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Effects of Al_2O_3 phase composition on AlON powder synthesis via aluminothermic reduction and nitridation

Using micro-sized aluminum powder (11 wt.%) and nano-sized Al_2O_3 powder (89 wt.%) with five different phase compositions, AlON powders were synthesized at different temperatures in flowing-nitrogen atmosphere. Our results suggest that for starting materials with low γ-Al_2O_3/total Al_2O_3 ratio R (0 and 0.15), a calcination temperature of 1 750 °C is required to obtain single-phase AlON. This temperature is about 50 °C higher than for other batches starting with larger R values (0.5, 0.85, and 1.0). The AlON powders fabricated from reactants with a high R value in this work show narrower particle size distribution and better particle homogeneity than those prepared from batches with lower R values.

Keywords: Single-phase AlON powder; Aluminothermic reduction and nitridation method; Raw materials composition; Reaction process

1. Introduction

Aluminum oxynitride spinel (γ-AlON) is a very important phase of the Al_2O_3–AlN pseudobinary solid-solution system with a composition of $Al_{23}O_{27}N_5$ ($9Al_2O_3 \cdot 5AlN$). Due to its isotropic cubic structure, AlON can be sintered to a fully dense ceramic with high in-line transmittance and wide wavelength transmission range. Its unique mechanical and chemical properties make AlON a promising candidate for many scientific, technological, and environmental applications under extreme conditions, such as high-temperature infrared (IR) windows, illumination-saving domes, and highly transparent armors [1–3].

Despite a large number of research investigations, the application of highly transparent ceramic remains limited due to the lack of economic and feasible fabrication methods for high-quality AlON powder. Specifically, previous studies have shown that as a non-oxide ceramic material, AlON can only be synthesized by means of high-temperature solid-state reaction methods [4–8] because strong crystalline coarsening can hardly be avoided under high synthesis temperature (above 1 500 °C). Therefore, reduction and precise control of the synthesis temperature is crucial in the preparation of AlON powder.

Compared with other methods [4–8], it is easy to fabricate AlON compounds through a preeminent solid-state synthesis method called aluminothermic reduction and nitridation (ARN), in which Al_2O_3 and aluminum (high-reactivity) powders are mixed as starting materials [7, 8]. However, there remain several issues to be addressed, one of which is the influence of the composition of raw starting materials. The weight ratio, phase composition, and particle size of reactants, which are acknowledged to be crucial factors in determining the phase composition and morphology of powder products [5, 6], have not been studied and reported.

In this study, we prepared AlON powder using the ARN method using micro-sized aluminum and nano-sized Al_2O_3. Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) were utilized as the main characterization techniques. The weight ratio of γ-Al_2O_3 in total Al_2O_3, R, the particle size of the starting materials, and the thermodynamic and kinetic factors that might affect the phase composition and morphology of the final powder products are discussed in detail.

2. Experimental

Industrial-standard micro-sized aluminum powder (particle size, 1 ~ 2 μm; purity, 99+ %; Yuanyang Aluminum Industry Co., Ltd, Henan, P.R. China) and nano-sized α- and γ-Al_2O_3 powders (average crystal size for α and γ-Al_2O_3, 80 nm and 20 nm, respectively; purity, 99.99+ %; Luming Nanomaterials Co., Ltd, Liaoning, P.R. China) were used as starting materials. These were ball milled to a certain weight ratio (11 wt.% for aluminum and 89 wt.% for Al_2O_3) and R value (see Table 1) in a 500 ml polyurethane jar with ZrO_2 balls (diameter, 5 mm) for 24 h in nitrogen atmosphere. Subsequently, the well-mixed powders were placed in a high-pur-

Table 1. Phase compositions of as-made AlON powders calcined at various temperatures with different *R* values.

	R = 0	*R* = 0.15	*R* = 0.50	*R* = 0.85	*R* = 1.0
1 650 °C	AlON + Al_2O_3 + AlN	AlON + Al_2O_3 + AlN	AlON + Al_2O_3	AlON + Al_2O_3	AlON + Al_2O_3
1 700 °C	AlON + Al_2O_3	AlON + Al_2O_3	AlON	AlON	AlON
1 750 °C	AlON	AlON	AlON	AlON	AlON

ity corundum crucible, transferred into a graphite furnace (Model ZT-40-20Y; Shanghai Chenxin Electric Furnace Co., Ltd, Shanghai, P.R. China), and heated to pre-programmed temperatures (1 650 °C, 1 700 °C, and 1 750 °C) for 3 h of ARN reaction in nitrogen flow. Finally, the final calcined products were ground, passed through a 250-mesh sieve, and ball milled for another 24 h under the same conditions as the raw material preparation.

