RAPID NITRIDING OF ALUMINUM UNDER NITROGEN GLOW PLASMA

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Applying a low pressure nitrogen r.f. plasma, large-sized aluminums were completely nitrided to produce aluminum nitride. The compact prepared from atomized powder was nitrided by positioning it at 1.0 cm above the lower end of r.f. coil and by applying a plate power of 1.85kW. In this case, nitriding of the compact was accomplished in a short period of time; 10 min and at a relatively low temperature; 1000℃, giving 96% of conversion. Different shaped aluminums such as cylindrical, rectangular, plate and grains were also successfully nitrided in a short time at a low temperature. The product consisted of aluminum nitride whiskers with ca. 1μm in dia. This nitriding may be characterized with the nitrogen plasma containing activated nitrogen species such as N, N^+, N_2^+ , which would penetrate into the inner part of the sample to produce the aluminum nitride whiskers. Nitrogen glow plasma was very effective for the rapid production of pure aluminum nitride from large-sized aluminums in low cost.

1. Introduction

Aluminum nitride ceramics are excellent in their thermal conductivity and are expected as substrates for LSI. To obtain aluminum nitride ceramics with high thermal conductivity, high purity is required for the starting powders. Aluminum nitride powders have been commercially produced by two methods; direct nitriding of aluminum and carbothermal reduction of alumina. In these processes, the direct nitriding has been extensively used. Direct nitriding of aluminum has been also studied by plasma processing, especially using a thermal plasma, in which atomized powder or aluminum ingot [1] has been heated by thermal plasma to generate aluminum vapor, reacting with nitrogen. Small particles of atomized powder are preferred in the conventional nitriding, because the aluminum nitride layer on the aluminum melt has been considered to be too stable to proceed further nitriding [2-4]. On the other hand, the aluminum surface was generally covered with the thin oxide layer of aluminum. Therefore, the atomized powder has relatively large amount of oxygen, compared with an aluminum block with the same weight. If the large-sized aluminum is completely nitrided, atomized process of aluminum will be removed and the product will contain less amount of oxygen impurity. Based on these ideas, Scholtz et al. [4] reported that the aluminum alloy containing 2.3wt% lithium was completely nitrided in the form of cylindrical sample with 15 mm dia. and 9 mm in height. In this process, lithium in the alloy vaporizes and disappears from the product. We also reported that the aluminum grains with 2mm in size and the wires with 2mm in dia. and 50 mm in length were completely nitrided by the addition of 0.1 to 3.0 wt% of yttrium oxide and by the pretreatment of electrolytic etching of the surfaces, respectively[5]. Yttrium oxide has been used as an additive for the sintering to produce aluminum nitride ceramics. The product from electrolytically etched aluminum wires must be of no impurity in principle. Though the nitride layer on the aluminum melt has been considered to prevent further nitriding, the reaction of aluminum melt and nitrogen gas has been successfully proceeded in our process. The thickness of the layer grew up to be about 100-200 μm. The most important point of these processes is that the reaction of aluminum melt and nitrogen gas was remarkably accelerated by the additive effect of yttrium oxide or by the surface morphology of aluminum pretreated. It is expected from our previous results that the reaction of aluminum melt and nitrogen is also accelerated by the active nitrogen species in glow plasma to produce pure aluminum nitride at relatively low temperature. In this study, the nitridings have been studied for the large-sized aluminums, applying nitrogen glow plasma.

2. Experimental

Several shaped aluminums were used as starting materials; compact of aluminum powder(65 μm in av. dia., purity 99.97%, 0.4g) pressed under 150 Pa (ϕ 13 mm x 1.7 mm), and aluminum blocks with cylindrical (ϕ 6.2mm x 5.5mm, purity >99%), rectangular (4.0mm x 10.0mm x 10.0mm, purity >99%), plate (0.5mm x 10.0mm x 10mm, purity 99.2%), and grain (2mm, purity 99.5%) shapes.

Figure 1 shows the apparatus for the generation of the r.f. plasma (4MHz, max 10kW). The sample was placed on a sample holder in a double walled and water cooled cylindrical quartz tube and heated by the nitrogen glow plasma generated inductively. Considering the stoichiometric amount of nitrogen gas for 0.5 g of aluminum, flow rate of nitrogen gas (99.9999%) was determined as 100 sccm. The pressure in the apparatus is maintained at ca. 75Pa. The plate power of r.f. generator and the position of the sample in the plasma were especially studied as important factors. The product was analyzed by Kjeldahl method to determine the conversion to aluminum nitride.

