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Modification of alumina bubbles with ammonium aluminum sulphate

Jiabang Wang[a,*], Lianbang Wang[b], Hui Yang[a], Xiaoyun Fu[b], Deyu Kong[a,b]

[a] *Department of Materials Science and Engineering, Institute of Inorganic and Non-metal Materials, Zhejiang University, Hangzhou 310014, PR China*
[b] *Zhejiang University of Technology, Hangzhou 310014, PR China*

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Abstract

Ammonium aluminum sulphate was introduced to modify alumina bubbles by the wet chemical method. Distribution of ammonium aluminum sulphate, in situ decomposition characteristics, microstructure and mechanical properties of the modified alumina bubbles were investigated by SEM, XRD, BET and by a purposely designed experimental device for the measurement of compressive resistance. Experimental results showed that an ammonium aluminum sulphate thin film was formed on the surface of the alumina bubbles, at the same time, ammonium aluminum sulphate also infiltrated into the flaws and cavities of the alumina bubbles. After heat-treated at 900 °C, the ammonium aluminum sulphate on the alumina bubbles could be in situ decomposed to γ-Al_2O_3 with high activity. The compressive resistance of the modified alumina bubbles was enhanced from 15.6N to 38.7N after heat-treatment at 1700 °C for 2 h.

Keywords: Alumina bubble; Ammonium aluminum sulphate; Compressive resistance

1. Introduction

Alumina bubble ceramics as high-temperature insulation materials have attracted much attentions because of light weight, high strength, high refractoriness, good heat-insulating performance and abundant raw material [1–4]. Compared with the dense refractory materials [5,6], alumina bubble ceramics have light weight, high-thermal shock loading, well-heat insulating and low-thermal capacity, while compared with the common heat-insulating refractory materials [7], they have high-compressive resistance, high-softening temperature at load and low-linear shrinkage ratio on reheating. Alumina bubble ceramics can be used as heat-insulating layer and contact with flame directly; it is an ideal inner constructional material for light-weight structural ultra-temperature kiln.

At present, the studies of alumina bubble ceramics mainly focus on their macroscopic nature and give different conclusions by different researchers. It suggests that the stability of the material is poor in use [8]. So a systemic and profound research is required about the bubble's mechanical characteristic, filling characteristic, bonding agent formulation [9], preparation technology and microscopic structure of alumina bubble ceramics.

In this work, the alumina bubbles have been modified with ammonium aluminum sulphate by wet chemical method, and then heat-treated at various temperatures. The microscopic structure and mechanical properties of the alumina bubbles after heat-treatment have been investigated in detail.

2. Experimental

2.1. Preparation of samples

Alumina bubbles (Zhengzhou Yuli Co. Ltd, China, Al_2O_3 99.36%) with 3–4 mm in size were immersed into 13.04 wt.% and 8.89 wt.% ammonium aluminum sulphate (Shanghai Jinshan Chemical Plant) solution containing 1.46 wt.% and 1 wt.% Al_2O_3, respectively. After 2 h immersion, the alumina bubble was dried at 80 °C for

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[*] Corresponding author. Tel.: +86 571 87951408; fax: +86 571 87953054.
E-mail address: wangjiabong@163.com (J. Wang).

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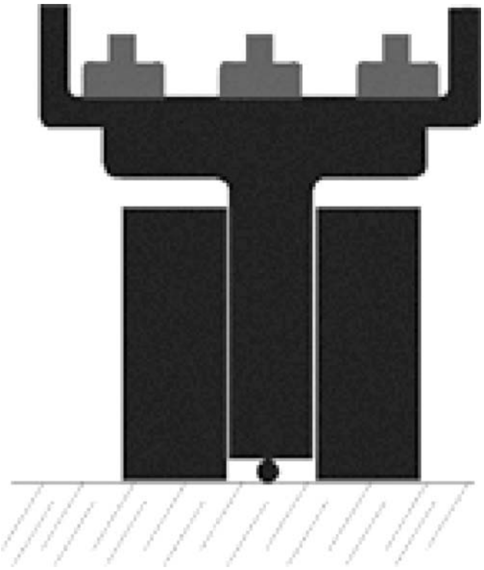

Fig. 1. Experimental device for the measurement of compressive resistance of alumina bubbles.

