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Reaction sintering and microstructural development in the system Al_2O_3–AlN

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Abstract

The reaction sintering and microstructural development of alumina with additions of 1–25 mol% AlN have been investigated by heating under 1-atm nitrogen gas at 1600–1800°C. Sintering Al_2O_3 with 1 mol% AlN addition at 1750°C, resulted in a ceramic with close to theoretical density of α-Al_2O_3 (3.98 g/cm^3). For the different compositions, the sintered densities decreased with increasing AlN content. This trend was attributed to the presence of secondary phases such as AlON($9Al_2O_3 \cdot 5AlN$) and ϕ($5Al_2O_3 \cdot AlN$) formed by reacting Al_2O_3 with AlN. For a given AlN addition, densification increased with sintering temperature, due to Al_2O_3 and/or AlON grain growth control. The stability of the individual crystalline phases depends on both sintering temperature and batch composition. © 2001 Published by Elsevier Science Ltd.

Keywords: AlN; Al_2O_3–AlN; AlON; Microstructure-development; Reaction sintering

1. Introduction

Dense polycrystalline aluminum oxide, (Al_2O_3), and aluminum oxynitride spinel, (AlON), are useful structural ceramics. The phase stability of Al_2O_3 is well established, however, there are disagreements concerning the range of the stable region of AlON in the Al_2O_3–AlN system. This is believed to be due to AlON being found only under a limited range of oxygen and nitrogen pressures, in conjunction with the formation of AlON being too slow to reach equilibrium at temperatures less than 1750°C.[1] AlON itself has a stoichiometric composition $5AlN \cdot 9Al_2O_3$ and melts incongruently into an alumina-rich, stable liquid and a second nitride-rich, unstable (volatile) liquid, at approximately 2050°C.[2]

It has been reported[3] that there are at least four techniques for the preparation of aluminum oxynitride phases:

1. the simultaneous reduction and nitridation of Al_2O_3;
2. the oxynitridation of metallic aluminum by combustion reaction;
3. the gas phase reaction involving $AlCl_3$;
4. the direct reaction between AlN and Al_2O_3.

Of the process routes, the fourth method is the most commonly used. Al_2O_3 reacts with AlN and the formation of AlON results at temperatures above 1650°C.[2,4,5] The few papers in the published literature, reporting the sintering behavior of AlON have concluded:

1. an evaporation-condensation mechanism governs densification during an initial reaction-sintering stage;[6]
2. the sintering aids present, intentionally or otherwise, form a transient liquid phase, resulting in the promotion of liquid phase sintering during the early sintering stage;[7]
3. densification occurs by volume diffusion at >1600°C;[8]
4. bulk ionic diffusion occurs at temperatures in the range 1300–1500° C.[9]

In the present work, reaction sintering, phase stability and the microstructure present in the 1–25 mol% AlN–

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Al_2O_3 system after heating at 1600–1800°C in 1-atm of nitrogen are discussed.

2. Experimental procedure

Al_2O_3 (AES-11C, Sumitomo Chemicals) and AlN (grade F, Tokuyama Soda Ltd.), powders were used as starting materials. The agglomerated Al_2O_3 (99.8% pure) and AlN particles (Fig. 1) exhibited an average particle size of 0.6 and 2.1 μm, and the specific surface area of 8.2 and 4.2 m^2/g, respectively. The AlN powder analysed as Ca 75 ppm, Mg 2 ppm, $Cr < 10$ ppm, $Fe < 10$ ppm, Si 36 ppm, $Ni < 10$ ppm, Al 65.4%, O 1.0%, C 0.06% and N 33.5%. Al_2O_3 powder was mixed with 1–25 mol% of AlN, 0.3 wt.% deflocculant (DARVAN-C, R.T. Vanderbilt Company) and 0.5 wt.% binder (PVA, Aldrich), by ball milling in an ethanol suspension for 48 h, using a high density polyethylene bottle with alumina ball media. After drying, the mixed powder was preformed into pellets of 11 mm diameter and 3–7 mm thickness, using a stainless steel die; the green compacts were then cold isostatically pressed (CiPed) at 200 MPa. The compacts were then calcined at 500°C in air to remove organic residue. Subsequently the samples were placed in a graphite crucible, embedded in aluminum nitride powder, and then sintered in a graphite resistance furnace at a temperature in the range 1600–1800°C for 2 h, at 1-atm nitrogen pressure. The apparent sintered density was measured by the Archimedes (water immersion) method. Individual crystalline phases were identified by X-ray diffraction analysis

