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Preparation and properties of AlON powders

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ABSTRACT

Aluminum oxynitride (AlON) powders were synthesized using the raw materials of γ-Al_2O_3 and carbon black through the carbothermal reduction and nitridation process. The carbon content in the γ-Al_2O_3/C mixture and heating temperature were investigated. The AlON powders were synthesized by calcination for 2 h at 1750 °C when the carbon content in the γ-Al_2O_3/C mixture was 5.8 wt%. The particle size of powder is important to the transparency of ceramics, but the size of the synthesized powder was large. Therefore, a few methods, such as freeze-drying, ultrasonic dispersion, and liquid nitrogen ball milling, were used to reduce the particle size of powders. Among the three methods, liquid nitrogen milling had the best results.

1. Introduction

Transparent aluminum oxynitride (γ-AlON) is an important single-phase, stable solid-state ceramic in the Al_2O_3-AlN binary system. It was widely used in military and commercial fields due to excellent physical, mechanical, and chemical properties, as well as good optical transmittance from ultraviolet to mid-infrared range (wavelength 0.2–5.0 μm with transmittance of up to 80%) [1–4]. At present, AlON transparent ceramics have become one of the preferred candidate materials for high-temperature infrared windows and bulletproof materials for armors and head gears [5,6]. AlON has attracted increasing interest since it was found by Yamaguchi in 1959. Many researchers have studied the preparation of powders and sintering additives to fabricate highly transparent AlON ceramics. Martin et al. used 0.5 wt% Y_2O_3 as an additive to fabricate AlON ceramics [7]. Liu et al. fabricated transparent AlON ceramics using 0.25 wt% MgO and 0.04 wt% Y_2O_3 as sintering aids and gained a transmittance of 83% at 2000 nm [8]. Sintering additives can reduce sintering temperature and promote densification of ceramics by inhibiting grain growth and grain boundary migration. With the exclusion of sintering additives, many factors affect the transparency of AlON ceramics, such as the purity, dispersion and particle size of raw materials, and sintering temperature.

In general, there are two ways to prepare AlON transparent ceramics. The one is a one-step method which involves the simultaneous process of solid-state reaction and densification of Al_2O_3 and AlN powder. The other one is a two-step method for reactive sintering, which involves the sintering of AlON powders [9]. Solid-state reaction sintering is a simple method but it requires homogeneous composition and high temperature due to its high energy consumption. The two-step method is commonly used to fabricate AlON transparent ceramics. At present, carbothermal reduction nitridation, aluminothermic reduction nitridation, and solid-state reaction are common methods for the preparation of AlON powders [10–16]. The most widely used method is carbothermal nitridation, which was also used in the present study.

Regardless of the method used to synthesize the AlON powder, all methods require high temperatures, which result in agglomeration of powders and grain growth. The agglomerated powders may produce pores that are difficult to remove during the sintering process, thereby resulting in the decreased transparency of the ceramic [17]. When the particle size of the raw material is small, the pores between the particles are all small, and atoms can easily diffuse in the process of sintering. The elimination of pores is more conducive to the improvement of the sintering properties of raw materials, which allow the product has a uniform structure and high transparency. Several researchers have studied the preparation of powders and sintering additives, but few have reported on the preparation of powders with smaller particle size.

In this study, AlON powders were prepared by carbothermal reduction nitridation, and the effects of different ratios of raw materials and sintering temperature on the preparation of powders were discussed. The prepared powders underwent freeze-drying, ultrasonic dispersion, and liquid nitrogen ball milling to reduce the particle size and their morphology and particle size were analyzed.

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2. Experimental section

AlON powders were prepared by carbothermal reduction nitridation. The starting materials were nanosized γ-Al_2O_3 (99.99%, Macklin Biochemical Co.,Ltd, Shanghai, China) and carbon black (99.5%, Macklin Biochemical Co.,Ltd, Shanghai, China). The γ-Al_2O_3 and carbon black (5.4–6.0 wt%) were ball-milled with zirconia balls and anhydrous ethanol at 200 rpm for 12 h. The resulting slurry was dried for 4 h at 80 °C, ground in a mortar, and passed through 200-mesh nylon sieve.

Then, the obtained mixture of γ-Al_2O_3 and carbon powder was placed into BN crucible and was heated in the atmosphere of nitrogen within the graphite furnace. The mixture was first heated at a heating rate of 10 °C/min to 1550 °C for 1 h to produce AlN, and then heated at a heating rate of 3 °C/min to 1650, 1750 and 1800 °C for 2 h to obtain AlON powders. The resulting powders were treated for 4 h in air at 700 °C to remove excess carbon or impurities.

The size of the synthesized AlON powder was large and required further treatment. The particle size of AlON powder was reduced by freeze-drying, ultrasonic dispersion, and liquid nitrogen milling method. The AlON powder was dispersed in deionized water and then freeze-dried for 24 h at − 80 °C to produce Sample No. 1; The obtained AlON powder underwent ultrasonic dispersion with absolute ethanol for 2 h to produce Sample No. 2; The AlON powder was milled by liquid nitrogen for 6 h to produce Sample No. 3. Then the particle sizes of the three samples obtained by the above three methods was compared.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the reaction process (TGA/DSC1, Metter Toledo Co., Switzerland) in a nitrogen atmosphere with a heating speed of 10 °C/min. The raw material, AlON powders, and post-treatment powders were measured by a laser particle size analyzer (L8 13320, Beckman Coulter Inc. Co. Ltd., United States). The phases of the powders were identified by X-ray diffraction (AXS D8 advance, Bruker Co., Germany). The microstructures of the raw materials and the powders synthesized were analyzed by the energy dispersive spectrometer (EDS) (X-MAX-50, Oxford Co., Britain) and the scanning electron microscope (QUANTA FEG 250, FEI Co., United States).

