

# SYNTHESIS OF ALUMINUM OXYNITRIDE SPINEL POWDERS BY ALUMINOTHERMIC REACTION UNDER REDUCING CONDITIONS

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*Aluminum oxynitride spinel (AlON) powders were synthesized by aluminothermic reaction under reducing conditions provided by  $N_2$ -CO atmosphere using low cost and easily available aluminum and  $\gamma$ - $Al_2O_3$  alumina micron-sized powders as starting materials. The influence of Al/ $\gamma$ - $Al_2O_3$  ratio and sintering temperature on the phase composition and microstructure of sintered samples was explored. The experimental results showed that when Al/ $\gamma$ - $Al_2O_3$  mass ratio equal to 3, AlON phase with AlN as a minor phase can be formed at 1600°C using this method. And we attributed the presence of small amounts of AlN to the displacement of oxygen atoms from AlON phases by nitrogen atoms at high temperature under carbon embedded condition. At the same time, grains of AlON were tabular in shape and whiskers can be found in samples after sintered at 1600°C because of elevated amount o non-stoichiometric species (Al,  $Al_2O$ , AlO) produced in strongly reducing atmosphere.*

## INTRODUCTION

Spinel-structure aluminum oxynitride (AlON) is an important single-phase and stable solid solution ceramic in the  $Al_2O_3$ -AlN system [1-2]. In its solid solution range, the molar content of  $Al_2O_3$  is 62.4%-72.5% [3]. AlON has good resistance to high temperature, corrosion, and oxidation, makes it useful in advanced temperature structural ceramics, cutting tools and refractories [4-6]. At the same time, AlON has favorable optical properties. It is suitable for use in infrared and visible window applications [7-8]. Therefore, AlON ceramic has broad prospects for applications in modern national defense and economic construction, but its high cost of production severely limits its applications. The industrial way for synthesis of AlON of different compositions is high-temperature sintering of AlN and  $Al_2O_3$  in pure nitrogen or a vacuum [9-10]. The major difficulty with this technique is in obtaining AlN powders with a high purity and a fine particle size. Relatively novel method of AlON synthesis is carbothermal nitridation of  $Al_2O_3$  ( $C+Al_2O_3$ ) and aluminothermic reduction by  $Al+Al_2O_3$  [11-13]. However, these methods of AlON synthesis still required the very pure nitrogen (oxygen content: 7 p.p.m). This makes its high cost of production.

In order to reduce the oxidation of the carbonaceous phases, charcoal-protected method was widely used in the

preparation and application of carbonaceous materials. This method has the advantages of simple process and low cost. Li Yuanbing et al [14] synthesized  $TiB_2$  based composite in charcoal-protected condition and found CO and  $N_2$  are the main gases in this atmosphere. In order to overcome the shortcoming of synthesis AlON in very pure nitrogen and reduce production cost of AlON, the main purpose of the present investigation of AlON synthesis, is to explore the possibility of synthesis of AlON using aluminum and  $\gamma$ - $Al_2O_3$  as raw materials in charcoal-protected condition. At the same time, we will study the effect of variation of different synthesis parameters on conversion rate and particle morphology. To this end, powder mixtures of different of aluminum and  $\gamma$ - $Al_2O_3$  starting materials were heat-treated at different temperature in charcoal-protected condition.

## EXPERIMENTAL

Commercially available aluminum and  $\gamma$ - $Al_2O_3$  powders were used as raw materials. The average particle size and purity of aluminum powders were 50  $\mu m$  and more than 99.5% in mass percent and those of  $\gamma$ - $Al_2O_3$  powders were 1.18  $\mu m$  and more than 99% in mass percent. The  $\gamma$ - $Al_2O_3$  was produced from boehmite heated at 700°C for 4 h.

Aluminum powders were mixed with 88, 70 and 25 wt.%  $\gamma$ - $\text{Al}_2\text{O}_3$ . The samples were classified as A, B, and C, respectively. Different powders batches were mixed and homogenized by ball milling in ethanol for 2h in a nylon bottle with alumina balls. After drying at 60°C for 24 h, the powder cake was crushed in an agate mortar and passed through a 100 mesh sieve. The granules were formed into cylinders 20mm in diameter and 15mm in thickness pressed at 200 MPa in a stainless-steel die. The cylinders were then covered with carbon granules (5-0.5 mm) in a sagger and heated in a furnace at 1600 °C for 3 h (Fig. 1), respectively.

