Mechanism and Research on Preparation of AlN Powder by Carbon Thermal Reduction Method

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Abstract. The alumina and activated carbon used as raw materials were prepared by chemical precipitation method. The uniformed aluminum nitride precursor was synthesized by mechanical mixing process. The effects of nitride temperature and time on the diameter of the particle were studied in detail. Ultrafine aluminum nitride powder was prepared by carbon-thermal reduction method. The results show that the precursor has better activity and nitride reaction proceeds rapidly. The complete conversion can be got at 1600°C for 2h. After calcination, it can be seen from the XRD graph that the powder with uniform size distribution has high AlN content.

1. Introduction

Aluminum nitride with high temperature corrosion resistance and temperature stability, higher strength and hardness has potentialities on the application of high temperature structural materials.

At present, with the development of China's national economy, the demand for aluminum nitride shows an increasing trend year by year, so the preparation of ultra-fine aluminum nitride powder has very important practical significance [1].

In this paper, AlN powder is prepared by carbon thermal reduction method to solve the technical problems such as insufficient research on ultra-fine aluminum nitride produced in mass production, unsuitable technological process for industrial production and poor dispersibility of products.

2. Reaction mechanism for synthesis of AlN powder by carbon thermal reduction

The AlN powder prepared by carbothermal reduction has higher purity, smaller size and active soybean. For its inexpensive starting material and stable process, the carbothermal reduction method becomes an absorbed synthesis method and attracts people's widespread attention. However, due to the poor binding property between alumina and carbon, it is difficult to achieve uniform mixing. In addition, the low reactivity of alumina itself requires high reaction temperature, which increases the production cost, which restricts the promotion and application of AlN powder.

Improving the bonding property of aluminum and carbon and exploring the reaction mechanism of the system are the key points of carbon thermal reduction. As intermediate phases such as Al(g), Al₂O(g) and Al₂O₃(g) will be produced in Al₂O₃-C-N₂ system, other substances other than AlN phase, such as AlON, may also appear in the reaction products, so the research on reaction mechanism of preparing AlN by carbon thermal reduction becomes complicated and there are many differences. In
general, the reaction mechanism can be divided into gas-solid reaction and solid-solid reaction according to the types of the first reaction in the process of carbon thermal reduction [2].

Different hypotheses were exist for the specific reaction process in the Al₂O₃-C-N₂ reaction system. For the gas phase reaction mechanism, the carbonation reduction reaction of alumina is divided into several processes [3],[1] Migration of material through a gas layer on the surface of a particle,[2] Material migration of stomata between particles within particles,[3] Reduction and nitride of alumina particles mixed with CO-N₂ gas; CO/N₂ mixture diffuses through the AlN layer on the particle surface; Diffusion of CO₂ gas products and reactions at the interface.[4] CO₂ is reduced by carbon. CO and N₂ diffuse inward through the product layer. The release of CO₂ products controls the reaction process.

The chemical reaction formula of the gas reaction mechanism is:
\[ \text{Al}_2\text{O}_3 \rightarrow 2\text{Al}(g) + \text{O}_2(g) \]
\[ \text{Al}_2\text{O}(g) + \text{N}_2 \rightarrow 2\text{AlN} \]

For the solid phase reaction mechanism, another reaction model was proposed by H K Chen[4] et al. The reaction is as follows.[1] \text{Al}_2\text{O}_3 and C first undergo a solid-solid reaction, producing \text{Al}_2\text{O} and CO gases.[2] \text{Al}_2\text{O} is adsorbed on the surface of \text{Al}_2\text{O}_3 and reacts with CO and N₂ to form AlN nucleus and generate CO₂.[3] Once the AlN nucleus is formed, it begins to grow. At this time, the gas can be adsorbed on the surface of \text{Al}_2\text{O}_3. Then AlN nucleus formed.[4] CO₂ which was formed in the reaction is then absorbed to the carbon and reacts with it to produce CO.

The chemical reaction formula of the solid phase reaction mechanism is:
\[ \text{Al}_2\text{O}_3 + 2\text{C} \rightarrow \text{Al}_2\text{O}(g) + 2\text{CO} \]
\[ \text{Al}_2\text{O}(g) + \text{C} + \text{N}_2 \rightarrow 2\text{AlN} + \text{CO} \]

According to different experimental conditions, there are problems with the mechanism of carbon-thermal reduction whether is explained by gas-solid reaction mechanism or solid-solid reaction mechanism. It is difficult to explain a specific carbon-thermal reduction reaction perfectly by a single mechanism, so it is proposed that two reaction mechanisms coexist.

Wengluqian[5] et al. believed that the zero-order reaction mechanism controlled by the evaporation of alumina exists simultaneously with the diffusion control of the solid reaction mechanism. Therefore, we believe that there are two reaction mechanisms in different stages of the carbon-thermal reduction reaction, which is more reasonable than other single reaction mechanisms.

3. Experimental materials and methods

3.1 Experimental materials
The details of materials used in the experiment are shown in Table 1.

| Reagent            | Molecular formula       | Specification | Manufacturer                                   |
|--------------------|-------------------------|---------------|-----------------------------------------------|
| Ammonia            | NH₃·H₂O                 | A.R           | Shenyang chemical reagent factory             |
| Ammonium bicarbonate | NH₄HCO₃                 | A.R           | Tianjin kemeiou chemical reagent development center |
| Polyvinyl alcohol  | PEG4000                 | A.R           | Shenyang chemical reagent factory             |
| Aluminum nitrate   | Al(NO₃)₃·9H₂O           | A.R           | Shenyang chemical reagent factory             |
| Ethanol            | C₂H₅OH                  | A.R           | Shenyang economic and technological development zone reagent factory |
| Deionized water    | H₂O                     |               | Laboratory homemade                           |
| Sucrose            | C₁₂H₂₂O₁₁               | A.R           | Tianjin ruijin chemical co. LTD              |
3.2 The experimental process

Synthesis of AlN precursor by mechanical hybrid method: Alumina and activated carbon prepared by chemical precipitation method are used as raw materials. The molar ratio of carbon to aluminum is C/Al=6. Ethanol was used as the ball grinding medium for wet grinding. The ball grinding speed was set as 1000r/min, the ball material ratio as 5:1, and the ball grinding time was 36h. After the mixture is ball-ground, the AlN precursor can be obtained. The aluminum nitride powder is obtained after the carbon removal of the precursor.

