Mechanism and kinetics of combustion-carbothermal synthesis of AlN nanopowders

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ARTICLE INFO

ABSTRACT

In this work, the carbothermal reduction-nitridation process of low-temperature combustion synthesis (LCS) (Al_2O_3+C) precursor was investigated in detail. Compared with conventional precursor, the LCS precursor possesses many advantages such as amorphous structure, nanosized particles, homogeneous mixing at molecular level. The experimental results indicate that the methods for preparing precursor exert great influence on phase transformation of Al_2O_3, onset temperature of nitridation and reaction activity. During the calcination, the phase transformation of Al_2O_3 is hindered by a large amount of surrounding C particles rendering Al_2O_3 maintains high reactivity. Accordingly, the nitridation reaction initiates at 1300 °C and completes at 1500 °C for 2 h. Furthermore, the reaction mechanism was also discussed on the basis of experiments. More significantly, it is established that the activation energy of carbothermal reduction-nitridation reaction using LCS precursor is Eα=336 KJ/mol.

1. Introduction

In recent years, aluminum nitride (AlN) has been attracting considerable attention owing to its various excellent properties [1], such as high intrinsic thermal conductivity (330 W/m·K), high electrical resistance (> 10^{14} Ω·cm), low dielectric constant and loss, and low thermal expansion coefficient (3.2×10^{-6}/K) close to that of silicon [2,3]. These excellent properties make AlN an extremely practical material for electronic application [2,4]. In particular, AlN has been widely applied in heat-dissipation field for its outstanding thermal conductivity [5,6]. There are various methods to prepare AlN including direct nitridation [7,8], chemical vapor deposition [9–11], self-propagating high-temperature synthesis [12,13] and carbothermal reduction-nitridation [14–18]. The direct nitridation and carbothermal reduction-nitridation have been widely used in industry. However, the granule shape of AlN prepared by direct nitridation is irregular, and the follow-up ball grinding process is inevitable. As a result, a large number of impurity elements are introduced into the final product. Conventional carbothermal reduction nitridation method (CRN) can yield AlN powders exhibiting high purity, facile sinterability, and excellent stability against humidity. Nevertheless, this method has confronted several limitations such as the requirement of raw materials containing high purity Al_2O_3 and carbon black, the notorious difficulty in homogeneously mixing the raw materials, the high cost based on the

high calcination temperature (> 1580 °C). A lot of works has been done recently to ameliorate the CRN method [19,20]. These studies have concluded that the particle size and mixing homogeneity of the raw materials exert significant influence on the reaction condition as well as on the properties of the synthesized AlN powders. Therefore, the elaborate selection of the raw materials and the preparation of a homogeneous (Al_2O_3+C) precursor have become two essential tasks for the preparation of AlN by CRN method [21–27].

It is well known that LCS method is considered to be one of the most appropriate methods to prepare the oxide-based materials [28,29]. In our previous works [5,30,31], a precursor, consisting of homogeneously mixed amorphous Al_2O_3 and carbon with ultrafine particle size, was prepared through LCS method. Subsequently, the ultrafine AlN powders with superior sintering performance was obtained by carbothermal reduction–nitridantion of the as-synthesized precursor. Simultaneously, the onset temperature for nitridation was as low as 1300 °C.

The overall reaction equation of the carbothermal reduction-nitridation process can be described as follows:

$$Al_2O_3(s) + 3C(s) + N_2(g) = 2AlN(s) + 3CO(g) \qquad (1)$$
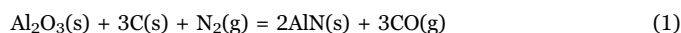
The Gibbs free energy is ΔG=689.9−0.353 T+RTln(P_{CO}^3/P_{N^2}) KJ· mol^{-1}. Where P_{CO} and P_{N^2} is the equilibrium partial pressure of CO and

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N_2 respectively.

According to above thermodynamic calculation, the onset temperature for formation of AlN is about 1680 °C if the reaction take place in a closed system. Under flowing nitrogen atmosphere, i.e., if P_{CO}^3 is maintained below P_{N^2}, it is possible to decreases the onset temperature of nitridation reaction.

The reaction mechanism and kinetics of CRN has been widely reported. Sakai et al. [32] considered that a solid-phase reaction occurs through oxycarbides. Hirai et al. [33,34] confirmed a solid-gas mechanism and assumed that the rate-limiting step was gaseous diffusion through the pore of the nitride scale formed above alumina. Lefort et al. [16] investigated the effects of reaction time, calcination temperature, particle size of raw materials and N_2 flow rate on nitridation. The kinetics showed that the rate-limiting process was the combustion of carbon. Chen et al. [17,18] concluded that the reaction rate could be increased by decreasing the sample size, the grain sizes of alumina and carbon or initial bulk density. The reaction steps and reaction-rate expressions were also discussed.

However, these reports just concentrated on the conventional CRN method. Our previous works only aim at exploring the impacts of various experimental parameters and obtaining well-behaved ultrafine AlN powders. No systematic studies have been conducted to investigate the mechanism and kinetics of the carbothermal reduction-nitridation of the LCS precursor. In this paper, the emphasis focuses on these aspects to expound the reasons for advantages of LCS precursor.