XRD analysis(D/MAX2500PC model, Rigaku Co., Japan) was conducted using Ni filtered Cu  $K_\alpha$  under the following conditions: scanning speed of 2°  $\text{min}^{-1}$  and temperature of 16°C. The microstructure was carried out using scanning electron microscopy (SEM) (KYKY-2800B). Particle size of raw materials was measured using a laser diffraction method (Mastersizer 2000E, Malvern Instruments Ltd., England).

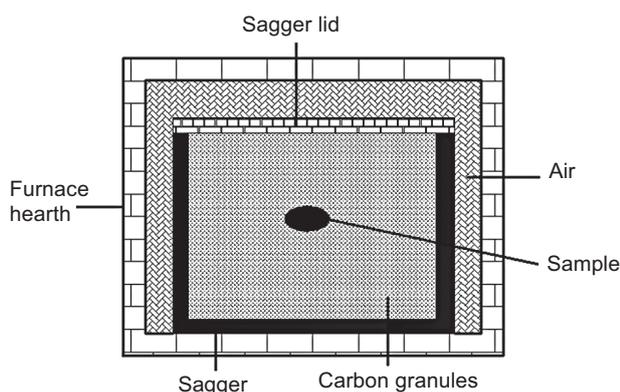
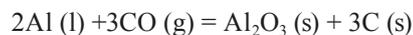


Figure 1. Schematic diagram of preparation process.

## RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of samples with different mass ratio of Al and  $\gamma$ - $\text{Al}_2\text{O}_3$  sintered at 1600°C for 3h. It is evident from the figure that AION peaks appear in all samples and the peak intensity of AION increases to a maximum in samples C. When Al/ $\gamma$ - $\text{Al}_2\text{O}_3$  mass ratio equal to 0.14 and 0.43, a large amount of  $\text{Al}_2\text{O}_3$  phases remained indicating the inappropriate Al/ $\gamma$ - $\text{Al}_2\text{O}_3$  mass ratio. In case of sample C, only a small amount of AlN existed as well as large amounts of AION phases. Therefore, we concluded that AION phase with AlN as a minor phase can be formed at 1600 °C in charcoal-protected condition when Al/ $\gamma$ - $\text{Al}_2\text{O}_3$  mass ratio equal to 3. This temperature is lower than its synthetic temperature in the phase diagram of McCauley [15]. We attributed this decrease to two reasons. One side, in charcoal-protected condition, CO and  $\text{N}_2$  are the main gases. Carbon monoxide is produced by the reaction between

atmospheric oxygen and carbon granules in the sagger and the nitrogen is from the atmosphere. According to literature [16], Al and CO can react to form  $\text{Al}_2\text{O}_3$  and C in charcoal-protected condition. Reaction equation as follows:



This is an exothermic reaction. Therefore, the actual temperature around samples is higher than 1600°C. The oxidation of aluminum in charcoal-protected condition also coincided well with the higher content of aluminum required in this paper than that of other paper which AlON was synthesized by aluminothermic reduction [12]. On the other hand, alumina obtained by oxidation of aluminum has higher activity and the volatility of alumina is several orders of magnitude greater in reducing conditions [17]. These are helpful for AlN which obtained by aluminum and  $\text{N}_2$  in the furnace react with  $\text{Al}_2\text{O}_3$  to AlON.

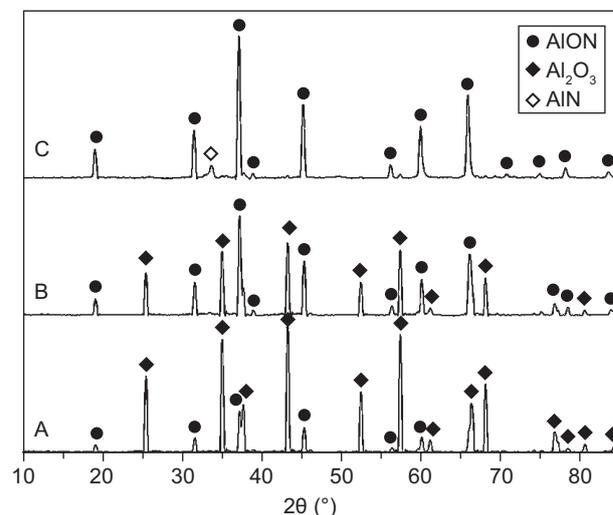


Figure 2. XRD patterns of specimens sintered at 1600°C for 3 h: A – Al/ $\gamma$ - $\text{Al}_2\text{O}_3$  mass ratio equal to 0.14, B – Al/ $\gamma$ - $\text{Al}_2\text{O}_3$  mass ratio equal to 0.43, C – Al/ $\gamma$ - $\text{Al}_2\text{O}_3$  mass ratio equal to 3.

