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Full Length Article

Phase, microstructure and sintering of aluminum nitride powder by the carbothermal reduction-nitridation process with Y_2O_3 addition

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ABSTRACT

Aluminum nitride powders were synthesized by carbothermal reduction-nitridation method using $Al(OH)_3$, carbon black and Y_2O_3 as raw materials. The change of phase, microstructure and densification during the AlN synthesis and sintering process were investigated and the effects of Y_2O_3 was discussed. The results showed that Y_2O_3 reacted with Al_2O_3 to form yttrium aluminates of $YAlO_3$ (orthorhombic and hexagonal phases), $Y_4Al_2O_9$ and $Y_3Al_5O_{12}$ at the low temperature of 1350 °C. $YAlO_3$ could firstly be transformed into Y_2O_3 and then completely into YN when the firing temperature and holding time increased. However, YN could be oxidized into Y_2O_3 again after the carbon removal at 700 °C in the air atmosphere. There were two ways generating AlN when adding Y_2O_3 and the possible mechanism was proposed. Y_2O_3 from YN oxidation favored the densification of AlN ceramics because the liquid had better flowability and distribution in the sintering process at 1800 °C.

1. Introduction

In the last twenty years, an increasing amount of attention has been paid to AlN in the electronic industry due to its high thermal conductivity, high electrical resistivity, good electrical insulation, nontoxicity and thermal expansion coefficient close to that of silicon [1–3]. Recently, the demand for low cost is becoming more and more urgent with the expansion of the application field.

The commercial AlN powders were synthesized in two primary ways: carbothermal reduction-nitridation (CRN) of Al_2O_3 and direct nitridation (DN) of Al metal [4]. Comparatively, the CRN process had more advantages of high purity, high stability against humidity and high sinterability in the preparation of AlN powder [5,6]. However, the highly pure AlN powders had high cost because of the high reaction temperature, long reaction time and the requirement of Al_2O_3 and carbon black with high purity. Much work has been done in the past few years to improve CRN method and lower the nitridation temperature. It has been reported that $Al(OH)_3$ used as a starting material of CRN has drawn more and more attention as the nitridation reaction rate from $Al(OH)_3$ was higher than that from conventional α-Al_2O_3 [7–10].

It was well known that additives were always used to reduce the synthesis temperature of AlN powders [11–13]. Molisani et al. [13] proved that some additives, such as CaF_2, Y_2O_3, $LiCO_3$, $SrCO_3$, could reduce the synthesis temperature of AlN powders by CRN method. Particularly, Y_2O_3 was one of the most commonly used additives to promote the densification of AlN ceramics in the sintering process since it reacted with Al_2O_3 to form liquid yttrium aluminates [14,15]. The effects of Y_2O_3 on the phase compositions, reaction rate and spherical granules of AlN powders by carbothermal synthesis had also been studied by several researchers using Al_2O_3 or its precursor [16–19]. However, the relationship between the phase change during the carbothermal synthesis and the carbon removal and the following sintering process was seldom studied when Y_2O_3 was used in the solid reaction.

In this study, AlN powders was prepared from $Al(OH)_3$ by the CRN process, using Y_2O_3 as the promoting additive. Some interesting phenomena between the phase and morphology were observed. The effects of Y_2O_3 on the phase composition, microstructure and sintering property of AlN powder were systematically investigated.

2. Experimental procedure

Commercially available $Al(OH)_3$ powder (Chalco Shandong Co., China, H-WF-1, 99.9% purity), carbon black powder (Hangzhou Juy New Materials Technology Co., China, N124, 99.9% purity) and Y_2O_3 powder (Ganzhou Shangyuan New Material Co., China, 99.9% purity) were used as the starting materials. The particle size distribution of $Al(OH)_3$ powder was approximately 1–3 μm as shown in Fig. 1(a). Y_2O_3 particles were irregular flakes with particle size range of 1–6 μm as

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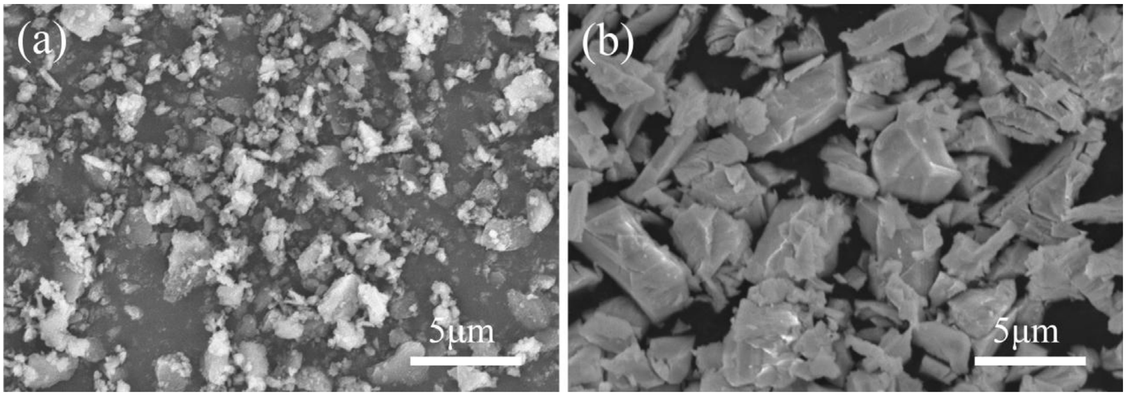

Fig. 1. SEM photographs of the raw materials. (a) $Al(OH)_3$; (b) Y_2O_3.

