

Direct nitridation of aluminum compacts at low temperature

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Direct nitridation of aluminum compacts (relative density 65%) consisting of commercial atomized powder was examined at temperatures from 500 to 700 °C, near or below the melting point of aluminum, and under a pressured nitrogen atmosphere between 0.5–7 MPa. Complete nitridation was achieved at a temperature as low as 540 °C by controlling the nitrogen pressure. The nitridation process and the structures of generated aluminum nitride (AlN) were drastically influenced by nitrogen pressure. Considering the relations between the reaction conditions and the reaction processes, it is suggested that low nitridation temperature and pre-heating in vacuum have a good effect on the nitridation ratio. © 2000 Kluwer Academic Publishers

1. Introduction

Aluminum nitride (AlN) is an attractive material for use as substrate and heat sink in electronic devices due to its excellent properties, such as high thermal conductivity, high electrical resistivity, a thermal expansion coefficient that matches well with that of silicon, a moderately low dielectric constant, and a low loss tangent [1–3]. In addition, because of its excellent thermal properties AlN powder is going to be used as a filler for high-heat-conductive plastic packages [4].

AlN has been synthesized as powder using many kinds of processes [5]. Carbothermal reduction of alumina powder is a representative method already applied industrially, and it has the advantage of synthesis of uniform particles. However, this method requires a reaction temperature as high as 1700–1800 °C. Also, high purity alumina powder as a reactant is necessary for synthesis of high purity AlN powder making it an expensive material. Chemical vapor deposition of AlN by the reaction of an aluminum gaseous compound such as aluminum chloride with nitrogen or ammonia is also being studied [6–8]. Although it is a candidate as a method for production of AlN sub-micro or nano particles with good sintering properties, this method seems to be costlier than carbothermal reduction because of the difficulty to produce in commercial-scale. Organometallic precursor method using a polymeric precursor such as tri-alkylaluminum is also being studied, but it is still in developmental stage [9].

Direct nitridation also has already been performed industrially. It has the advantage of low-costs due to its simple reaction system and lower reaction temperature. The reaction for direct nitridation, namely, the reaction between metal aluminum and nitrogen is highly exothermic. It is reported that the reaction starts from

475 °C [10]. Taking these into account, direct nitridation of aluminum metal would proceed easily without severe reaction conditions. In the practice, however, direct nitridation of aluminum metal powder is performed in the temperature of 1500 °C [5]. The reason for this is that the large heat of nitridation reaction makes unreacted aluminum melt and coalesce, which in turn prevents nitrogen from diffusing into aluminum and stops nitridation [4]. Perfect nitridation of such coalesced aluminum needs heating at high temperature for long time. Moreover, nitridation ratio is increased by mixing AlN powder in aluminum reactant as a reaction diluent. These treatments cause high energy consumption and high costs that, although not so high as of carbothermal reduction [4], are among the main barriers to large-scale use of AlN.

In our group, direct nitridation of pure aluminum compacts have been tried at a much lower reaction temperature than conventional methods under pressured nitrogen atmosphere, and without any reaction additives or diluents [11, 12]. In this paper, the nitridation was examined in a wide range of reaction temperatures, below the melting point of aluminum, and of nitrogen pressures. The limit of reaction conditions enough for the complete nitridation of aluminum powder compacts and the relation between the condition and the generated AlN structure were investigated. The nitridation processes were also investigated and the mechanism discussed.

2. Experimental procedures

Commercial aluminum atomized powder (with an average particle size of 24 μm by coulter-counter method, and a surface area of 0.4 m²/g) was used as starting

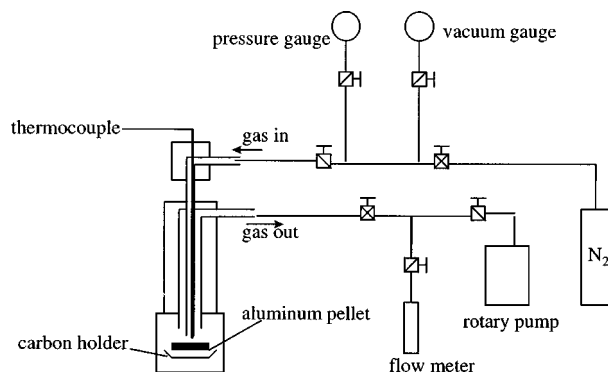


Figure 1 Schematic illustration of the equipment.