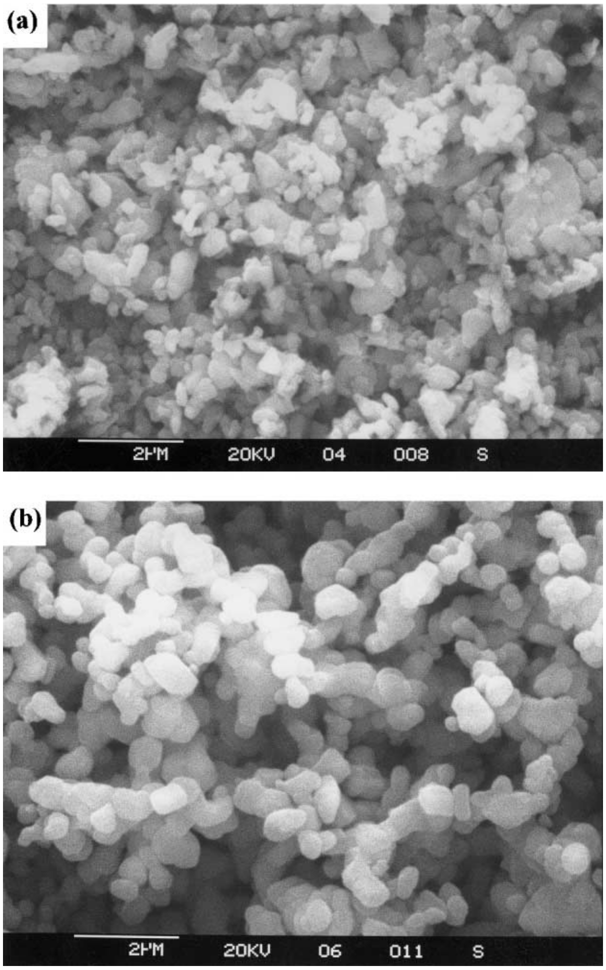

Fig. 1. Scanning electron micrographs of starting (a) Al_2O_3 and (b) AlN powders.

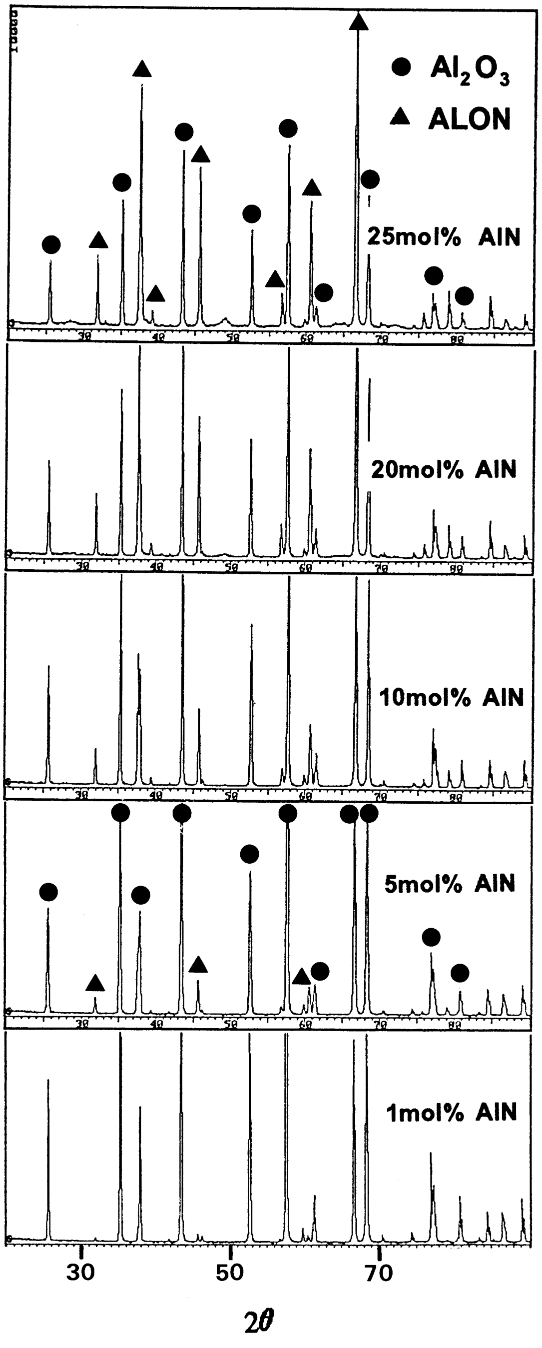

Fig. 2. XRD patterns of AlN–Al_2O_3 specimens sintered at 1600°C for 2 h.

(XRD, D-MAX 1400, Rigaku). The surface microstructure of the sintered specimens were observed using a scanning electron microscope (SEM, MK3, Cambridge) after polishing with 1 μm diamond slurry and thermal etching at 1400°C for 30 min, and the detailed structure by means of a scanning transmission electron microscope (STEM, JEM-200CX, Jeol). The grain size of the sintered Al_2O_3 specimens was measured with an Image Analyzer (Quantimet 570, Cambridge). Nitrogen content in the sintered specimens was determined using a nitrogen/oxygen determinator (TC-230, Leco).

