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# Combustion synthesis and characteristics of aluminum oxynitride ceramic foams

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**Abstract**

Aluminum oxynitride (AlON) ceramic foams were prepared by combustion synthesis using Al and $Al_2O_3$ as starting materials under high nitrogen pressure. By introducing $Al(NO_3)_3{\cdot}9H_2O$ into reactants as active pore-forming agent, AlON ceramic foams with well-distributed pores were cost-effectively fabricated. The influences of $Al(NO_3)_3{\cdot}9H_2O$ content on the combustion process, pore content and structure were studied systematically. The experiment results showed that porous AlON ceramics containing evenly distributed and noncontiguous pores were obtained when $Al(NO_3)_3{\cdot}9H_2O$ content was 30%, in which the closed porosity of 80% was found by Archimedes' method. Pore distribution measured by mercury intrusion porosimetry indicated that pores with several types of diameter were formed in the foams because of the different conditions of pore fusion and molten viscosity.



*Keywords:* B. Porosity; D. $Al_2O_3$; E. Structural applications

## 1. Introduction

Aluminum oxynitride (AlON), as a solid solution of AlN and $Al_2O_3$, has the advantages of good high temperature properties, thermal shock and oxidative resistance and chemical inertness [1–3], which make it an ideal candidate for a variety of applications under high temperatures. So AlON ceramic is attracted by many researchers, and has been prepared by various methods, such as hot-press sintering [4], carbothermal reduction [5,6], solid phase reaction [7], self-propagating combustion [8], spark plasma sintering (SPS) [9], microwave reactive sintering [10], and so on. However, AlON foam, which can be used in the field of molten metal filter, catalyst carriers and high-temperature thermal-insulation components, has seldom been studied systematically. High porosity (70–90%) and low density (0.3–0.6 g/cm$^3$) are the main characteristics of the ceramic foams, and the common preparation methods include the addition of pore-forming agent, foaming process, polymeric sponge impregnation and sol–gel process [11–14]. These preparation methods are highly involved and complicated to fabricate foam ceramics, resulting in low productivity, high costs and manufacturing problems during scale-up.

Combustion synthesis (CS) (self-propagating high temperature synthesis, SHS) provides a cheap and efficient method for the manufacture of inorganic refractory materials due to the advantages of high reaction temperatures, fast heating rates, short reaction times and no external power supply. AlON ceramics have been prepared by combustion synthesis under low air pressure using Al and $Al_2O_3$ powder as starting materials [8,15–17]. However, only a few papers have reported the preparation of AlON foam ceramics by combustion synthesis [18]. In this experiment, gas–solid combustion synthesis was adopted to prepare AlON foam ceramic. Due to the characteristic features of gas–solid combustion process, the products prepared by this process are typically porous, and the manufacturing process is energy saving and cost effective. By adding pore-foaming agent of $Al(NO_3)_3{\cdot}9H_2O$, the porosity of the foam ceramic can improved obviously.

In this study, foam AlON ceramics with high porosity and well-distributed pores were prepared by combustion synthesis, and the effects of active pore-forming agent of $Al(NO_3)_3{\cdot}9H_2O$ on the combustion synthesis process and foam structure were studied in detail.

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## 2. Experimental procedure

Raw materials used in this experiment included Al powder (free Al > 98%, average grain size is 6 μm, Fine materials Corp. Xi'an, China); α-$Al_2O_3$ (purity ≥ 99.99%, average grain size is 2 μm, Dalian Rall Fine Ceramic Co., LTD., China) and pore-foaming agent $Al(NO_3)_3\cdot 9H_2O$ (purity > 99.9%, analytical reagent). After dried for 12 h at 60 °C, the powder mixture was processed by mechanical ball milling for 24 h with the ball to powder mass ratio of 3:1. The thoroughly mixed powder was uniaxially pressed to cylindrical shape with a diameter of 24 mm and relative density of 60%.

The combustion synthesis reaction in this study can be expressed as follows:

$$Al + Al_2O_3 + Al(NO_3)_3 + N_2 \rightarrow AlON(foam) + Q \quad (1)$$

where $Q$ is the heat released by the exothermic chemical reaction. In above reaction, $Al(NO_3)_3\cdot 9H_2O$ was not only used as a strong oxidizer to participate in reaction, but also as pore-forming agent to produce pore structure in the product. The reactant composition in this experiment was shown in Table 1.