material. Samples were pressed to form disk pellets with a diameter of 12 mm and thickness of 0.8 mm, that is nearly equal to the thickness of the device substrate. Their relative densities to theoretical were 65%. High purity nitrogen (99.999%) was used as reaction gas. The schematic illustration of the apparatus is shown in Fig. 1. The aluminum pellet, sustained by a graphite holder, was set in a reactor. A thermocouple was inserted to 0.5 mm above the pellet to record the temperature change during the reaction. The reactor was put into a furnace and pre-heated to the desired temperature with a constant rate of 10°C/min. The reactor was evacuated by a rotary pump during heating. The vacuum pressure was about 1 torr. After keeping the desired temperature for 30 min in vacuum, nitrogen gas was induced to the desired pressure. Here, the temperature means the furnace temperature, but it was nearly equal to the sample temperature at the beginning of the reaction. The nitrogen pressure was kept for 120 min. The experiments were performed at various temperatures from 500 to 700 °C, and under nitrogen pressures between 0.5 and 7 MPa. The nitridation ratio was calculated from the weight gain of the pellet after the reaction according to the following equation:

$$\text{Nitridation ratio (\%)} = 100 \times \left(\frac{M_{\text{Al}}}{M_{\text{N}}} \right) \times \frac{(m_{\text{rp}} - m_{\text{Al}})}{m_{\text{Al}}} \quad (1)$$

where M_{Al} and M_{N} are the atomic weights of aluminum and nitrogen, and m_{Al} and m_{rp} are the weights of the original aluminum compact and of the reacted compact.

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) and transmission electron microscopy (TEM), simultaneously energy dispersive spectroscopy (EDS) was used for elements distribution relative quantitative analysis.

3. Results and discussion

3.1. Nitridation ratio

The effects of reaction temperature and nitrogen pressure on the nitridation ratio were examined for the pellets. The reaction temperatures were set between 500 and 700 °C. The dependence of nitridation ratio, calculated from the weight gain, on reaction temperature

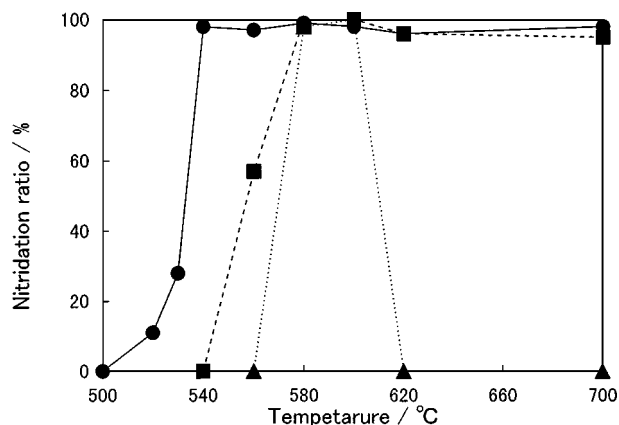
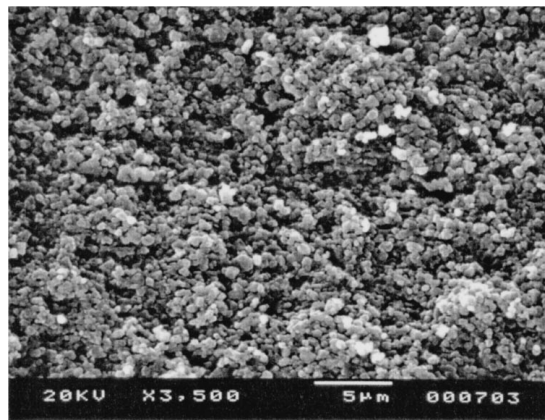


Figure 2 Effect of temperature and N₂ pressure on nitridation ratio. (●: 7 MPa, ■: 4 MPa, ▲: 0.5 MPa).