3. Results and discussion

XRD patterns for the sintered materials with additions of 1–25 mol% AlN to the Al_2O_3 are shown in Figs. 2–5. After sintering at 1600°C (Fig. 2), all specimens

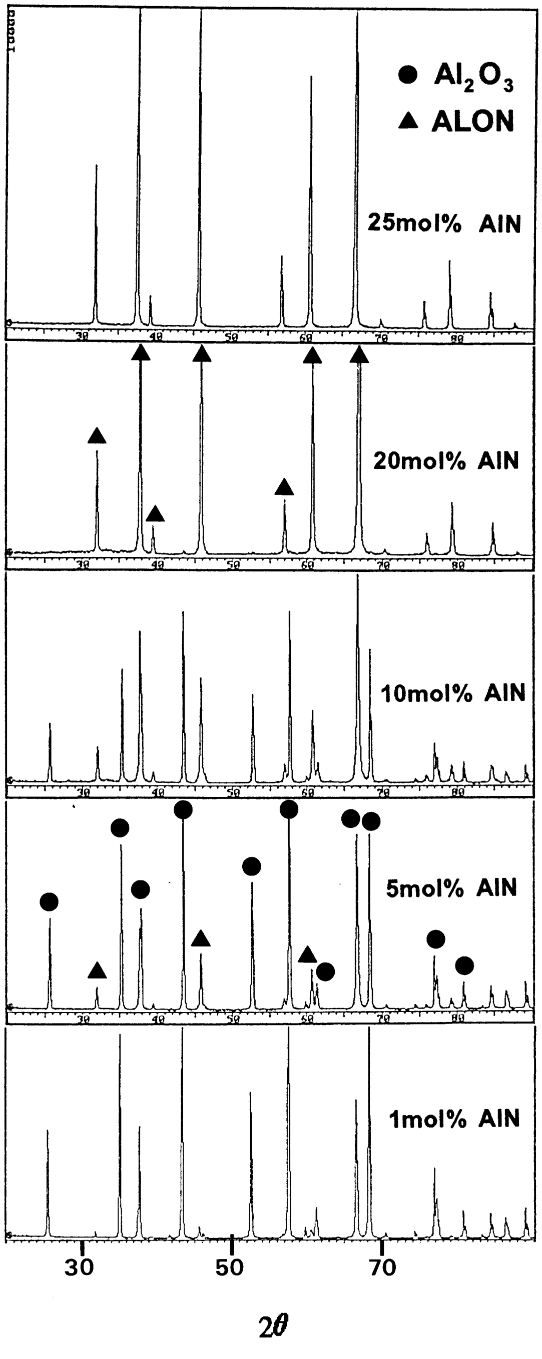

Fig. 3. XRD patterns of AlN–Al_2O_3 specimens sintered at 1700°C for 2 h.

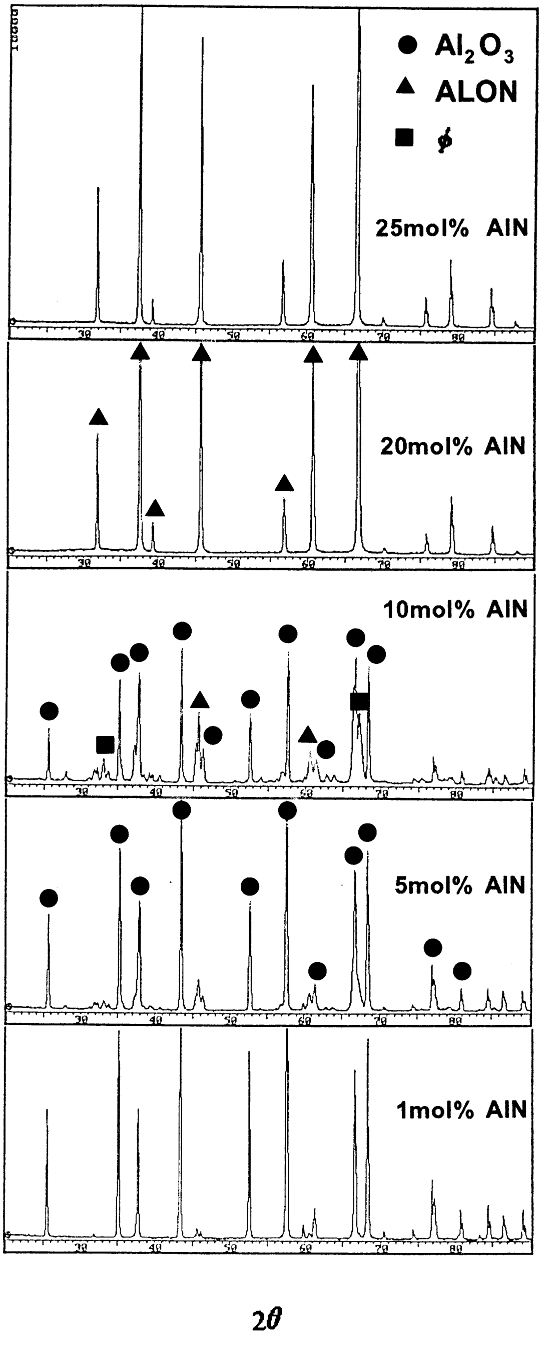

Fig. 4. XRD patterns of AlN–Al_2O_3 specimens sintered at 1750°C for 2 h.

were found to consist of α-Al_2O_3 and AlON phases; the diffraction intensity of the AlON peak increased with increasing AlN addition until the major phase in the specimen with 25 mol% AlN addition was AlON. The present results are in agreement with those of Lejus,[10] and Gauckler and Petzow,[11] who have reported that the formation of AlON in the system Al_2O_3–AlN starts at 1600°C. However, there are disagreements about the stability region (composition and temperature) of AlON in the system Al_2O_3–AlN.[2,10,12]