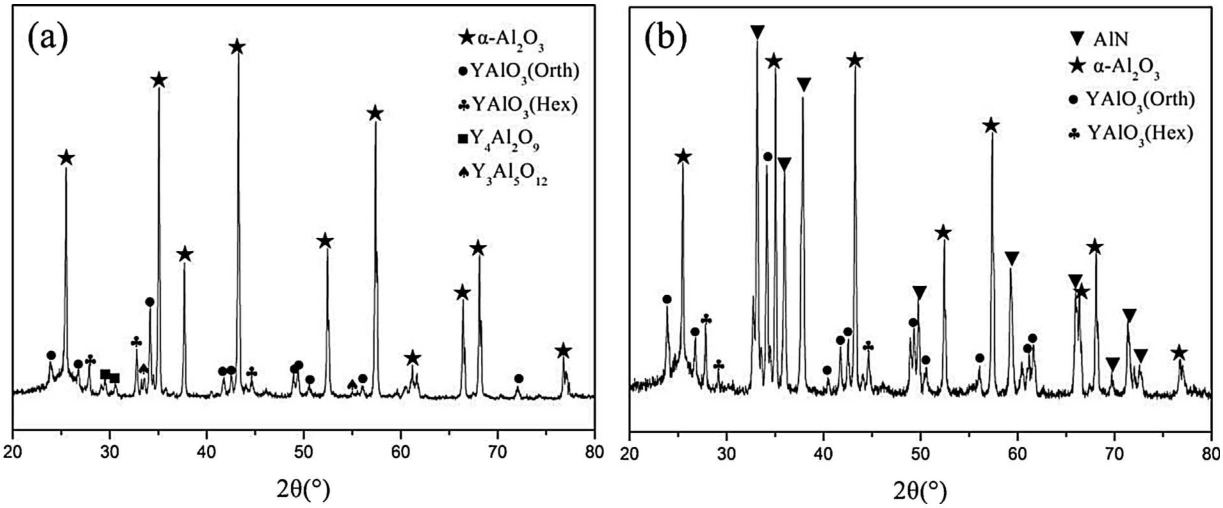

Fig. 2. X-ray diffraction patterns of the products with 8 wt% Y_2O_3 addition synthesized at different temperatures. (a) 1350 °C; (b) 1400 °C.

shown in Fig. 1(b). The contents of Y_2O_3 additive varied within the range of 0–8 wt% of $Al(OH)_3$. The mass ratio of $Al(OH)_3$ to carbon black was 2.5.

The three raw materials with the total weight of 20 g were mixed firstly and then fired in an experimental graphite furnace with the highly pure nitrogen atmosphere and normal pressure at the flowing rate of 2L/min at the temperatures ranging from 1350 °C to 1550 °C for 1–6 h. Subsequently, the residual carbon was removed by heat treatment in air at 700 °C for 2 h using an electric furnace (KBF1700, Nanjing University Instrument Plant). YAN was labelled as the product with 8 wt% Y_2O_3 addition which was achieved at 1550 °C for 6 h.

To investigate the sintering properties of YAN, the single AlN powder was prepared at 1550 °C for 6 h without Y_2O_3 addition and labelled as AN. After the excessive carbon was removed, YAN powder and AN powder with the commercial Y_2O_3 addition by the same adding content as YAN with the weight of 10 g each batch were ball-milled by planetary milling for 3 h respectively, using ethanol as the mixing medium with ratio of alumina balls to powders of 10:1. After dried in vacuum oven, the powders were granulated with polyvinyl butyral (PVB) and then were pressed into pellet with the weight of 0.4 g and the diameter of 12.41 mm under the pressure of 200 MPa. The green bodies de-waxed at 600 °C were put in the BN crucible which was covered with coarse AlN powder in the bottom. Then, the two samples were sintered in a graphite furnace at 1800 °C for 2 h in a flowing nitrogen atmosphere. The sintered samples from YAN and AN/Y_2O_3 powders were labelled as sample A and B respectively.

The phase compositions of the powders achieved in different conditions were identified by X-ray diffraction (XRD, PANalytical X'Pert PRO) with Cu Kα radiation. The particle morphologies of the powder and the fractural surfaces of sintered pellets were detected by scanning electron microscopy (SEM, Hitachi SU1510) and field emission scanning electron microscopy (FESEM, FEI Nova NanoSEM 450) with EDS analysis. The TG analysis (TA Instruments, Q5000IR) between 50 and 700 °C were carried out to detect the weight change during the carbon removal in the air and nitrogen atmospheres with the flowing rate of 50 ml/min at the heating rate of 10 °C/min. The shrinkages and the densities of the sintered pellets were measured by Vernier caliper and Archimedes displacement method respectively.

3. Results and discussion

3.1. Phase compositions

Fig. 2 showed the X-ray diffraction patterns of the products with 8 wt% Y_2O_3 addition synthesized at different temperatures for 1 h. It was found that most products displayed α-Al_2O_3 phase at 1350 °C which were decomposed by $Al(OH)_3$. AlN and α-Al_2O_3 phases were detected when the temperature increased to 1400 °C. This indicated that the starting formation temperature of AlN was 1350–1400 °C in the condition of adding Y_2O_3, followed by the corresponding chemical reaction:

$$\alpha\text{-}Al_2O_3(S) + 3C(S) + N_2(g) \rightarrow 2AlN(S) + 3CO(g) \quad (1)$$

As shown in Fig. 2(a), two phases of orthorhombic $YAlO_3$ (YAP) and hexagonal $YAlO_3$ (YAH), $Y_4Al_2O_9$ (YAM) and small amount of $Y_3Al_5O_{12}$ (YAG) were detected at 1350 °C. This suggested that Y_2O_3 could react