12 h, then the alumina bubble was heat-treated at various temperatures for 2 h.

2.2. *Testing programs*

Sample modified by the in situ decomposition of ammonium aluminum sulphate at 900 °C was determined by X-ray diffraction (XRD) using a D/max-RA (Rigaku Denki Co. Ltd., Tokyo, Japan) and scanning electron microscopy (SEM) using a PHILIPS XL Series. Surface-to-volume ratio of the sample was analyzed using a specified surface instrument (Ominsorp 100CX). Compressive resistance of single alumina bubble was examined with self-prepared equipment shown in Fig. 1.

3. Results and discussion

3.1. *Structure characteristic of alumina bubbles before modification*

Fig. 2 shows the SEM morphologies of alumina bubble before modification. The thickness of the alumina bubble wall is around 250 μm. It is clear that the alumina bubble is composed of small crystal with average size around 50 μm. It can be seen that there are flaws and cavities between crystals, which would obviously lower the compressive resistance of the alumina bubble.

3.2. *Microstructure of alumina bubble after modification*

Fig. 3 shows the surface morphology of modified alumina bubble after being dried at 80 °C. It can be seen that the surface of alumina bubble was coated by a thin film of ammonium aluminum sulfate shown in Fig. 3a. The flaws and cavities between the crystals shown in Fig. 2 were covered up. After heat-treatment at 900 °C for 2 h, XRD patterns in Fig. 4 shows that γ-Al_2O_3 was formed on the surface of the alumina bubbles due to the decomposition of ammonium aluminum sulphate. The size of γ-Al_2O_3 particles on the surface of alumina bubbles was

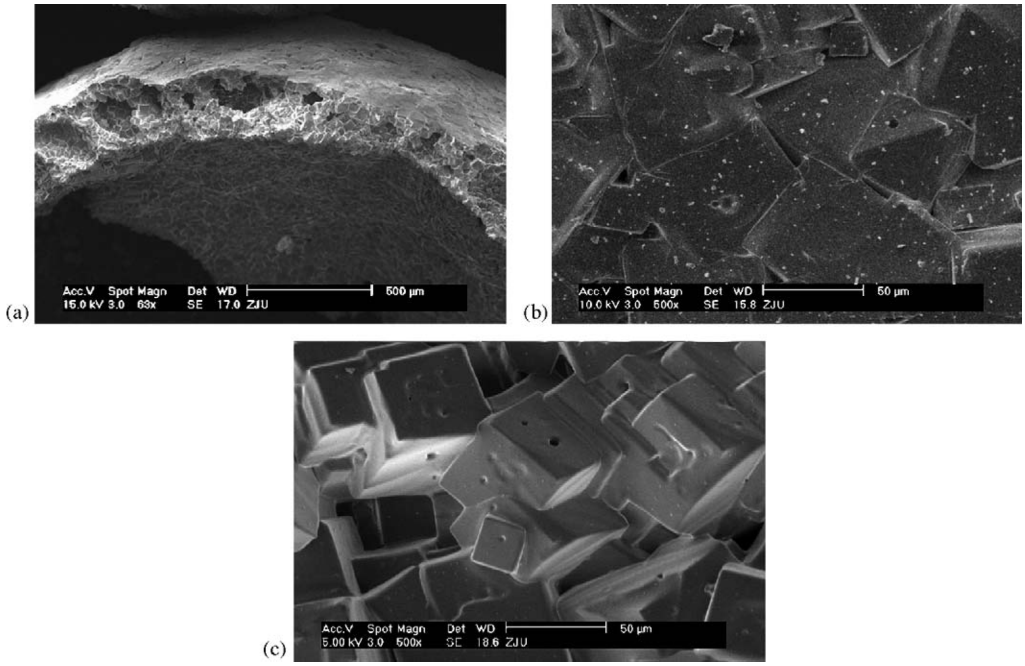

Fig. 2. SEM morphologies of alumina bubble before modification: (a) fractured crust; (b) outer surface; and (c) inner surface.