at reaction nitrogen pressures of 7, 4, and 0.5 MPa is shown in Fig. 2. Nitridation ratio depended on both reaction temperature and nitrogen pressure. In 7 MPa, nitridation occurred at temperature as low as 520 °C, but the nitridation ratio was low. Full nitridation was achieved over 540 °C in 7 MPa. In 4 MPa, nitridation started from 560 °C, and full nitridation was achieved over 580 °C. In 0.5 MPa, the temperature range of nitridation was very narrow. Full nitridation was achieved between 580 and 600 °C. Samples were also investigated by XRD and synthesis of AlN was ascertained. As for the samples with almost 100% nitridation ratio, there was no peak except for AlN. These results prove that complete nitridation of aluminum compacts is achieved below the melting point of aluminum in only a few MPa of pressured nitrogen atmosphere. The temperature range at which nitridation completely proceeded was dependent on nitrogen pressure. As the nitrogen pressure was higher, the nitridation started at lower temperature, which suggests that pressured nitrogen atmosphere remarkably enhances nitridation progress. In 0.5 MPa, nitridation stopped at higher temperature, over 620 °C. The reason may be excessive growth of the oxide layer on the surface of aluminum due to residual oxygen during heating in vacuum. Such oxide layer would hinder the permeation of nitrogen into aluminum at low nitrogen pressure.

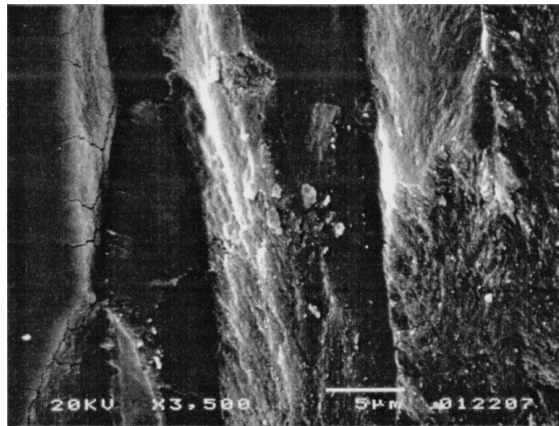
3.2. Synthesized microstructure

The microstructure formation of the nitridation product was found to be strongly influenced by the nitrogen pressure. Representative microstructure of the products synthesized in nitrogen pressure of 7, 4 and 0.5 MPa is shown in Fig. 3. In the case of 7 MPa, shown in Fig. 3a, isotropic particles appeared with about 1 μm in size. As for 4 MPa, the structure was an aggregation of extremely small fragment pieces with nano-scale, apparently columnar and dense, as shown in Fig. 3b. The microstructure synthesized in 0.5 MPa also consisted of small fragments, but the columnar feature was not found. XRD spectra for each product are shown in Fig. 4. The product in 7 MPa exhibited sharp diffraction peak, indicating large crystal size. On the other hand, the spectra for 4 and 0.5 MPa were rather broad,



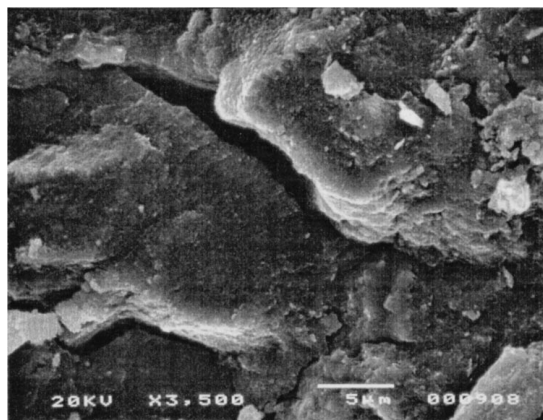
(a)

5 μ m



(b)

5 μ m



(c)

5 μ m

Figure 3 SEM images of the fracture cross-sections of AlN products. (N_2 pressure: (a) 7 MPa, (b) 4 MPa, (c) 0.5 MPa).

which would indicate small crystal size. There was a slight orientation to (002) in 4 MPa, that seems to reflect its columnar structure. TEM images of the product synthesized in 7 and 4 MPa are shown in Fig. 5. The crystal size synthesized in 7 MPa was about $1 \mu\text{m}$ and isotropic, whereas the one synthesized in 4 MPa was as