3. Results and Discussion

3.1 Nitriding of aluminum compact by low pressure nitrogen plasma

At first, a compact of atomized powder, which was thought to be relatively active, was used as a starting material. When the compact with 8 mm in dia. was put at 2.0 cm below the lower end of r.f. coil (-2.0cm), aluminum compact was not nitrided under the plate power of 3.5 kW. On the other hand, the upper part of the compact was nitrided by positioning it at 1.0 cm above the lower end of r.f. coil (+1.0cm) and by applying the minimum plate power of 1.85kW. Furthermore, enlarged compact with 13 mm in diameter was wholly nitrided in these conditions. Single phase of aluminum nitride was detected in x ray diffraction pattern of the product. It was confirmed that the compact of atomized powder was able to be nitrided by nitrogen r.f. plasma. The highest conversion (96%) for the aluminum compact with 13 mm diameter was obtained at the sample position of +1.0 cm, applying 1.85kW of nitrogen glow plasma. When the sample was lifted higher, the state of plasma became unstable. The nitriding did not proceed at -2.0 cm. At the sample position of +1.0 cm, high conversion (94 - 96%) was obtained in every plate power (1.85 - 5.00 kW). However, as-nitrided state of the product were dependent on the plate power. The products were tightly sintered at higher plate powers. These products may be able to be used as-nitrided. On the other hand, the products obtained at lower plate powers were easy to be pulverized. The low power is fascinating for the industry. Therefore, the plasma power 1.85kW and the sample position +1.0 cm are considered to be the favorable conditions for the glow plasma nitiriding of aluminum compact with 13 mm in diameter

Figure 2 shows the temperature of the sample as a function of reaction time. As the sample is heated by the nitrogen plasma, the temperature of the sample exceeds the temperature without sample. This exothermic reaction is due to the reaction heat of nitriding ($Al + 1/2N_2 \rightarrow AlN$ ΔH°=-329 kJ/mol at 1000℃). The temperature reaches to the maximum of 1000℃ in 5 min and then decreases to the temperature without sample. In accordance with the exothermic reaction, pressure decrease due to the rapid nitriding was also observed. The conversion at every stage is also indicated in Fig.2. After the exothermic reaction at C point in Fig. 2, the conversion reaches up to 93.2%. This means that the glow plasma nitriding is almost completed in 10 min. This may be due to the activatednitrogen (N, N^+, N_2^+, etc.) in the glow plasma.

Figure 3 shows the cross section and microstructures of the product. The product consisted of the black upper layer with 0.6 mm in thickness and the white or gray inner part. As shown in Fig. 3 (c), white or gray part consisted of aluminum nitride fibers with ca. 1 μm in diameter and in the upper layer (b) the fibers were tightly sintered. The aluminum nitride whiskers may be applicable to the high thermal conductivity filler. The conversion in the surface layer is measured to be 94.3%, which is lower than that of the inner part(97.5%). Aluminum nitride decomposes above 2200℃. The surface exposed in the plasma is tightly sintered, but at the same time, decomposition may occur a little. The color of pure aluminum nitride is white. The oxygen content in the surface layer was measured to be 0.22%, which is lower than that of inner part(0.32%). These oxygen contents are very low compared to those of commercial ones. The black layer seems to reveal the existence of decomposed Al in aluminum nitride.

It is concluded that using nitrogen glow plasma fibrous aluminum nitride with low oxygen content was obtained at relatively low temperature in short period of time.

3.2 Nitriding of different shaped aluminums

Because the particles in the compact melt to be an aluminum block, different shaped aluminums will also be able to be nitrided. Figure 4 shows the products from the other shaped aluminums under the favorable conditions obtained for the compacts (1.85kW and +1.0 cm of sample position). The nitridings were also successfully accomplished in the different shaped aluminums; cylindrical (ϕ 6.2mm x 5.5mm), rectangular (4.0mm x 10.0mm x 10.0mm), plate (0.5mm x 10.0mm x 10mm), and grains (2mm).