A new chemical reaction mechanism for the synthesis of aluminum nitride by carbothermal reduction of aluminum oxide is as follows:

\[
\text{Al}_2\text{O}_3 + \text{N}_2 \rightarrow \text{AlON}
\]

\[
\text{AlON} + \text{C} + \text{N}_2 \rightarrow \text{AlN} + \text{CO}
\]

The route diagram of the synthesis process is shown as Figure 1.

![Figure 1. The flow sheet of AlN powder preparation](image)

4. Synthesis of aluminum nitride powders

The chemical reaction equation of AlN powder prepared by carbothermal reductive nitriding is shown in equation (1).

\[
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) + \text{N}_2(g) \rightarrow 2\text{AlN}(s) + 3\text{CO}(g)
\]  

(1)

Calculate the free change energy of the reaction, and then determine the temperature at which the reaction starts spontaneously. It can be found from literature [6] that: when the reaction that can occur at about 1400 °C. According to the theoretical calculation, the research group aluminum nitride powder was calcined under the four groups of samples such as 1450°C, 1500°C, 1550°C and 1600°C respectively, and studied the reaction products at different temperatures.

4.1 Effect of synthesis temperature on the content of AlN powders

| Table 2. Effect of synthesis temperature on synthesis powder by mechanical mixing method |
|-----------------------------------------------|
| Number | Temperature/°C | Heating time/h | O wt% | C %  |
|--------|----------------|----------------|-------|------|
| 1      | 1450           | 2              | 1.28  | 0.62 |
| 2      | 1500           | 2              | 1.11  | 0.59 |
| 3      | 1550           | 2              | 0.93  | 0.55 |
| 4      | 1600           | 2              | 0.75  | 0.48 |
| 5      | 1450           | 1              | 2.20  | 0.79 |
| 6      | 1500           | 1              | 1.70  | 0.78 |
| 7      | 1550           | 1              | 1.20  | 0.74 |
| 8      | 1600           | 1              | 1.36  | 0.71 |

Effect of synthesis temperature on synthesis powder by mechanical mixing method is shown as Table 2. When the insulation time was increasing, the oxygen content and carbon content of the products decreased under unchanged synthesis temperature. It indicated that the 1h insulation reaction time
cannot make the products completely nitrify. And the carbon content was getting smaller as the temperature rises up.

4.2. Effect of calcining temperature on phase composition of ALN powders

The XRD diagram of the reaction products of aluminum nitride precursor synthesized by mechanical mixing at different temperatures is shown as Figure 2. Aluminum nitride precursor was synthesized by mechanical mixing method, the AlN phase was formed under 1450 °C, some Al₂O₃ are also exist in the products as can be seen from Figure 2. There are still a small amount of Al₂O₃ in the reaction product under 1500 °C and 1550 °C. But at 1600 °C AlN phase and a small amount of carbon were exist in the reaction product without any Al₂O₃ phase.

![XRD patterns of the products synthesized at various calcination temperature](image)

Figure 2. XRD patterns of the products synthesized at various calcination temperature (a)1450°C (b)1500°C (c)1550°C (d) 1600°C

Aluminum nitride precursor which prepared by ball milling method is calcined at 1600 °C for 2h under flowing nitrogen (10L/h). Aluminum nitride powder was finally synthesized after the powder was carbonized by 650°C for 4h. The final aluminum nitride powder has only a single aluminum nitride phase and its purity is high as shown in Figure 3.

As can be seen from Figure 2, the synthesized powder had secondary AlON phase besides main AlN phase before 1600°C. It indicates that there are a large number of AlN synthesis at this temperature, but the reaction is not complete. At the same time, it can be seen that with the increase of temperature, the characteristic peak of AlON crystal phase decreases until it disappeared.
**Figure 3.** XRD patterns of aluminum nitride prepared by mechanical synthesis of aluminum nitride precursor.

**Figure 4.** The scanning electron microscope image of aluminum nitride powder.

4.3 **Effect of calcining temperature on microstructure of ALN powders**

Taking the aluminum nitride precursor synthesized by mechanical mixing method as raw material, calcining and holding for 2h under flowing nitrogen at 1600°C at 10L/h, the prepared powder was subjected to 650°C and kept carbonized for 4h before the final synthesis of aluminum nitride powder.

Figure 4 shows the scanning electron microscope image of aluminum nitride powder synthesized by holding it at 1600°C for 2h with a magnification of 20,000 times. It can be seen from Figure 4 that the grain grains are relatively complete and clear in profile after 2 hours of insulation, indicating that the crystallinity is good under this process condition, which is conducive to the growth of grains.

5. **Conclusion**

According to the mechanism analysis of the carbon-thermal reduction method combined with the theoretical numerical experiment analysis, it is concluded in the experiment that aluminum nitride powder with good crystallinity and high purity can be obtained by keeping the temperature at 1600°C for hours.

**Acknowledgments**

The project was supported from Natural science foundation of Liaoning province (2018011155-301) and key laboratory of environment and geotechnical of Liaoning province. The authors thank the support of Northeastern University and Centre for Microscopy, Characterization and Analysis.

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