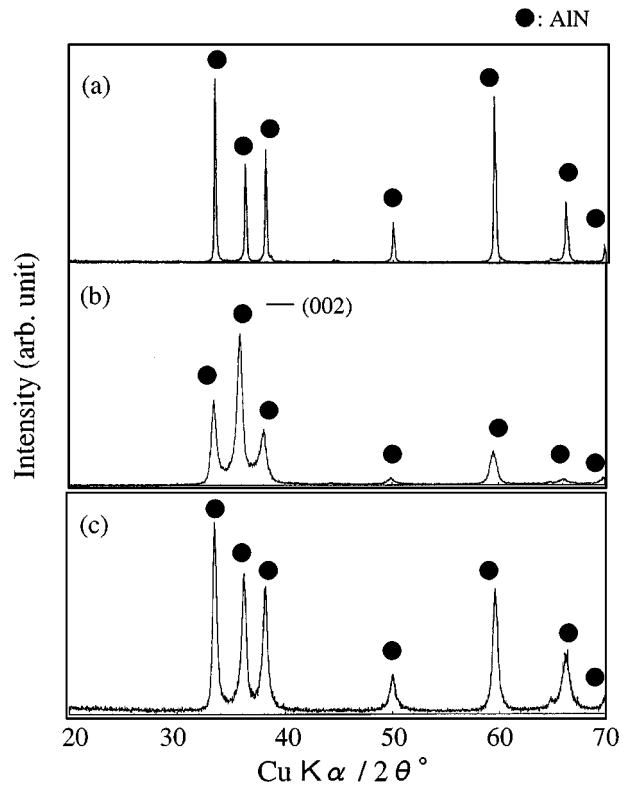


Figure 4 XRD spectra of AlN products. N_2 pressures were (a) 7 MPa, (b) 4 MPa and (c) 0.5 MPa.

small as about 10 nm width and 100 nm length. This is consistent with the XRD result.

Reaction temperature scarcely had an effect on microstructure formation in the temperature range of this study. This seems to be because the heat of the nitridation reaction compensates the difference of reaction temperature.

The relation between nitridation and reaction conditions is summarized in Fig. 6.

3.3. Nitridation processes

Nitridation process was investigated for the case of reaction temperature of 580°C and nitrogen pressure of 7, 4 and 0.5 MPa. The temperature at 0.5 mm above the sample was recorded, and the structure of the pellets in the middle of nitridation was observed by SEM. The detected increase of the temperature is considered to show the occurrence of nitridation reaction since direct nitridation of aluminum (e.g. reaction of aluminum with nitrogen) is an exothermic reaction. (No temperature change was detected after inducing nitrogen without setting of an aluminum pellet).

The processes also differed with the nitrogen pressure. Fig. 7a shows the temperature change during nitridation under 7 MPa nitrogen atmosphere. The nitridation process is divided into three stages. At the first stage, the temperature increased a little at the moment pressured nitrogen is induced into the reactor, suggesting the start of nitridation. At this point, nitridation ratio was about 5%. Next, in the second stage, the temperature remained constant or increased slightly. This would indicate that nitridation proceeded gradually. Nitridation ratio increased from 5 to about 40% in this stage.