XRD patterns of sample C in Fig. 2 show the presence of very small amount of AlN. In order to further investigate the effect of sintering temperature and Al content on the peak intensity of AlN, four more samples, having the same composition as sample C, were prepared and sintered at 1550 °C, 1650 °C, 1700 °C and 1750 °C for 3 h, respectively. XRD patterns of these samples are presented in Fig. 3. It is evident from the figure that AION is the main phase in all samples. The diffractogram A in Fig. 3 shows the presence of  $\text{Al}_2\text{O}_3$  and AlN at 1550 °C. Therefore, we concluded that  $\text{Al}_2\text{O}_3$  and AlN is not completely reaction at 1550 °C. When sintering temperature is higher than 1600 °C,  $\text{Al}_2\text{O}_3$  phase disappears, the peak intensity of AlN decreases to the lowest at 1600°C and then increases above this

temperature up to 1750 °C. This shows that the optimal synthesis AION temperature under reducing conditions is 1600 °C. In addition, two more samples having Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 2.70 and 3.35 (Al content below and above 75 wt%), respectively were prepared and sintered at 1600 °C for 3 h. XRD patterns of these samples are presented in Fig. 4. It is seen that the predominant phase is AION. A small amount of AlN appears in Fig. 4B and 4C but in Fig. 4A both AlN and Al<sub>2</sub>O<sub>3</sub> phases are present. Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mass ratio has little effect on the peak intensity of AION. Therefore, we can attribute the presence of AlN to the displacement of oxygen atoms from AION phases by nitrogen atoms at high temperature under carbon embedded condition.

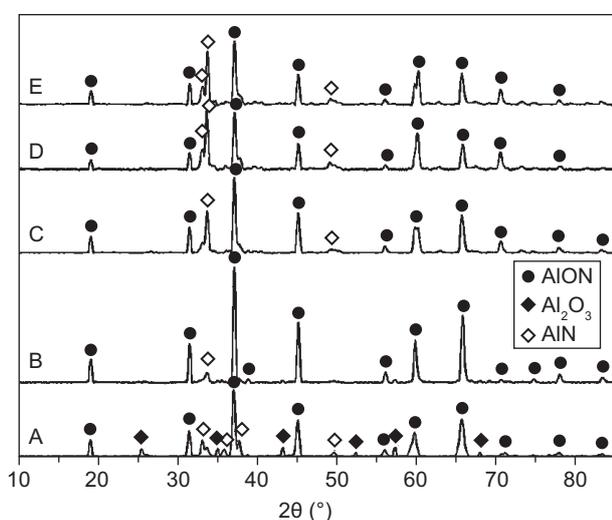


Figure 3. XRD patterns of specimens with Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 3 sintered at different temperature: A – 1550 °C, B – 1600 °C, C – 1650 °C, D – 1700 °C, E – 1750 °C

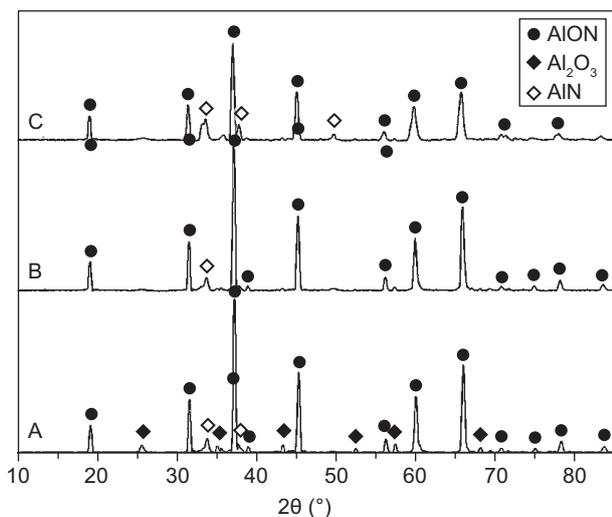


Figure 4. XRD patterns of specimens sintered at 1600 °C for 3 h: A – Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 2.70, B – Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 3, C – Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 3.35.

This is also the cause of peak intensity of AlN increasing with sintering temperature (in Fig. 3). The temperature dependency of AlN peak intensity of sample C was similar to that for the AION synthesized under flowing nitrogen atmosphere [13].