Phase identification of the samples was carried out by means of XRD with a DX-2500 diffractometer (Dandong Fangyuan Instrument Co., Ltd, Liaoning, P.R. China). SEM was used to reveal the morphology of the final powder products. The grain size distribution for each sample was calculated by averaging the data obtained from the SEM images.

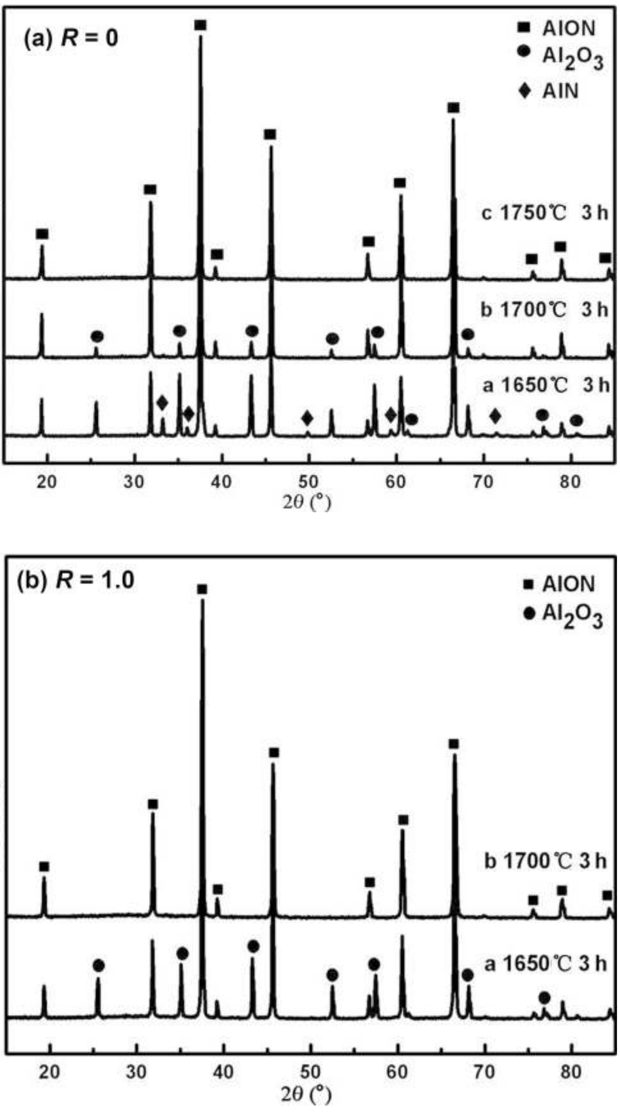

Fig. 1. Powder X-ray diffraction patterns of powder product calcined at various temperatures with different *R* values.

3. Results and discussion

Figure 1 presents the XRD patterns of the powders prepared under different conditions (*R* value and calcination temperature). Table 1 shows the phase compositions of the products. For all products, AlON was the dominative phase. Specifically, after calcination at 1 650 °C, both Al_2O_3 and AlN were still present in reactants with low *R* values (0 and 0.15), whereas those with high *R* values (0.5, 0.75, and 1.0) showed Al_2O_3 as the only impurity. Heating at 1 700 °C eliminated AlN from the products; however, Al_2O_3 remained in samples with low *R* values. At about