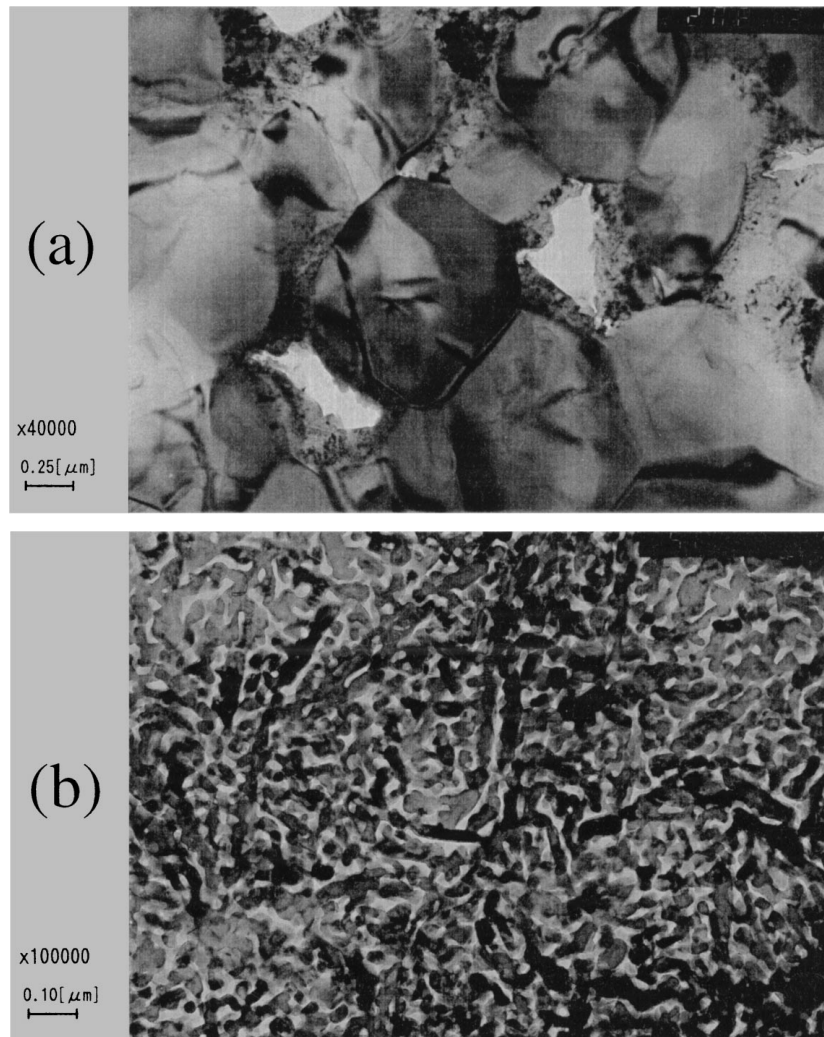


Figure 5 TEM images of AlN products. (N₂ pressure: (a) 7 MPa, (b) 4 MPa).

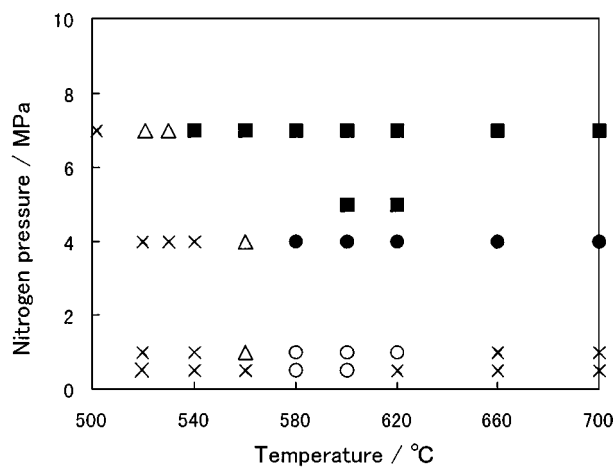


Figure 6 Reaction conditions and nitridation. X: no nitridation, Δ: incomplete nitridation, O: complete nitridation (resulting in small crystal), ▲: complete nitridation (resulting in small crystal with columnar feature), ■: complete nitridation (resulting in large crystal).

Finally, at the third stage, the temperature increased rapidly by over 100 °C. The temperature of the pellet itself is considered to reach 1300 °C, at least, because a stainless steel rod in contact with the pellet was melted. No temperature change was detected thereafter. Such

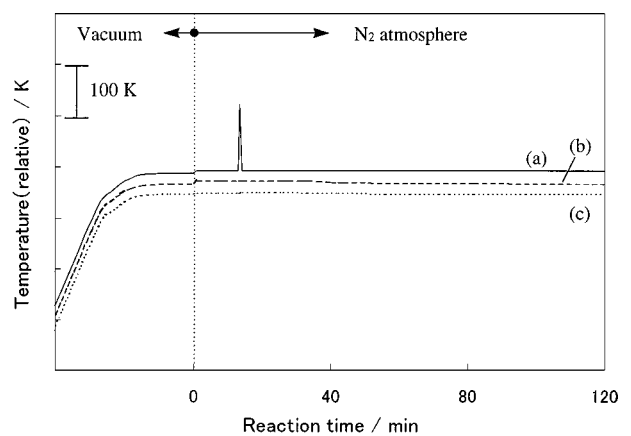
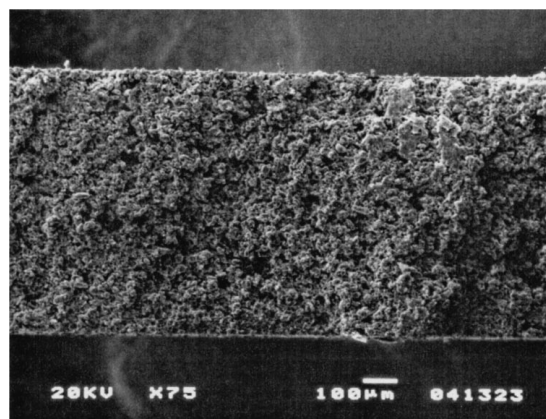