2. Experimental

Two kinds of precursors were prepared in this study and designated Precursor I and Precursor II, respectively. The preparation process is described as follows. They express different features of crystallinity, particle size, specific surface area, tap density, impurity levels with the different methods. These factors will exert a great influence on the reaction thermodynamics and kinetics.

2.1. Preparation of (Al$_2$O$_3$+C) precursor

Aluminum nitrate (Al(NO$_3$)·9H$_2$O) (oxidizer and Al source), urea (CO(NH$_2$)$_2$) (fuel) and glucose (C$_6$H$_{12}$O$_6$·H$_2$O) (C source) were commercially purchased and of analytical reagent grade. The initial solution was prepared by dissolving above materials in 100 ml of deionized water. In the solution, the amount of aluminum nitrate was 0.1 M and the molar ratio of urea to aluminum nitrate (U/Al) was fixed at 1, whereas the amount of carbon source was explored for the C/Al atomic ratio of 10. The solution was poured into a 1000 ml breaker and heated in air on an electrical furnace whose temperature could be controlled. And the furnace could be operated up to peak temperature of 550 °C. In the temperature range of 90–100 °C, a gelatinous mass was formed by the evaporation of water. As heating continued, the resultant gel started to swell and then a smoldering combustion reaction suddenly took place, accompanied by the release of a large number of gases. The whole process of swelling and combustion appeared to undergo a nonexplosive self-propagating exothermic reaction and took only several minutes, leading to the formation of a fragile and foamy mass of (Al$_2$O$_3$+C) precursor (Precursor I). The specific surface area and tap density of Precursor I is 10.3 m^2/g and 0.079 g/cm^3.

Commercial γ-Al$_2$O$_3$ and carbon black powders were used as the raw materials, and their characteristics were listed in Table 1. The atomic ratio of C to Al was fixed at 2, which is larger than the theoretical value of 1.5 for the sake of complete conversion of Al$_2$O$_3$. The γ-Al$_2$O$_3$ powders were mixed with the carbon black in alcohol by high-purity zirconia ball milling for 12 h, then dried in oven at 80 °C (Precursor II). The tap density of Precursor II is 0.160 g/cm^3. These two precursors were both grinded in a quartz mortar for 1 h.

Table 1
Characteristics of the raw materials.

Material	γ-Al$_2$O$_3$	Carbon black
Medium size(nm)	150	40
Specific surface area(m^2/g)	117. 95	71. 21
Tap density(g/cm^3)	0. 129	0. 056
Purity(%)	99. 9	99. 9

2.2. Preparation of AlN

The carbothermal reduction-nitridation of two precursors were performed in an alundum tube furnace. A strict temperature program was followed in all runs, with heating at a constant rate of 10 K/min up to the plateau temperature, 1100–1500 °C. The precursors were heated in a flowing nitrogen gas at various temperatures for 2 h with the flow rate was 1 L/min. The residual carbon in the calcined product was removed by firing at 650 °C in air for 2 h. To investigate the Kinetics, the carbothermal reduction-nitridation of Precursor I was completed under different temperatures from 1300 °C to 1450 °C for different time from 1.0 h to 2.5 h. The chemical analysis was employed to measure the amount of N in the powder by the melting method and then the amount of AlN in powder can be calculated.

2.3. Characterization

The phase composition of the precursors and calcined products were identified by X-ray diffractometer using CuKα radiation (XRD, Rigaku, D/max-RB12). The morphology and size of Precursor I were observed by scanning electron microscopy (SEM, JSM-6510). The morphology and size of the calcined products were observed by transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN) and field emission scanning electron microscopy (FE-SEM, ZEISS ULTRA55). The specific surface area (SSA) of the precursors were determined by the BET method by using an Automated Surface Area & Pore Size Analyzer (QUADRASORB SI-MP, Quantachrome Instruments, Boynton Beach, FL). The content of nitrogen in AlN powders was determined by a LECO TN-114 nitrogen-oxygen analyzer (LECO, Corporation, Joseph Charter Township, MI).

3. Results and discussion

3.1. Phase transformation

Fig. 1 displays the SEM image of Precursor I and the corresponding element distribution. It can be clearly observed that there are Al, O, C elements and each element is uniformly distributed in the sheet-like precursor. The XRD pattern of Precursor I is presented in Fig. 2. It is evident that no apparent Bragg peak has been detected in Precursor I. On account of these results, it can be concluded that Precursor I consists of homogeneously mixed amorphous Al$_2$O$_3$ (hereafter referred to as A-Al$_2$O$_3$) and carbon. During the preparation process of Precursor I, the raw materials were dissolved in deionized water, and apparently all the ions and molecules evenly dispersed in the solution. With the rapid development of combustion process, there was not enough time for atoms or ions to regularly arrange to crystallize, leading to the formation of amorphous structure. Which preserves the uniform distribution of various elements come from the solution. Fig. 2 depicts the XRD patterns of the products calcined at 1100 °C –1500 °C under a flowing nitrogen atmosphere for 2 h. As can be clearly seen, still no obvious Bragg peak is detected in the product calcined at 1100 °C. It implies that the calcined product remains amorphous structure. It can be easily concluded that neither the crystallization nor the nitridation of A-Al$_2$O$_3$ have occurred at 1100 °C. When the temperature reaches 1200 °C, weak and broad diffraction peaks of γ-Al$_2$O$_3$ are detected in