3.3 Nitriding process of aluminum in nitrogen glow plasma

In the previous report [5], the large-sized aluminums with 2mm in size were completely nitrided at 1000-1300℃ by the addition of yttrium oxide. The mechanism of this process was suggested as follows; in the first step, the nitriding of aluminum melt is accelerated by the additive effect of yttrium. The temperature of the sample is then raised by the reaction heat of nitriding enough to generate the aluminum vapor. In the second step, the aluminum vapor generated reacts with nitrogen in vapor phase to produce fine powder of aluminum nitride. As the result, hollow, spherical shells covered with the fine particles of aluminum nitride are formed. Based on this idea, vapor phase reaction (CVD reaction) can be also suggested in the plasma process. The formation of aluminum nitride whiskers was characteristic in this process. It is well-known that whiskers are rapidly produced from the vapor phase. In addition, it was observed that the sample was slightly expanded at the beginning of the nitriding. Therefore, in order to produce the aluminum nitride in the inner part, active nitrogen from the glow plasma must be supplied through the surface layer of the sample to react with aluminum vapor. The nitriding conditions of the inner part seem to be suitable for the formation of whiskers.

4. Conclusions

In this study, the direct nitridings of large-sized aluminums with different shapes were studied under low pressure nitrogen r.f. plasma. The results are summarized below.

1. It was confirmed that applying a nitrogen glow plasma large-sized aluminum was successfully nitrided without any promoter.
2. The favorable nitriding conditions for the compact obtained from the atomized powder are 1.85 kW of plate power and +1.0 cm of sample position. In this case, the compact was successfully nitrided at a low temperature of 1000℃ in a short period of 10 min, giving 96% of conversion.
3. Different shaped aluminum such as cylindrical, rectangular, plate and grains were also successfully nitrided in a short time and at a low temperature under the conditions of 1.85 kW of plate power and +1.0 cm sample position.
4. The product consisted of aluminum nitride whiskers with 1μm in dia., which may be applicable to the high thermal conductivity filler. This nitriding may be characterized by the nitrogen plasma containing activated nitrogen such as N, N^+, N_2^+ , which would penetrate into the inner part of the sample to produce the aluminum nitride whiskers.
5. Nitrogen glow plasma is very effective for the rapid production of pure aluminum nitride from various shaped aluminums in low cost.

References

1. H. Ageorges, S. Megy, K. Chang, J.-M. Baronnet, J. K. Williams and C. Chapman, "Synthesis of Aluminum Nitride in Transferred Arc Plasma Furnaces," Plasma Chemistry and Plasma Processing, **13**, 613-632 (1993).
2. H. Scholtz and P. Greil, "Nitridation Reactions of Molten Al-(Mg, Si) Alloys," J. Mat. Sci., **26**, 669-677 (1991).
3. K. Komeya, N. Matsukaze and T. Meguro, "Nitridation Behavior of Aluminum

Melt," Proceedings of the Fall Meeting of the Ceramic Society of Japan, p.232 (1991) (in Japanese).
4. H. Scholtz and P. Greil, "Synthesis of High Purity AlN by Nitridation of Li-Doped Al-Melt," J. Euro. Ceram. Soc., 6, 237-242 (1990).
5. S. Ito, K. Yoshida, S. Saito and K. Akashi, "Nitriding of Large-Sized Aluminum," Proceedings of Symposium XIX at the ACerS 97th Annual Meeting, Cincinnati, 1995 (to be published).

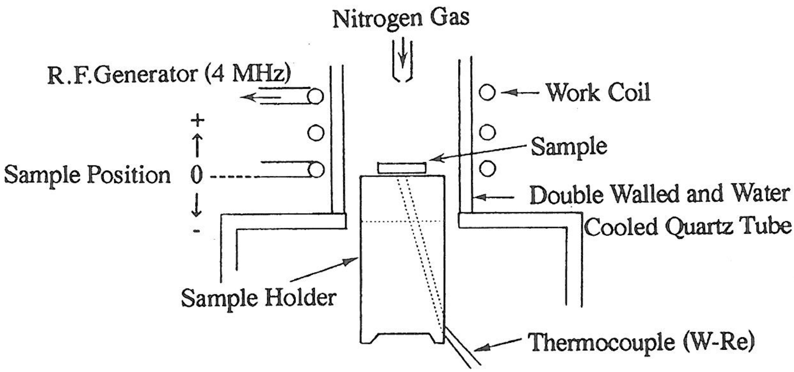


Fig. 1 Nitrogen plasma generator for the nitriding of large-sized aluminum.