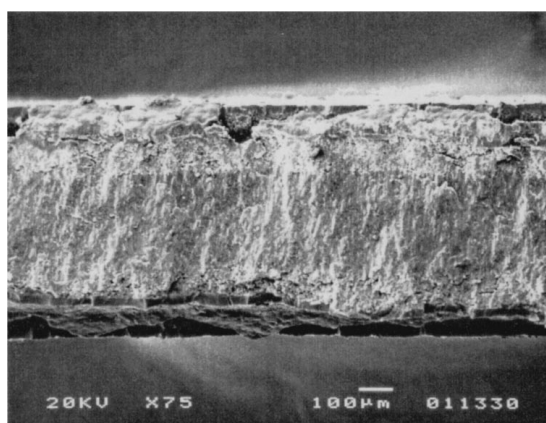
Figure 7 Temperatures of reaction systems during nitridation. (reaction temperature: 580 °C, N₂ pressure: (a) 7 MPa, (b) 4 MPa, (c) 0.5 MPa).

temperature record suggests that the nitridation proceeded rapidly to full nitridation ratio at this stage. The fracture cross section of the pellet in the first stage (nitridation ratio 5%) and the second stage (nitridation ratio 20%) are shown in Fig. 8b and c, respectively. At the first stage, aluminum particles at the surface of the pellet reacted with nitrogen and AlN was generated, while aluminum inside of the pellet was melted and



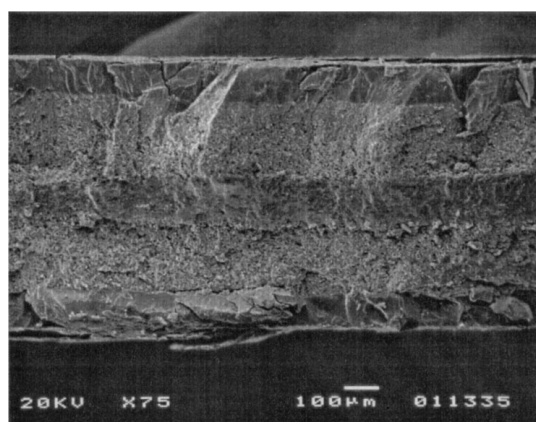
100 μ m

(a)



100 μ m

(b)



100 μ m

(c)

Figure 8 SEM images of the fracture cross-sections of (a) starting aluminum pellet, (b) the pellet with nitridation ratio of 5 wt% and (c) the pellet with nitridation ratio of 20%. (reaction temperature: 580 °C, N₂ pressure: 7 MPa).

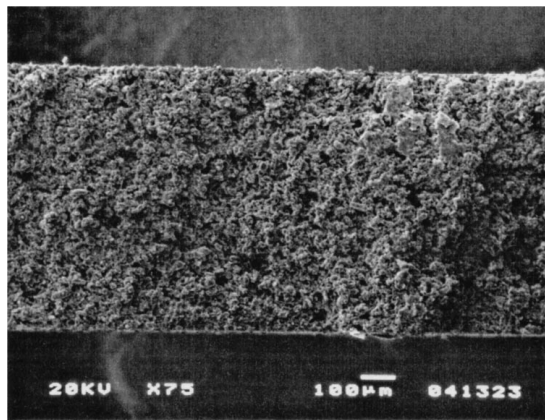
coalesced by the reaction heat. The pellet shrank and reached almost theoretical density. The shape of atomized aluminum powder disappeared. Next, in the second stage, the pellet consisted of three kinds of layers, surface, inner and center, as shown in Fig. 8c. The surface layers appeared columnar and dense, whereas the inner