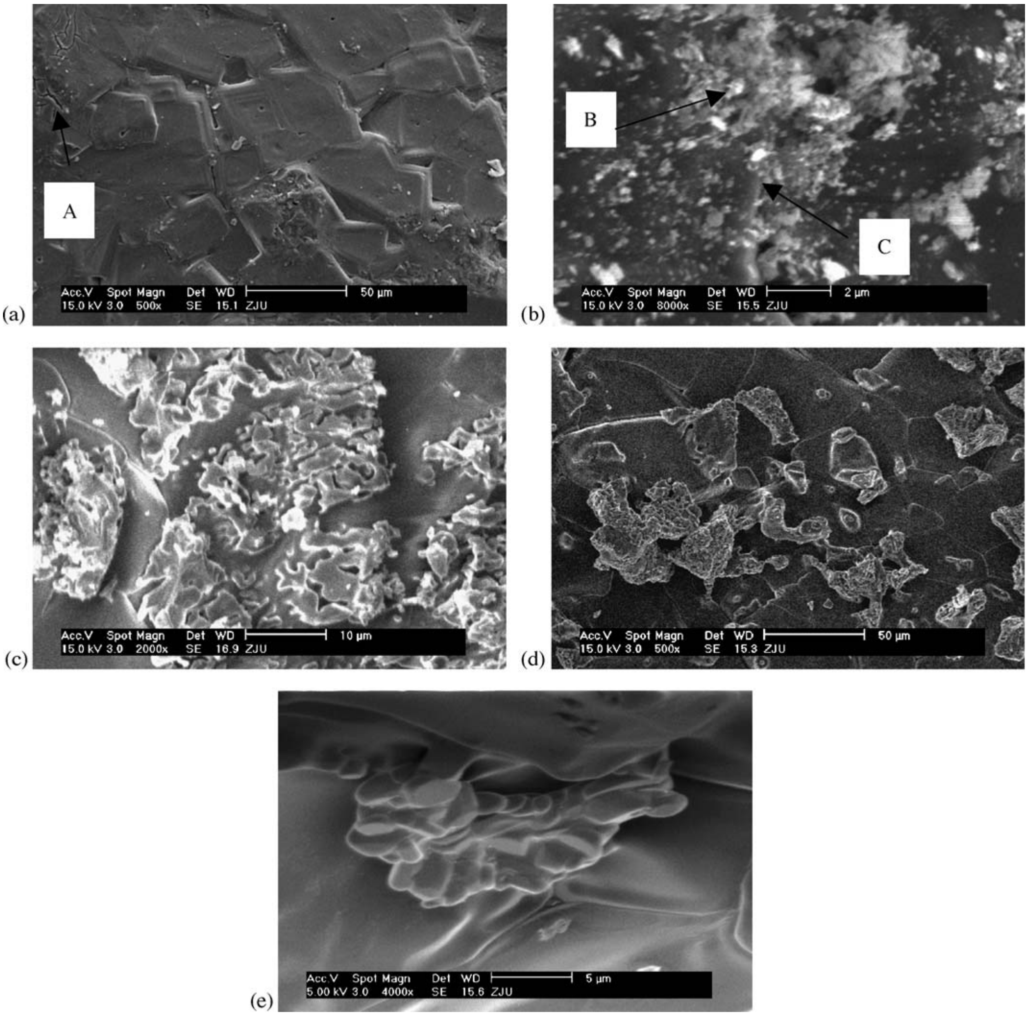

Fig. 3. Surface morphology of alumina bubble modified with ammonium aluminum sulphate: (a) after being dried at 80 °C; (b) after heat-treatment at 900 °C; (c) after heat-treatment at 1200 °C; (d) after heat-treatment at 1550 °C; and (e) after heat-treatment at 1700 °C.

around 200 nm shown in Fig. 3b. The decomposed γ-Al_2O_3 powders filled into and covered up the flaws and cavities of the original alumina bubbles, which cured the cracks and cavities of alumina bubbles. The BET result shows that the specific area of γ-Al_2O_3 powder formed due to the decomposition of ammonium aluminum sulphate was 255.2 m^2/g and the average particle size was 6.7 nm.