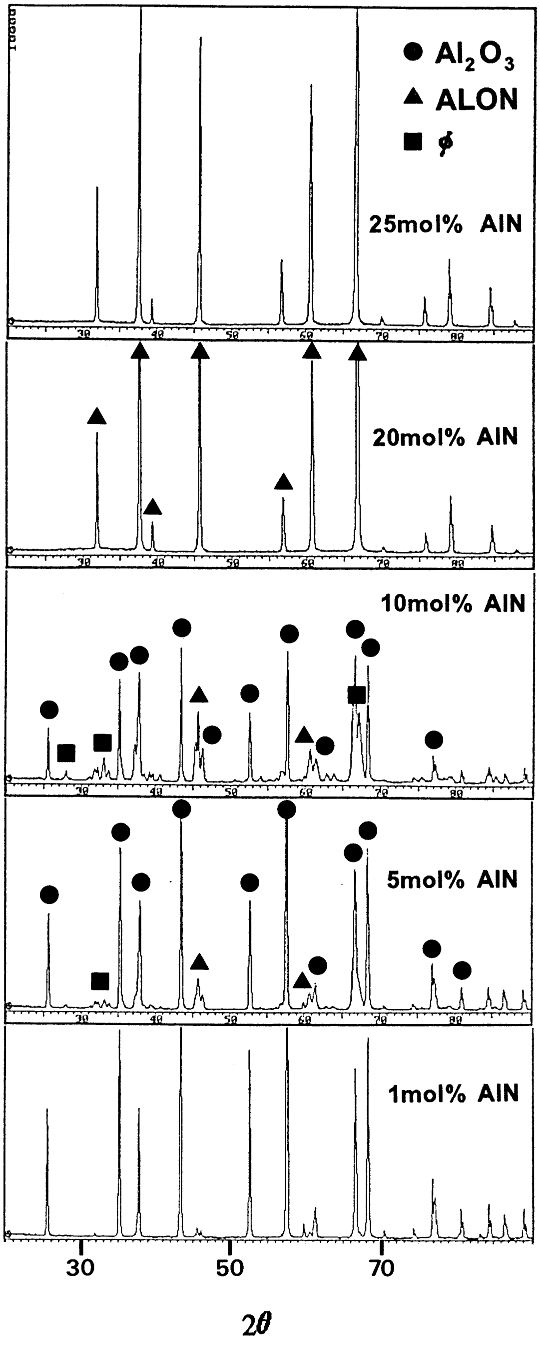

Fig. 5. XRD patterns of AlN–Al_2O_3 specimens sintered at 1800°C for 2 h.

On increasing the sintering temperature to 1650°C, the diffraction intensity of α-Al_2O_3 decreased. As a result, it can be concluded that the majority of the specimen with addition of 20 mol% AlN reacted to form AlON. In the case of 25 mol% AlN addition, the major AlON and Al_2O_3 XRD traces were confirmed. On sintering at 1700°C (Fig. 3), all α-Al_2O_3 in the specimens with 20 and 25 mol% AlN additions reacted to form AlON. These observations are consistent with Lejus' result,[10] that stable AlON is formed at 1700°C by additions in the range of 16–33 mol% AlN, but differ slightly with the report by Takebe et al.,[12] that its stable composition range is 28–31 mol% AlN at the same temperature. When the sintering temperature was increased to 1750°C (Fig. 4), and similarly to the 1700°C sintering, the minor AlON phase was identified

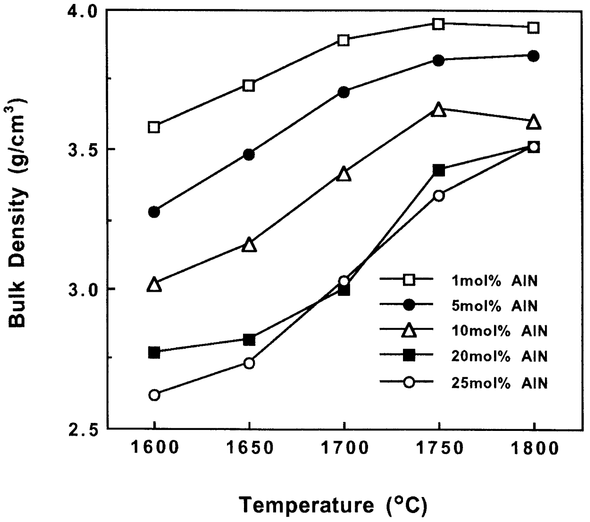

Fig. 6. Sintered density of AlN–Al_2O_3 specimens with various AlN content.