layers were porous. The center layer consisted of dense molten aluminum. The nitridation ratio of the surface layer was higher than of the inner porous layer. No nitrogen was confirmed in the center layer. The thickness of the pellet increased as nitridation proceeded. In detail, both the surface and inner layer got thicker, while the center layer became thinner and finally disappeared. This suggests that nitride layers grew outwardly by a kind of capillar growth of molten aluminum. Such capillar growth is considered to be characteristic of liquid-gas reaction between aluminum and nitrogen and similar phenomena were reported during the nitridation of aluminum molten alloy [13–15]. As it was described above, over 40% of nitridation ratio (the third stage), nitridation proceeded explosively. The microstructure drastically changed after the rapid nitridation. The pellet shrank to nearly the thickness of starting aluminum pellet and the resulting structure is shown in Fig. 3a. The large heat generated by rapid nitridation would cause the drastic structure change and particle growth in AlN.

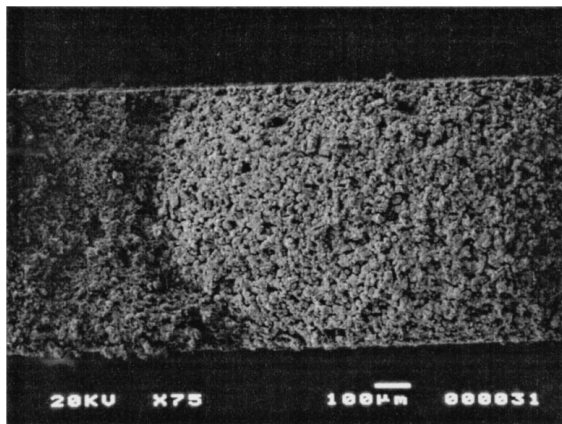
In the case of 4 MPa, the temperature record was as shown in Fig. 7b. Rapid temperature increase did not occur although the nitridation process was almost the same as in the case of 7 MPa. This indicates that nitridation continued gradually without large temperature increase. The microstructural changes during nitridation are almost the same as for 7 MPa until the second stage. The final microstructure shown in Fig. 3b resembled the structure at the end of this second stage, which consisted of an apparently columnar and dense structure, without the drastic structure change caused by the large temperature increase recorded under 7 MPa of nitrogen pressure.

In the case of 0.5 MPa, the temperature record during nitridation is shown in Fig. 7c. In this case, the increase of temperature at the moment of inducing nitrogen was smaller than for other cases. The temperature increased slowly and there was no peak that would indicate rapid nitridation. It suggests the nitridation proceeded slowly, as under 4 MPa. The structural transition, however, was different from 4 MPa. Fig. 9 shows the fracture cross-section of the pellet in the middle of nitridation in 0.5 MPa. Melting of aluminum was not observed in the structure throughout the reaction. Aluminum particles gradually broke down as nitridation progressed and finally resulted in the structure shown in Fig. 3c.

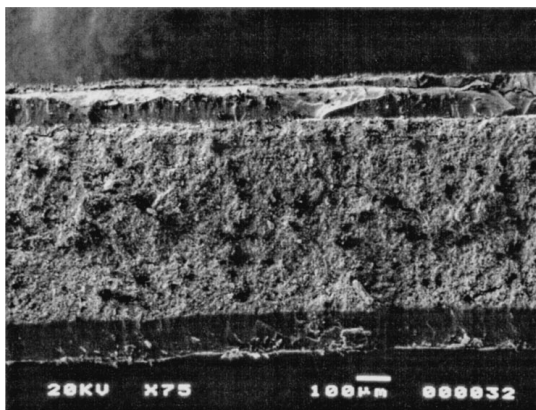
As described in the introduction, complete nitridation of aluminum powder is said to require a high reaction temperature since permeation of nitrogen into the molten and coalesced aluminum is difficult. It is also true that the complete nitridation of aluminum powder compacts or dense bulk, which is easier to coalesce, needs severe reaction conditions such as high nitrogen pressure of over 100 MPa [16–18], but in this study complete nitridation was achieved under nitrogen pressure of only 0.5–7 MPa without any additives or diluents such as AlN powder, although melting and coalescing of aluminum occurred in the case of 4 or 7 MPa. The reason for this is not clear, but key points to complete nitridation are guessed from several experimental results of nitridation ratio.