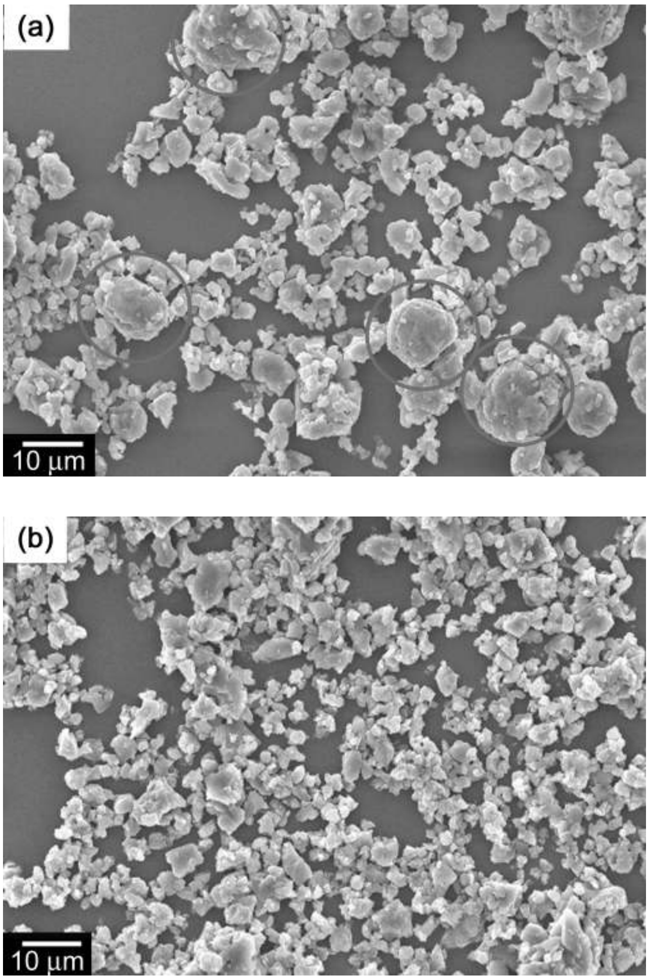

Fig. 2. SEM images of single-phase AlON powder with different *R* values after ball milling for 24 h. (a) *R* = 0, (b) *R* = 1.0.

1 750 °C, when all secondary phases had disappeared (see Fig. 1), the starting materials completely transformed into single-phase AlON. The above observations suggest that the synthesis temperature of single-phase AlON reported by us is significantly lower than that mentioned in previous studies [4, 5].

The morphology (see Fig. 2) and grain size distribution profiles (see Fig. 3) suggest that for all the powder products, the grain sizes fall within the range of 1 to 10 micrometers. Interestingly, powders calcined at lower temperatures have smaller particle sizes and preserve better particle uniformity. Additionally, the product particle distribution tends to be narrower and closer to its Gaussian distribution as the R value increases. Thus, our synthesis fabricated materials with better quality than that of samples prepared by means of other solid-state synthesis methods [4, 9]. Our method may further benefit the sintering of highly transparent ceramics [10]. Also, the experimental observations from reduced-temperature synthesis of single-phase AlON powder strongly suggest that our method has the advantages of reducing the agglomeration of the final AlON product powder and lowering production cost [4, 5, 9].

Due to the high reactivity of aluminum, the reaction between aluminum and Al_2O_3 usually selects a self-propagating high-temperature synthesis (SHS) pathway [8]; vapor–liquid and/or vapor–liquid–solid and two-step mechanisms were suggested during the materials formation process [8]. However, the high reactivity and the short, intensive reaction period of SHS usually lead to impurity phases and a coarsened AlON sample. A large body of research has been carried out to obtain single-phase and non-coarsened AlON. Miao et al. [7] found that the SHS reaction could be minimized by using a small amount of aluminum as starting material. In a later report, Wang et al. [11] did a thermodynamic analysis on the ARN method. Combining the conclusions from these two earlier studies and the interpretation of our current data, a schematic of the ARN reaction process is proposed, as shown in Fig. 4, which clearly suggests that the reaction may have two consecutive steps. First, after ball milling, the reactants are uniformly mixed and the large micron-sized aluminum particles are surrounded by small nano-sized Al_2O_3 particles. The melting and nitridation reactions to produce AlN start at about the melting point of aluminum, because a well-resolved X-ray diffraction peak of AlN can be observed once the reactants are calcined at 800 °C [11]. Al_2O_3 particles are segregated into aluminum particles and then to AlN with small particle sizes through gas–solid and/or gas–liquid–solid mechanisms. All the nitridation processes are completed at about 1 100 °C. Subsequently, the solid-state reaction between AlN and Al_2O_3 is initiated at about 1 600 °C, which is defined as the critical temperature for phase stabilization of AlON, providing enough thermodynamic driving force for the reaction. As the AlON-stabilized region expands with increasing temperature [11, 12], the formation of AlON accelerates accordingly. Therefore, our reaction at 1 700 °C with 3 h of isothermal calcination is more than enough for the formation of single-phase AlON with high R values.