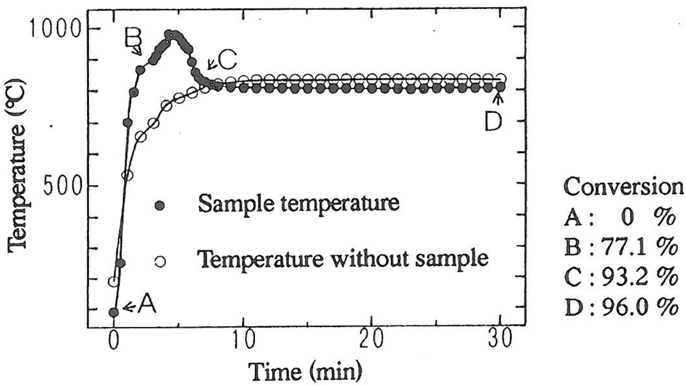
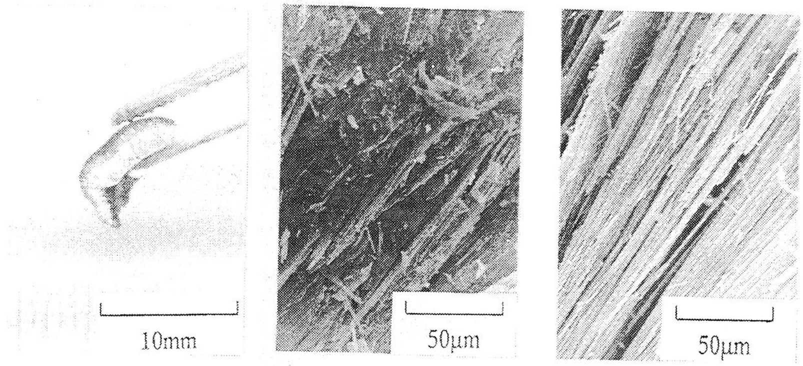
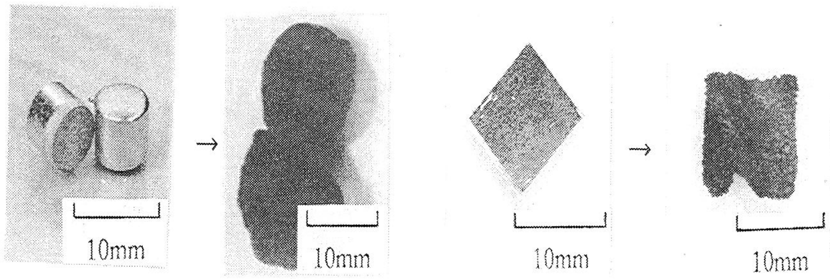


Fig. 2 Temperature of the sample vs. nitriding time.
Plate power: 1.85kW, Pressure: 75 Pa, Flow rate of nitrogen: 100sccm.



(a) Cross section (b) Upper layer (c) Inner part

Fig. 3 Cross section and microstructures (SEM) of the product.
Plate power: 1.85 kW, Sample position: +1.0 cm.

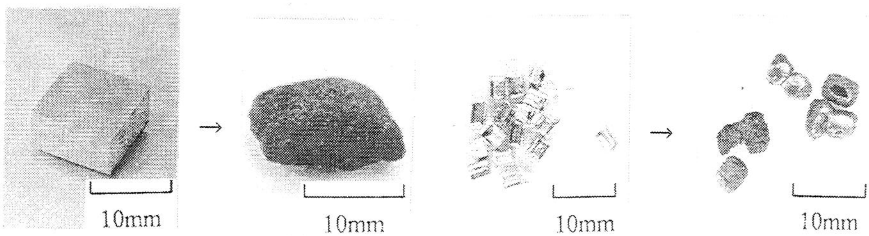


(a) Cylindricals
purity >99%

Conversion
93.8%

(b) Plate
purity 99.2%

Conversion
95.9%



(c) Rectangular
purity >99%

Conversion
89.0%

(d) Grains
purity 99.5%

Conversion
80.9%

Fig. 4 Nitriding for different shaped aluminums.
Plate power: 1.85 kW, Sample position: +1.0 cm.