(a)
100 μ m



(b)
100 μ m



(c)
100 μ m

Figure 9 SEM images of the fracture cross-sections of (a) starting aluminum pellet, (b) the pellet with nitridation ratio of 5 wt% and (c) the pellet with nitridation ratio of 20%. (reaction temperature: 580 °C, N₂ pressure: 0.5 MPa).

First, the effect of pre-heating atmosphere on nitridation ratio is shown in Table I. In the case of heating in vacuum, nitridation proceeded completely. On the other hand, in the case of pre-heating in pressured nitrogen atmosphere, nitridation ratio was low. The rea-

TABLE I Effect of the pre-heating atmosphere on nitridation ratio. (reaction temperature: 580 °C)

| Reaction N ₂ pressure | Nitridation ratio (%) | |
|----------------------------------|------------------------|--------------------------|
| | Pre-heating atmosphere | |
| | Vacuum | Pressured N ₂ |
| 4 MPa | 100 | 19 |
| 7 MPa | 99 | 0.2 |

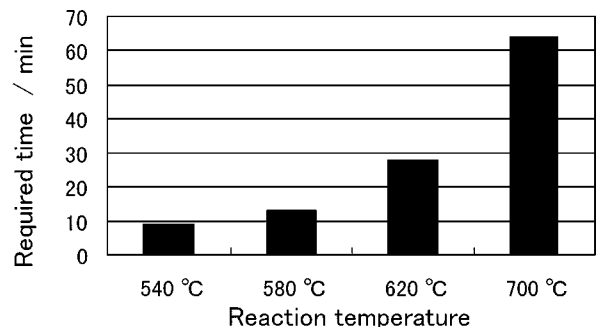


Figure 10 Required time for full nitridation at each reaction temperature. (N₂ pressure: 7 MPa).

son is considered to be as follows. In the case of heating in pressured nitrogen, it is expected that a nitride layer gradually grows at the surface of aluminum particles since nitridation of aluminum starts at 475 °C [10]. The diffusion coefficient of nitrogen in AlN is 1.23×10^{-17} m²/s at 1830 °C, and 2.55×10^{-17} m²/s at 1930 °C [19]. Assuming that the activation energy of diffusion of nitrogen in AlN does not change between 660 and 1930 °C, the diffusion coefficient is calculated to be extremely low, 2.63×10^{-25} m²/s at 660 °C. (The diffusion coefficient of nitrogen in molten aluminum is calculated to be 3.9×10^{-8} m²/s at 660 °C from the value at 2227 °C [17], assuming that the activation energy of the diffusion do not change between 660 and 2227 °C.) It indicates that formation of a surface nitride layer of even a few nm prevents the contact between nitrogen and inner aluminum. It is considered that the thin but rigid nitride layer gradually grows during pre-heating in pressured nitrogen and it prevents nitridation progress. From this reason, pre-heating in vacuum seems to have a good effect on nitridation progress.

Next, the required time for full nitridation is shown in Fig. 10. As the reaction temperature was lower, the required time was shorter. The reason is guessed as follows. Aluminum is melted by the reaction heat and a nitride layer is generated at the surface. Nitrogen can not come into contact with the inner aluminum without cracking the surface nitride layer due to extremely low diffusion coefficient of nitrogen in AlN. However, molten aluminum is cooled and might be solidified since the surrounding nitrogen temperature is rather lower than the melting point of aluminum. Phase transition between liquid and solid produces the large volume change. It would cause the nitride layer to crack and allow contact between aluminum and nitrogen. From this reason, the low reaction temperature also seems to have a good effect on nitridation progress.

4. Conclusions

Perfect nitridation of aluminum powder compacts was achieved at below the melting point of aluminum and under nitrogen pressures of 0.5–7 MPa. Nitridation progress and generated structures depended on nitridation conditions, especially nitrogen pressure. At nitrogen pressure of 7 MPa, rapid reaction and temperature increase occurred at the middle of nitridation and AlN with large crystal size of 1 μm was generated. At reaction nitrogen pressures of 4 and 0.5 MPa, nitridation proceeded gradually and the generated AlN had a small crystal size of under 100 nm. It was suggested that low nitridation temperature and pre-heating in vacuum had a good effect on the complete nitridation of aluminum compacts through prevention of excessive growth of the surface nitride or oxide layer, and through the difference of thermal expansion between liquid and solid aluminum.

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