The phase composition of Al_2O_3 reactant powder is also a crucial factor affecting the thermodynamic states and kinetic reaction pathways. The nano-Al_2O_3 powders used in this work provide an additional driving force because of their large surface area and high-energy disordered surfaces. McHale et al. [13, 14] reported that for γ- and α-Al_2O_3 nanoparticles with the same size, γ-Al_2O_3 is a thermodynamically preferable phase. In other words, α-Al_2O_3 is less stable on the nanoscale. This phenomenon also explains why nano-Al_2O_3 is more common in the γ phase. Interestingly, McHale et al. also suggested that coarsening of γ-Al_2O_3 happens at about 900 °C for γ-Al_2O_3 ($166\ m^2\ g^{-1}$) and at 500 °C ($156\ m^2\ g^{-1}$) for α-Al_2O_3. In our current work, γ-Al_2O_3 with an average particle size of 20 nm was used instead of α-Al_2O_3 (80 nm). The strong resistance to coarsening maintains a high surface area for γ-Al_2O_3 under high

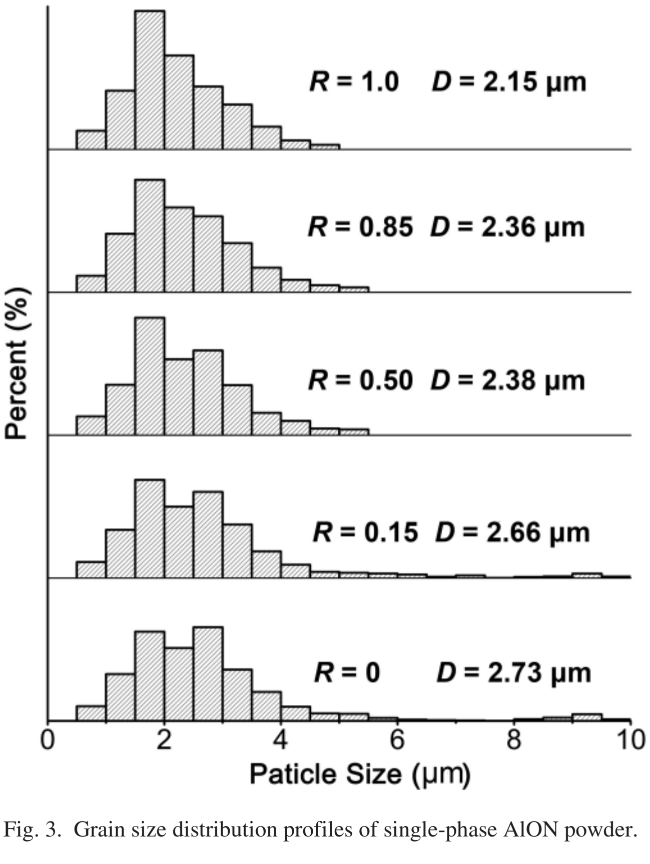

Fig. 3. Grain size distribution profiles of single-phase AlON powder.

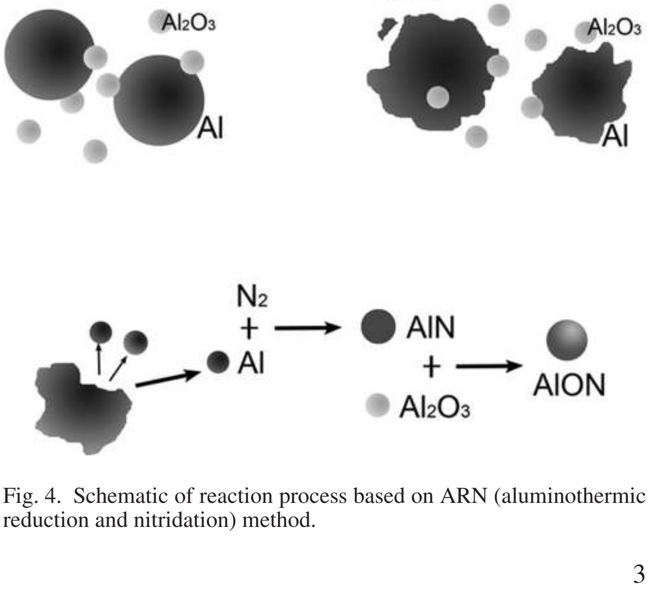

Fig. 4. Schematic of reaction process based on ARN (aluminothermic reduction and nitridation) method.

temperature, which enables the surface energy contribution during nitridation of aluminum. Additionally, although the solid-state reaction process is usually governed by the diffusion of solid materials, the γ-Al_2O_3 nanoparticles used in this work offer an effective free path necessary for transport, especially ion diffusion. Hence, compared with the conventional methods, the higher ratio of γ-Al_2O_3 used in this work can provide both a stronger thermodynamic driving force at the start of the reaction as well as better diffusion in later reaction processes. Moreover, the coarsening prohibition of γ-Al_2O_3 can avoid the formation of big AlON grains during the reaction process, as shown in the grain size distribution of single-phase AlON powders (see Figs. 2 and 3), in which big particles occur only with a low *R* value.

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