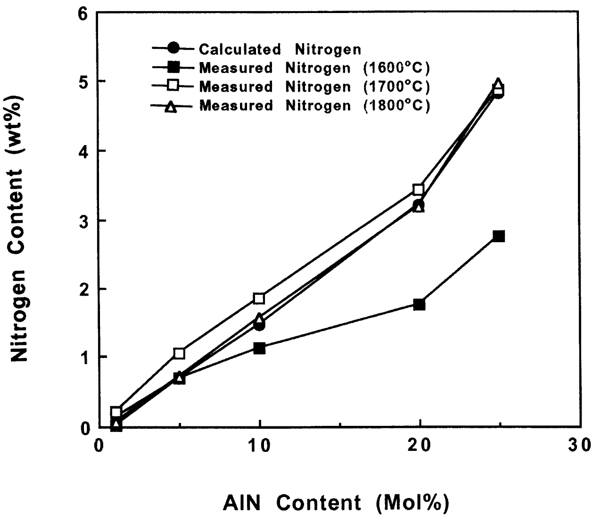

Fig. 7. Calculated and measured nitrogen content of the sintered specimens with AlN addition.

in the specimen with additions to the starting compositions as low as 1 mol% AlN. In the specimens with additions of 10 mol% AlN, there were not only major α-Al_2O_3 and AlON peaks, but ϕ phase, ($5Al_2O_3{\cdot}AlN$, monoclinic) was also identified in the diffraction patterns, $(122, 22\bar{1})$, (321), (040) and $(52\bar{5})$, as first proposed by Michel[13] in the system Al_2O_3–AlN. In the specimens formed on additions of 20 and 25 mol% AlN, only AlON could be identified. After sintering at 1800°C (Fig. 5), for the specimen with the addition of 5 mol% AlN, the major component was α-Al_2O_3 with minor amounts of AlON and ϕ phase also present. The specimen containing 10 mol% AlN, in contrast, showed that the majority of the primary α-Al_2O_3 had reacted and changed to AlON. However, only AlON was present in the specimen with the addition of 20 mol% AlN. In the specimen containing 25 mol% AlN, unidentified small peaks again appeared.

The effects of AlN addition and changes in the sintering temperature on the densification of the Al_2O_3–AlN powder compacts are shown in Fig. 6. The sintered bulk density of the compacts decreases with increasing AlN content and increases with increasing sintering temperature. For the specimen containing 1 mol% AlN, sintered at 1750°C, the density approximated the theoretical value (3.98 g/cm^3) of α-Al_2O_3. Similarly, for specimens with additions of 5 and 10 mol% AlN, the measured densities increased rapidly with increasing sintering temperature, in spite of the formation of AlON, which has a lower density than α-Al_2O_3. The density then tended to reach constant values (3.82 g/cm^3 for 5 mol% AlN and 3.63 g/cm^3 for 10 mol% AlN) when sintered above 1750°C. For the case of additions of 20 and 25 mol% AlN, in which almost all the α-Al_2O_3 reacted to form AlON at temperatures ⩾1700°C (Figs. 3–5), the densities of both specimens increased

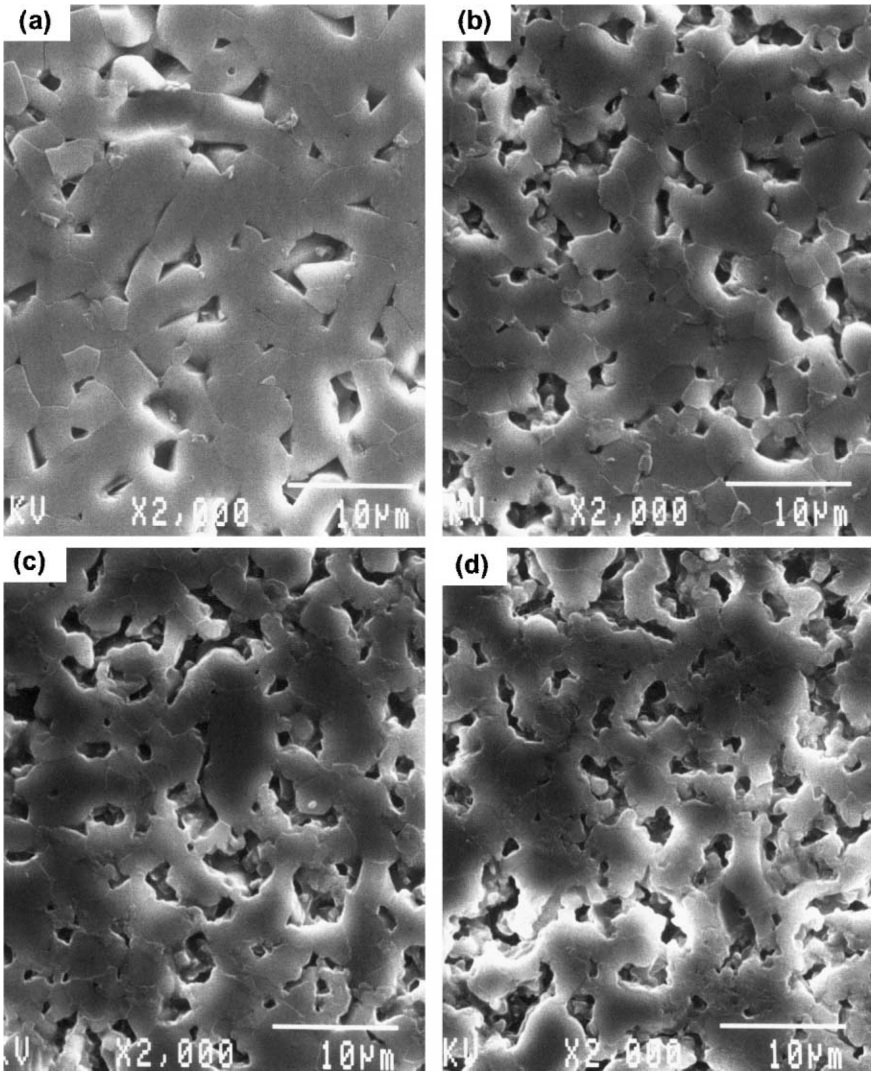

Fig. 8. SEM micrographs of polished and etched surfaces of AlN–Al_2O_3 specimens containing (a) 1, (b) 5, (c) 10 and (d) 20 mol% AlN, sintered at 1600°C for 2 h.

