1993, **9**, 463–473.
5. Weimer, A. W., Cocharn, G. A., Eisman, G. A., Hook, J. P. and Mills, L. K., *J. Am. Ceram. Soc.*, 1994, **77**, 3–18.
6. Munir, Z. A., *Ceram. Bull.*, 1988, **67**, 342–349.
7. Costantino, M. and Fipro, C., *J. Mater. Res.*, 1991, **6**, 2397–2402.
8. Marin-Ayral, R. M., Tedenac, J. C., Bockowski, M. and Dumez, M. C., *Ann. Chim. Fr.*, 1995, **20**, 169–180.
9. Scholz, H. and Greil, P., *J. Mater. Sci.*, 1991, **26**, 669–677.
10. Yuan, D. W., Chengn, V. S., Yan, R. F. and Simkovich, G., *Ceram. Eng. Sci. Proc.*, 1994, **15**, 85–94.
11. Komeya, K., Matukaze, N. and Meguro, T., *J. Ceram. Soc. Jpn.*, 1993, **101**, 1319–1323.
12. Matsuo, S., Komeya, K., Matsuki, Y. and Shikanai, S., *J. Ceram. Soc. Japan*, 1967, **75**, 241–246.
13. Okada, T., Obata, M., Toriyama, M. and Kanzaki, S., In *Proceedings of the 2nd International Symposium on the Science of Engineering Ceramics*, September 1998, ed. K. Niihara, T. Sekino, E. Yasuda and T. Sasa. Trans Tech Publications, 1999 pp. 129–131.
14. Okada, T., Toriyama, M. and Kanzaki, S. *J. Mater. Sci.*, in press.
15. Watari, K., Ishizaki, K. and Tsuchiya, F., *J. Mater. Sci.*, 1993, **28**, 3709–3714.
16. Slack, G. A., *J. Phys. Chem. Solids*, 1973, **34**, 321–335.
17. Ueno, F., *J. Mater. Sci. Soc. Jpn.*, 1994, **31**, 150–156.