After heat-treatment at 1200 °C and 1550 °C for 2 h, it was found that the formed γ-Al_2O_3 was coagulated and sintered. After heat-treatment at 1700 °C shown in Fig. 3e, the formed γ-Al_2O_3 has been sintered and grown together with crystals of the alumina bubble. The holes and cavities of the original alumina bubbles has been cured and covered. It is suggested that the coagulation and sintering of the γ-Al_2O_3 were enhanced with the increasing heat-treatment temperature. Both the self-sintering of the highly active γ-Al_2O_3 and sintering with the crystals on the surface of alumina bubbles happened at high heat-treatment temperature. γ-Al_2O_3 was crystallized and grown up during the sintering process.

3.3. Fracture morphology of modified alumina bubbles

Fig. 5 showed the fracture morphology of modified alumina bubbles with ammonium aluminum sulfate after heat-treatment at various temperatures. It can be seen in

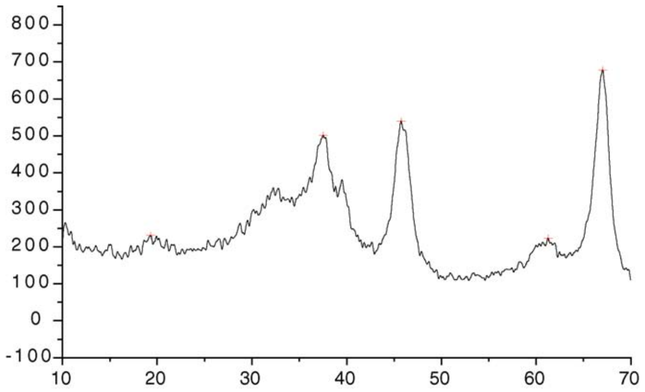

Fig. 4. XRD pattern of alumina bubbles modified by ammonium aluminum sulfate after heat-treatment at 900 °C.

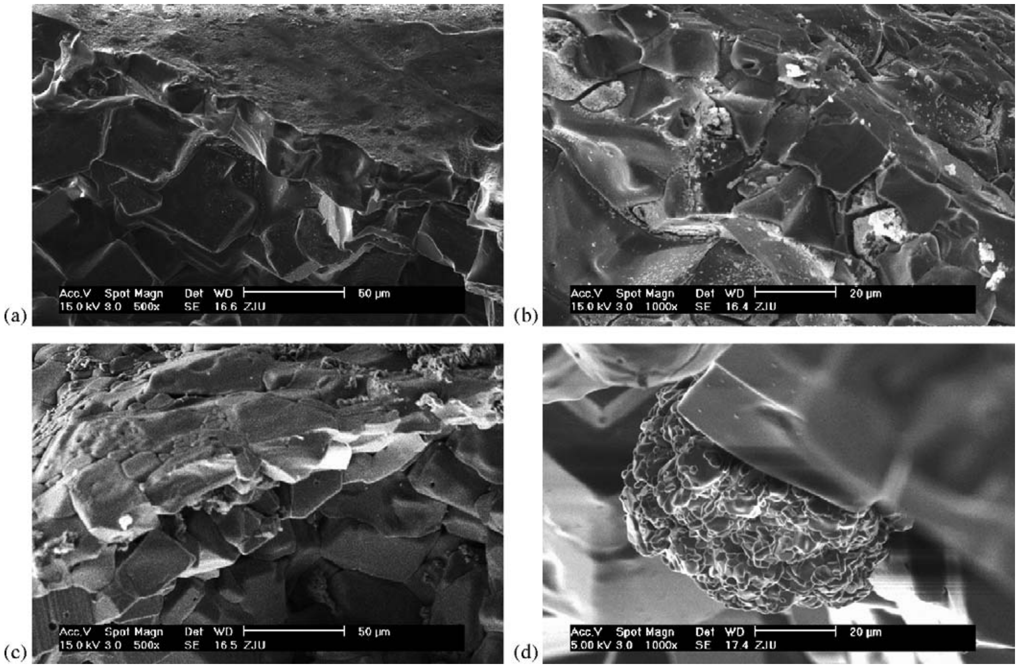

Fig. 5. Fracture morphology of the modified alumina bubble (a) after being dried at 80 °C; (b) after heat-treatment at 900 °C; (c) after heat-treatment at 1550 °C; and (d) after heat-treatment at 1700 °C.