with sintering temperature and had very similar values (~94.5% of theoretical density) at 1800°C. This result is in agreement with the work of McCauley and Corbin,[2] who reported that Al_2O_3 with 35.7 mol% AlN addition, sintered at 1825°C, exhibited a similar density.

The measured and calculated nitrogen content for the specimens with additions of 1–25 mol% AlN, after sintering at 1600, 1700 and 1800° C for 2 h under 1-atm nitrogen gas atmosphere are shown in Fig. 7. The evaporation of nitrogen in the 1600°C-sintered specimen was confirmed and its degree increased with increasing AlN content. In the 1700°C-sintered specimen, the measured nitrogen content was somewhat high compared with the calculated nitrogen content but for the 1800°C-sintered specimen, both were nearly same.

Microstructures of polished and thermally etched surfaces of materials obtained by sintering at 1600–1800°C for 2 h with additions of 1–25 mol% AlN were prepared and examined. After sintering at 1600°C (Fig. 8), the microstructure of the specimen with 1 mol% AlN was similar to that of sintered pure alumina except for the presence of localised AlON particles. With increasing AlN addition, from 5 to 25 mol%, the amounts of AlON and porosity present increased and at the same time the grain growth of Al_2O_3 was suppressed, with an overall poor densification of the compact on sintering (Fig. 6). At the lower end of the addition range, in the specimens with 5 and 10 mol% AlN, it was possible to distinguish the Al_2O_3 from AlON grains. However, in the specimens with 20 and 25 mol% AlN, it was no longer possible because the reaction of Al_2O_3 and AlN proceeded. On sintering at 1700°C (Fig. 9), in the specimen with 5 mol% AlN, AlON was mainly formed at the triple point regions of the alumina

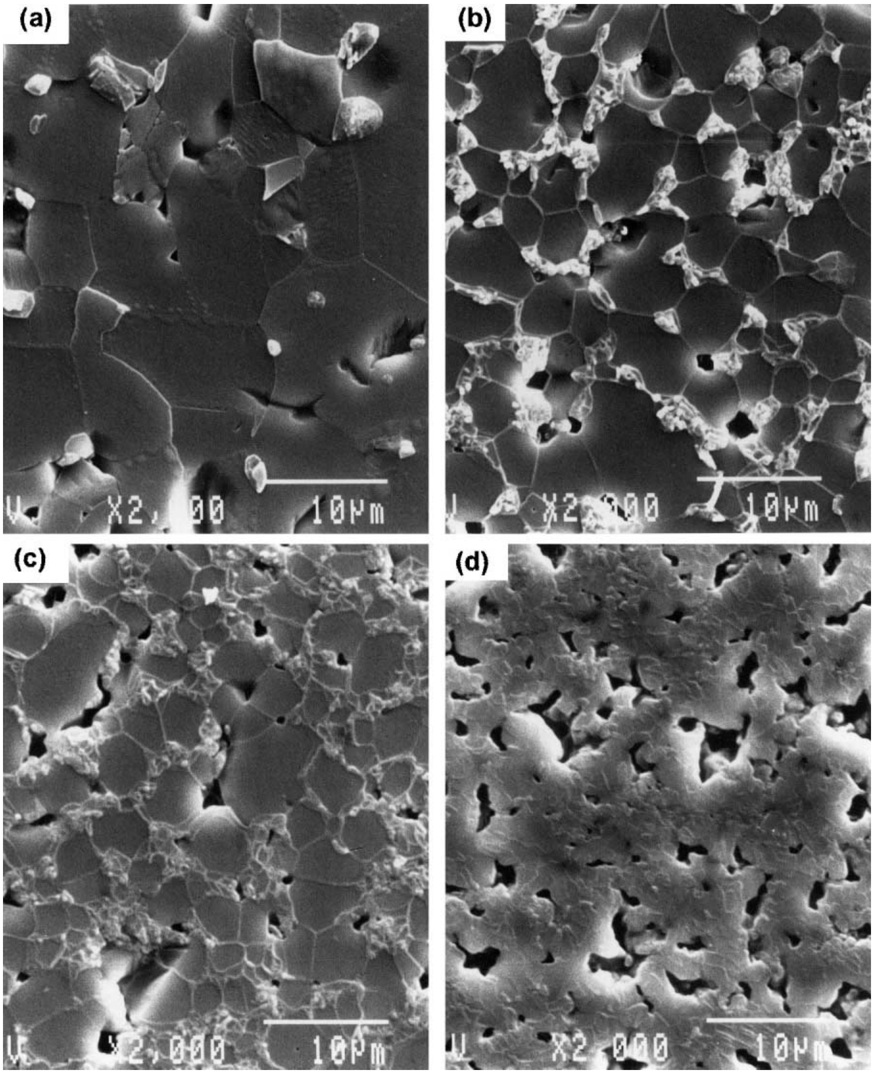

Fig. 9. SEM micrographs of polished and etched surfaces of AlN–Al_2O_3 specimens containing (a) 1, (b) 5, (c) 10 and (d) 20 mol% AlN, sintered at 1700°C for 2 h.