3. Results and discussion

Fig. 1 shows the particle size distribution of γ-Al_2O_3 and carbon black. The median diameter of γ-Al_2O_3 and the carbon powder are approximately 6.656 μm and 15.42 μm, respectively, as displayed in Fig. 1**(a)** and **(b)**. The particle size is larger than expected due to the agglomeration of powders. The scanning morphologies of the raw materials and γ-Al_2O_3/C mixture are shown in Fig. 2, and the morphologies were evident at high magnification. The particle size of γ-Al_2O_3 and carbon powder can evidently reach nanometer scale, as displayed in Fig. 2**(a)** and **(b)**. By comparing with Fig. 1, it is known that the agglomeration of the raw materials existed. The mixing degree of γ-Al_2O_3 and carbon powder is significant for the synthesis of single-phase AlON powders, however, the agglomeration and large particles of raw materials will hinder the mixing of γ-Al_2O_3 with carbon powder; therefore, it is necessary to improve the mixing degree of γ-Al_2O_3/C mixture and reduce the size of the raw material by ball milling. Fig. 2**(c)** shows the morphology of γ-Al_2O_3/C mixture after ball milling for 12 h. The particle size of γ-Al_2O_3/C mixture has been considerably reduced after ball milling for 12 h, as shown in Fig. 2**(c)**. The fine-grained and homogeneous distribution of γ-Al_2O_3/C mixture is conducive to the synthesis of single-phase AlON powders.

Fig. 3 indicates the EDS mapping for Al, O, and C of the γ-Al_2O_3/C mixture after ball milling for 12 h. It can be seen from Fig. 3**(a)** and **(b)**, the aluminum and oxygen elements are uniformly dispersed in the γ-Al_2O_3/C mixture. The carbon element is slightly small because carbon powder accounts for only 5.8 wt% of the mixture, however, the grain size of carbon powder is fine and nearly evenly distributed in γ-Al_2O_3/C mixture, as shown in Fig. 3**(c)**. Therefore, ball milling for 12 h is suitable for this experiment.

The TG-DSC-DTG curves of γ-Al_2O_3/C mixture are shown in Fig. 4. The mixture lost weight at approximately 90 °C, and an endothermic peak is evident at this temperature from the DSC curve, which were attributed to the evaporation of water that was absorbed on the surface of the raw material. An endothermic peak can be observed at approximately 940 °C from the DSC curve, but the quality of the mixture slightly changed, which can be attributed to the decomposition of a small amount of organic matter in the mixture. An exothermic peak occurred at around 1300 °C in the DSC curve, which indicates that the crystalline shape of alumina changed (γ-Al_2O_3 transformed into α-Al_2O_3) at this temperature. The weight slightly varies from 500 °C and is close to zero from the DTG curve. The mixture does not react at 1400 °C, as shown in Fig. 4.

Fig. 5 shows the XRD diagram of the powders synthesized at a second step heat treatment temperatures of 1650 °C, 1750 °C, and 1800 °C for 2 h, and the first step thermal treatment at 1550 °C for 1 h. The powders prepared contain AlON, Al_2O_3, and AlN at the temperature of 1650 °C, which indicates an incomplete reaction. At 1750 °C and 1800 °C, the powder is single-phase AlON, which shows that AlON can be acquired at such temperatures. However, the experiment used a temperature of 1750 °C due to cost and other factors.

Fig. 6 shows the XRD diagram of the powders synthesized by the first step thermal treatment at 1550 °C for 1 h, and a second step thermal treatment at 1750 °C for 2 h. It can be seen that if the carbon

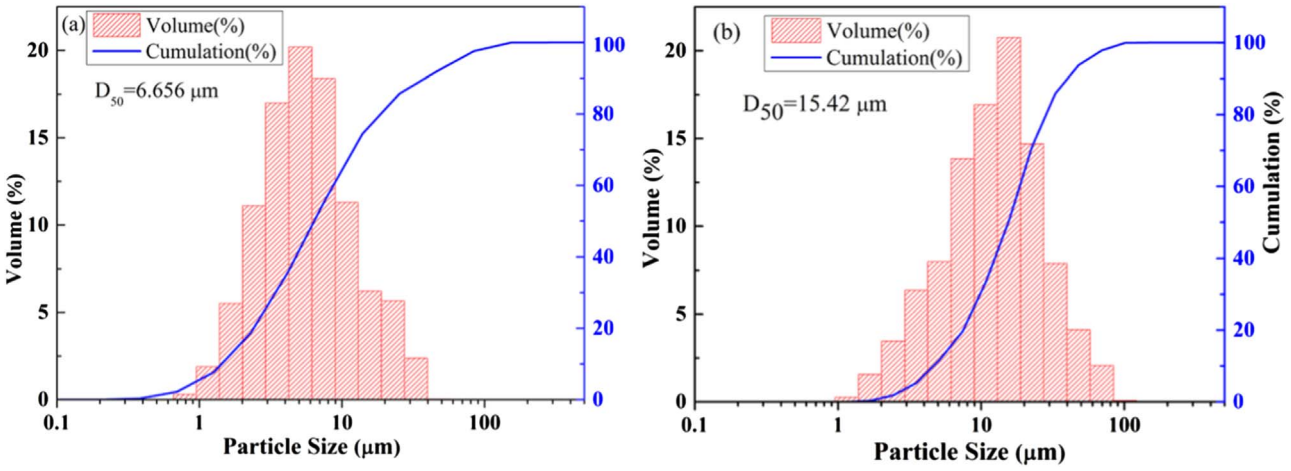

Fig. 1. Particle size distribution of the raw powders (a) γ-Al_2O_3 and (b) carbon black.