AlON foam ceramic was synthesized under 100 MPa $N_2$ pressure in the super-high pressure SHS reactor. The roughcast was placed into the combustion chamber of the SHS reactor and ignited by a Ni–Cr resistance coil at the top of the sample. Once an electrical current flows through the ignition coil, the Ni–Cr coil generates enough heat to ignite the self-sustained combustion reaction.

The temperature profile of the combustion reaction was recorded by an *X–Y* recorder through the potential difference obtained by W–5%Re/W–26%Re thermocouples inserted in the bottom center at a depth of 10 mm. Specimens were machined into required shape by inside diameter slicer. X-ray diffraction analysis was conducted on the X-ray diffraction device (Rigaku *D*/max-rB, Japan). The morphology of the products was observed by scanning electron microscopy (SEM, S4700 and FEI Quanta 2000F). Porosity of the foam ceramics was measured by mercury intrusion method (AUTOPORE 9420, Micromeritcs, USA).

## 3. Results and discussion

### 3.1. Reaction temperature

The powder compacts can be ignited easily under high nitrogen pressure and the combustion wave front propagated throughout the sample with high temperature and velocity. Fig. 1 shows the effect of $Al(NO_3)_3\cdot 9H_2O$ content on the

Table 1
Composition of the reactant used in the experiment.

| Samples | $Al(NO_3)_3\cdot 9H_2O$ (wt%) | Al (wt%) | $Al_2O_3$ (wt%) |
|---|---|---|---|
| A | 10 | 40 | 50 |
| B | 20 | 40 | 40 |
| C | 30 | 40 | 30 |
| D | 40 | 40 | 20 |

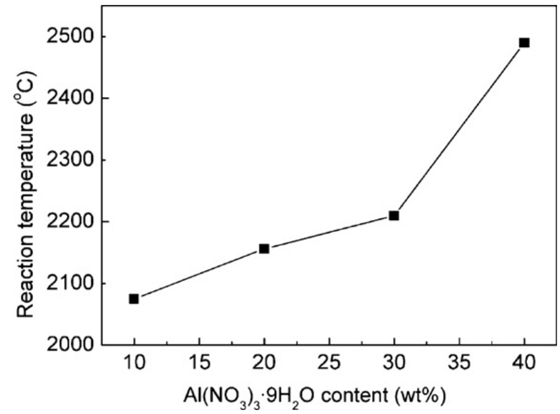


Fig. 1. Effect of $Al(NO_3)_3\cdot 9H_2O$ content on the temperature of the combustion synthesis.

temperature of combustion synthesis. With the increasing contents of $Al(NO_3)_3\cdot 9H_2O$ foam agent, the volume of decomposed gas increased, and thus Al powder in reactant can reacted entirely, and combustion temperature improved accordingly. The combustion temperature, ranging from 2165 °C to 2650 °C, was higher than the melting point of $Al_2O_3$ (2065 °C) and AlN (2150 °C, sublimating point). These molten phases, which existed in combustion reaction zone, can affect the foam structure in the ceramics. Combustion synthesis is a rapid process and only last for several to 10 s in the experiments. Although the operational temperature of the W–5%Re/W–26%Re thermocouples is under 2300 °C for working conditions, its instantaneous working temperature can reach 2800 °C.

Reaction (1) is an overall chemical process for the preparation of porous AlON ceramic, and it involves the following reactions.

At 110 °C, the dehydration reaction of the $Al(NO_3)_3\cdot 9H_2O$ occurs:

$$Al(NO_3)_3\cdot 9H_2O(g) = Al(NO_3)_3 + 9H_2O \quad (2)$$

When heated above 500 °C, the following reaction takes place:

$$2Al(NO_3)_3 = Al_2O_3 + 3N_2 + \frac{15}{2O_2} \quad (3)$$

Reaction between Al and oxygen is prior to the reaction between Al and nitrogen because of the higher oxidability of oxygen than nitrogen:

$$Al + \frac{3}{4}O_2 = \frac{1}{2}Al_2O_3 \quad (4)$$

The residual Al is reacted with nitrogen:

$$Al + \frac{1}{2}N_2 = AlN \quad (5)$$

At last, the solid solution reaction between $Al_2O_3$ and AlN happened to form AlON at the high combustion temperature:

$$(x+5y)AlN + (2x+y)Al_2O_3 \rightarrow xAl_5O_6N + yAl_7O_3N_5 \quad (6)$$

Once the combustion synthesis begins after the ignition, the exothermic reactions of Eq. (4) ($\Delta H = -1675$ kJ/mol) and