Fig. 5a, ammonium aluminum sulfate has permeated and filled into the flaws and cavities of alumina bubble wall. A thin film around 20 µm in thickness was coated on the surface of alumina bubbles. After heat-treatment at 900 °C, the γ-Al_2O_3 powders formed due to the decomposition of ammonium aluminum sulfate covered up the flaws and cavities of alumina bubbles. After heat treatment at 1550 °C, the formed γ-Al_2O_3 powders on the surface and in the flaws and cavities were sintered together with alumina crystals of the bubbles. After sintered at 1700 °C, the formed γ-Al_2O_3 powders were sintered together with the alumina bubbles completely.

3.4. Mechanical properties of the modified alumina bubbles

Table 1 shows the mechanical properties of alumina bubbles modified with ammonium aluminum sulfate at various experimental conditions. Without the modification, heat treatment gives a little effect on the compressive resistance of alumina bubbles. It is only an increase of 2.5N after heat treatment at 1700 °C. After the modification using ammonium aluminum sulfate, the compressive resistance of alumina bubbles has been changed due to the formation of γ-Al_2O_3 on the surface and in the cavities of alumina bubbles. After heat treatment at 900 °C, the compressive resistance of alumina bubbles modified with ammonium aluminum sulfate solution decreased due to the destroy of structure of bubbles resulted from the formation of γ-Al_2O_3 powder in the cavities of bubbles, which expanded the crack of bubbles. The compressive resistance of alumina bubbles decreased from 15.6N for original sample to 7.8N and 7.6N for the sample modified in 8.89 wt.% and 13.04 wt.% ammonium aluminum sulfate solution, respectively. After heat treatment at high temperature of 1550 °C and 1700 °C, the compressive resistance of alumina bubbles modified with ammonium aluminum sulfate increased remarkably because the γ-Al_2O_3 decomposed from ammonium aluminum sulfate sintered together with the crystals of alumina bubbles. After modification in 8.89 wt.% ammonium aluminum sulfate solution, the compressive resistance of alumina bubble increased from 15.6N for original sample to 30.1N and 34.8N for the modified sample after heat treatment at 1550 °C and 1700 °C, respectively, and it was 32.8N and 38.7N for the sample modified in 13.04 wt.% ammonium aluminum sulfate solution after heat treatment at 1550 °C and 1700 °C. It suggests that the decomposed γ-Al_2O_3 sintered both on the surface and in the cavities of

Table 1
Effect of concentration of ammonium aluminum sulfate and heat-treatment temperature on the compressive resistance of the modified alumina bubbles

Heat-treatment temperatures	900 °C × 2 h	1550 °C × 2 h	1700 °C × 2 h
Without modification	15.6N	16.0N	18.2N
8.89 wt.% ammonium aluminum sulfate solution	7.8N	30.1N	34.8N
13.04 wt.% ammonium aluminum sulfate solution	7.6N	32.8N	38.7N

alumina bubbles at high temperature could enhance the compressive resistance of alumina bubbles.

4. Conclusions

(1) While modified with various concentration of ammonium aluminum sulfate solution, a thin film was formed on the surface of the alumina bubble after drying at 80 °C, at the same time, the ammonium aluminum sulfate also permeated into the flaws and cavities of the bubbles.

(2) Ammonium aluminum sulfate on the surface and in the cavities of alumina bubbles would be in situ decomposed to high active γ-Al_2O_3 powder at 900 °C. The high active γ-Al_2O_3 powder could be sintered at higher temperature.

(3) Compressive resistance of the alumina bubble modified in 13.04 wt.% ammonium aluminum sulfate solution was enhanced nearly 1.5 times than that of bubbles without modification after heat-treated at 1700 °C due to the sintering of the in situ decomposed γ-Al_2O_3 with the crystals of alumina bubbles on the surface and in the cavities.

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