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 (AIN) 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 AIN powder is going to be used as a filler for high-heat-conductive plastic packages [4].

AIN 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 AIN 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 for a method to produce 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 precursors using a polymeric precursor such as trialkylaluminum 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 AIN 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 AIN.

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 AIN 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
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 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 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 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.