Scanning electron micrographs of samples with Al/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mass ratio equal to 3 sintered at 1600 °C for 3 h are shown in Fig. 5 and Fig. 6. Fig. 5 shows grains of AION are tabular in shape. This is attributed to elevated amount of non/stoichiometric species (Al, Al<sub>2</sub>O, AlO) produced in strongly reducing atmosphere. These low valence aluminum oxide gases make the growth of AION controlled by interface reaction because of the higher mass transport rate of gas. According to literature [18], the plate-like crystals increase when grain growth is controlled by the interface reaction. It is noted in Fig. 6 that some AION whiskers appear, especially the surface and hole of specimens. At the same time, most of the whiskers have sharp top and whiskers with hemispherical droplet are very few. Therefore, we suppose that the mechanism of whiskers growth was vapor-solid (VS) mechanism. The AION whiskers growth process may be as follows. As the reaction progresses, a large number

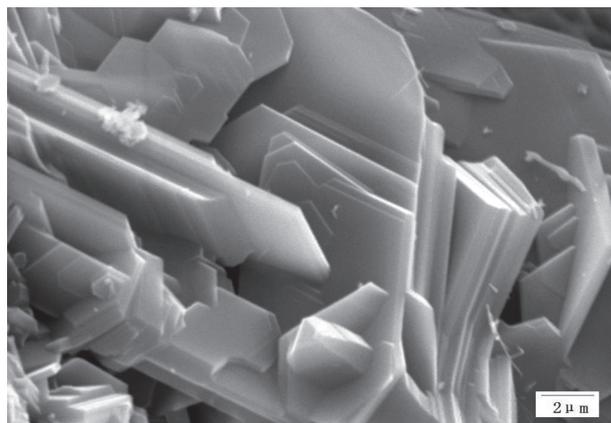


Figure 5. SEM micrographs of sample C sintered at 1600 °C for 3 hours.

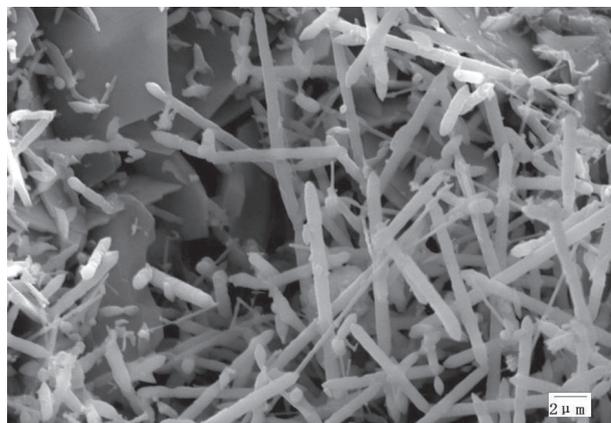


Figure 6. Secondary electron micrographs of AION whiskers of sample C sintered at 1600 °C for 3 hours.

of low valance aluminum oxide diffuse to the surface of specimens or hole in specimens and react with  $N_2$  and  $Al_2O_3$ . Then reaction products nucleate and grow on the surface of AION particle which has been generated. Thus, AION whiskers were produced in this paper. This also may be the reason that whiskers are mainly present at the surface and in the pores of the specimens.

### CONCLUSIONS

The main purpose of this paper was to explore the possibility of synthesis of AION powders using aluminum and  $\gamma-Al_2O_3$  as raw materials under reducing conditions. Influences of  $Al/\gamma-Al_2O_3$  mass ratio and sintering temperature in the phase composition and microstructure of sintered samples were studied. Based on the results above, it could be concluded as following:

- 1)  $Al/\gamma-Al_2O_3$  mass ratio of raw materials and sintering temperature played a great role in the synthesis of AION powders. When  $Al/\gamma-Al_2O_3$  mass ratio equal to 3, AION phase with AlN as a minor phase can be formed at 1600°C. We attributed the presence of AlN to the displacement of oxygen atoms from AION phases by nitrogen atoms at high temperature under carbon embedded condition. The peak intensity of AlN increased with sintering temperature when the sintering temperature is higher than 1600 °C.
- 2) The grains of AION synthesized in this paper were tabular in shape and whiskers can be found in samples sintered at 1600°C because of elevated amount of aluminum species (Al,  $Al_2O$ , AlO) produced in strongly reducing atmosphere.
- 3) It may be concluded that AION powders can be easily produced under reducing conditions. In order to obtain single-phase AION powder, research along these lines is in progress.

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