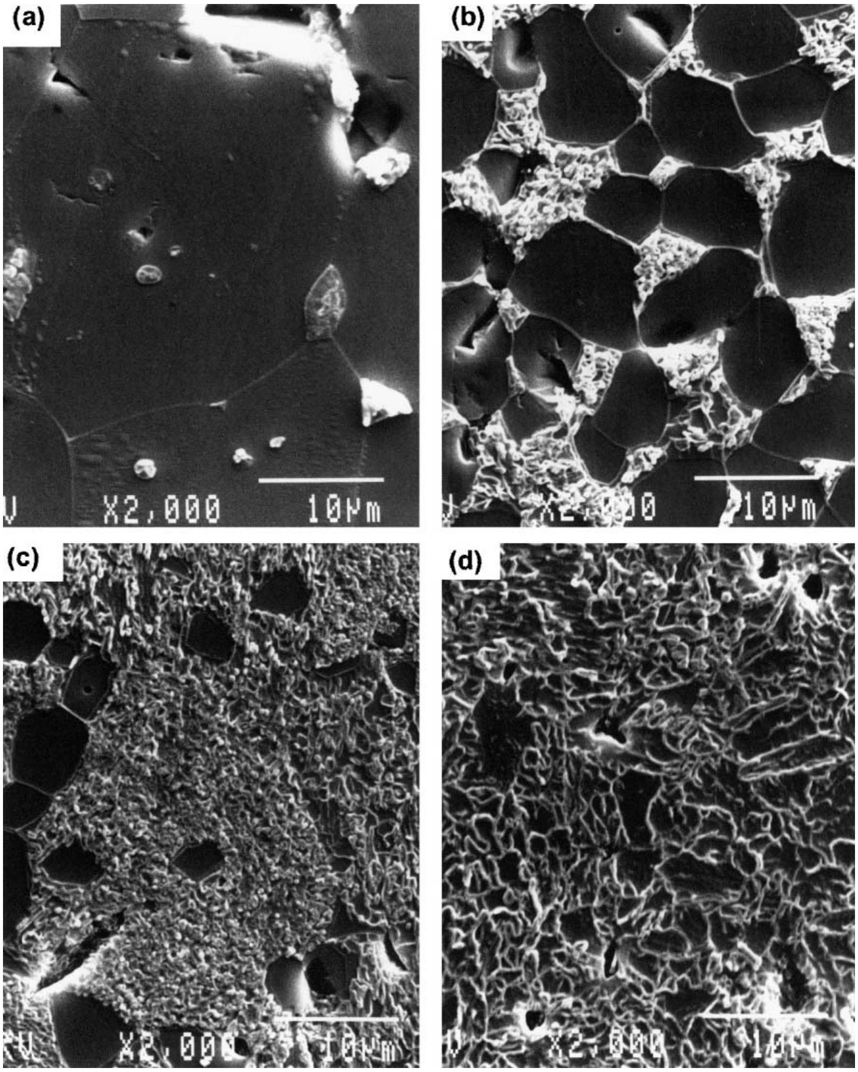

Fig. 10. SEM micrographs of polished and etched surfaces of AlN–Al_2O_3 specimens containing (a) 1, (b) 5, (c) 10 and (d) 20 mol% AlN, sintered at 1800°C for 2 h.

grains. However, in the case of addition of 25 mol% AlN, the reaction converted almost all the Al_2O_3 into AlON. The reaction and sintering process occurred simultaneously, to completion, but left large remnant pores (Fig. 9(d)). On sintering at 1800°C (Fig. 10), in the specimen with 5 mol% AlN, the alumina grains were homogeneous with a mean grain size of about 2 μm and the formation of AlON increased notably at the triple points. AlON and isolated alumina grains were present in the specimen with 10 mol% AlN addition. A further feature of interest was the decrease in porosity as the sintering temperature was increased, of specimens with 20 and 25 mol% AlN. After sintering mixed compacts of Al_2O_3 with additions of 1–20 mol% AlN at 1700° C, the microstructure was examined in detail using STEM (Fig. 11). It is apparent that on increasing the AlN content, the regions of AlON phase increased becoming extended around the Al_2O_3 grain boundaries.

The grain size of the Al_2O_3 in the specimens with 1, 5 and 10 mol% AlN addition, allowed the alumina grains to be distinguished from others (Figs. 8–10) is shown in Fig. 12. The Al_2O_3 grain size increased with increasing sintering temperature, regardless of the amount of AlN added. The incremental rate of Al_2O_3 grain growth in the specimens with 5 and 10 mol% AlN addition was clearly low compared with the specimen having 1 mol% AlN addition. There was little consistency in the relationship between the AlON content formed and the Al_2O_3 grain growth. The formation of relatively large amounts of AlON with increasing sintering temperature and AlN addition generates pores in the sintered body; under such conditions the presence of a further phase may not effectively suppress matrix grain growth.

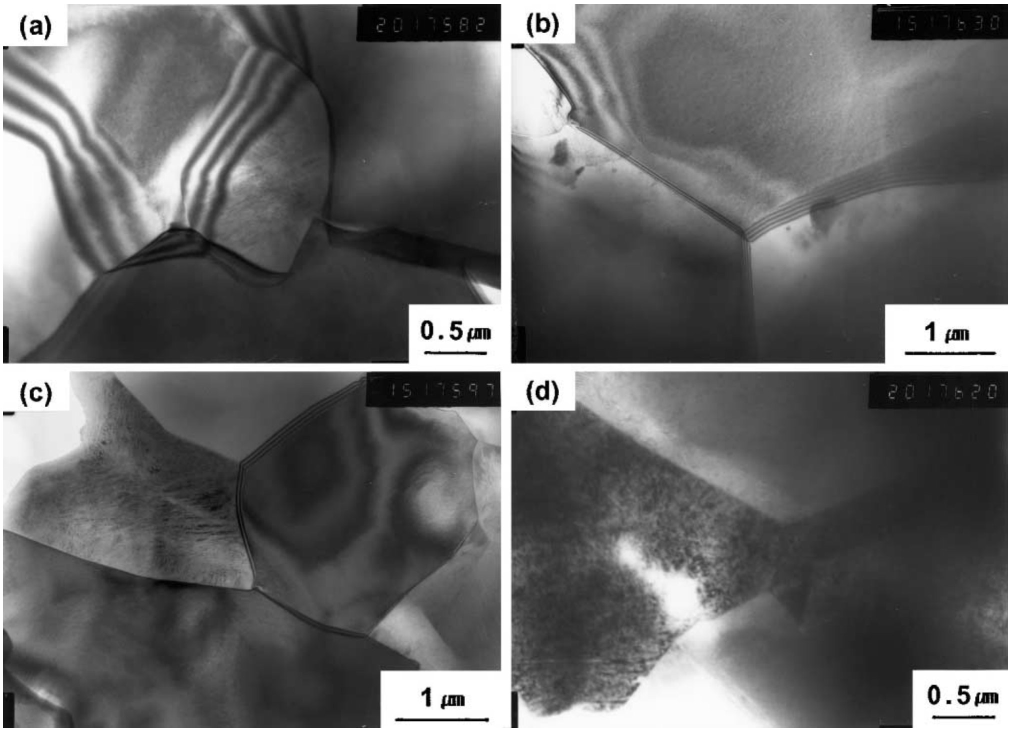

Fig. 11. STEM photographs of AlN–Al_2O_3 specimens containing (a) 1, (b) 5, (c) 10 and (d) 20 mol% AlN, sintered at 1700°C for 2 h.

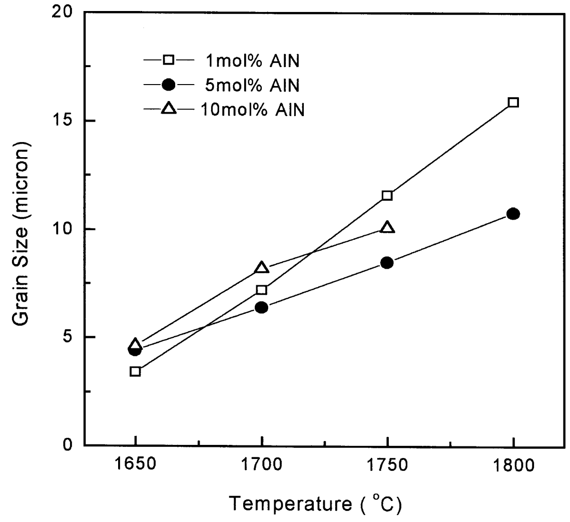

Fig. 12. Variation of Al_2O_3 grain size as a function of sintering temperature in AlN–Al_2O_3 specimens containing different AlN content.

4. Conclusions

Reaction sintering has been undertaken and the microstructure of compacts with 1–25 mol% AlN addition to Al_2O_3 has been characterized after pressureless sintering at 1600–1800°C in a nitrogen atmosphere. The densification of alumina with additions of 1–10 mol% AlN was nearly complete at 1750°C. The sintered densities of the specimens with additions of 20 and 25 mol% AlN reached ~94.5% of the theoretical value at 1800°C. As the AlN content and sintering temperature increased, increased volume fractions of the AlON phase formed, due to the enhanced reaction of Al_2O_3 and AlN. In the specimens with 5 and 10 mol% AlN, a ϕ phase formed at 1800°C. All the α-Al_2O_3 present in the samples with additions of 20–25 mol% became to be incorporated into the AlON product above 1650°C. The specimen with low AlN content (<10 mol%) showed a homogeneous microstructure and the AlON formed was situated primarily at the low energy triple points sites of the alumina grains. Specimens with higher AlN (>10 mol%) content developed AlON at the grain boundaries often surrounding all alumina grains.

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