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Preparation of $BaAl_2O_4$ by microwave sintering

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Abstract: The desulfurater ($BaAl_2O_4$) was successfully synthesized with $BaCO_3$ and $Al(OH)_3$ powders as raw materials by microwave sintering method. The mass loss of raw materials and the characterization of the outcome were investigated by means of TG-DSC, XRD and optical microscopy. The reaction mechanism was discussed. The experimental results show that synthesized $BaAl_2O_4$ by microwave sintering method is feasible. Compared with conventional sintering method, microwave sintering is a better way to synthesize $BaAl_2O_4$ with advantages of low temperature sintering, short time sintering and high synthesis rate.
Key words: $BaAl_2O_4$; microwave sintering; conventional sintering; synthesis rate

1 Introduction

China possesses about 150 million tons of high-sulfur bauxite, more than 57.2% of which is of high-grade[1]. This kind of bauxite is suitable for the Bayer process, but the problem of desulphurizing should be solved before it can be used. The desulphurizing methods include floatation[2−3], roasting[4−5] and wet process[6−9] at present. In a flotation or reverse flotation process, flotation reagents and washing water have an adverse effect on the Bayer process, and contamination will be caused by the tailing ore containing aluminum minerals. In a roasting process, there are still some serious problems such as high energy consumption and the release of SO_2 gas. In contrast, the alumina production capacity of Bayer process can be strengthened because the sodium aluminate solution can be purified in the wet desulfurization process. With the advantages of simple device, little pollution and high efficiency, the wet desulfurization process is the best way for desulfurization.

The barium salt is more effective in desulphurizing than other salt in wet process. In order to reduce desulphurizing cost and raise the efficiency, $BaAl_2O_4$ (BALO)[8−9] was used as desulfurater other than BaO[6] and $Ba(OH)_2$[7]. But BALO has only about 50% cost of BaO and $Ba(OH)_2$. Up to now, the report about preparation methods of BALO has not been seen yet. The single-phase BALO body is very difficult to obtain by conventional solid-phase sintering method, since it requires high temperature (1 300 °C) and long duration time (90 min). According to some reported results[10−15], microwave heating had a significant non-thermal effect in the stage of crystal growth compared with muffle heating.

In this work, the $BaAl_2O_4$ was successfully synthesized with $BaCO_3$ and $Al(OH)_3$ powders as raw materials by microwave sintering method. The experimental procedure and results analysis will be described in detail, and reaction mechanism will be discussed.

2 Experimental

The BALO was prepared by $BaCO_3$ (analytically pure, 99%) and $Al(OH)_3$ (micro-powder).The raw materials were weighed according to the mole ratio of 1.1:1 of Al_2O_3 to BaO. The powders were mixed for 30 min in ceramics mortar, and then subjected to sintering at 1 200 °C for 60 min using a muffle furnace or 1 300 °C for 90 min, respectively. In this process, 20 g mixed

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powders were put in alumina crucible which was located in a microwave oven (Fig.1). This device is capable of generating microwave power from 0 to 20 kW at operating frequency of 2.45 GHz. The temperature was measured by infrared pyrometer and controlled through adjusting input power. The sintering conditions were 800 °C for 20 min and 900 °C for 5 min, respectively.

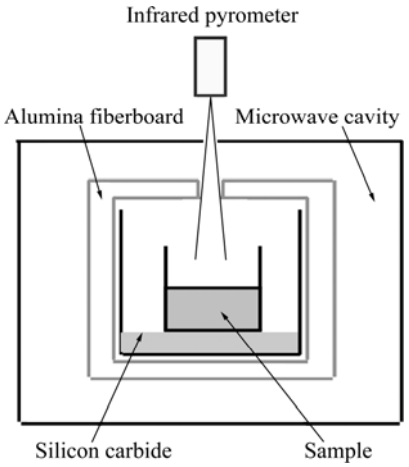

Fig.1 Arrangement of microwave furmace

The raw material powders of $BaCO_3$ and $Al(OH)_3$ were analyzed by thermogravimetric-differential thermal analysis (TG-DTA) on a Netzsch (Luxx, STA, 449C, Germany) analyzer using Al_2O_3 as the reference material in the temperature range of 25–1 450 °C with a heating rate of 10 °C/min in Ar atmosphere. The samples were also analyzed by XRD (D/max-2500PC) for determination of phase structures. The micro-morphologies of the samples were dispersed in ethanol using ultrasonic and analyzed by digital polarization microscope (AXIOSKOP 40, HAL 100, Czech Republic).

3 Results and discussion

3.1 TG-DSC analysis

TG-DSC was used to assess the degree of reaction occurred and stability of the powders with respect to thermal as well as chemical composition. It can be noted from TG and DSC curves (Fig.2), the first major endothermic and mass loss peaks observed below 600 °C are mainly caused by the evaporation of planar water and some crystallization water. The next major change occurs in the temperature range of 900−1 300 °C, which could be attributed to the decomposition of $BaCO_3$ and the continuous evaporation of crystallization water.

3.2 X-ray diffraction analysis

The sintered powders were examined by XRD in order to investigate the phase formation of BALO. The results are shown in Fig.3. Fig.3(a) shows the XRD

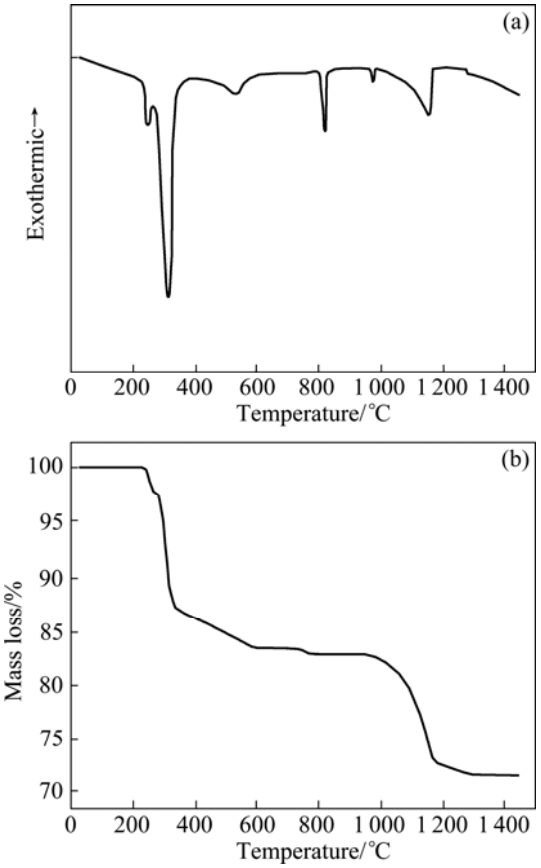

Fig.2 DSC (a) and TG (b) curves of $BaCO_3$ and $Al(OH)_3$ mixed powders

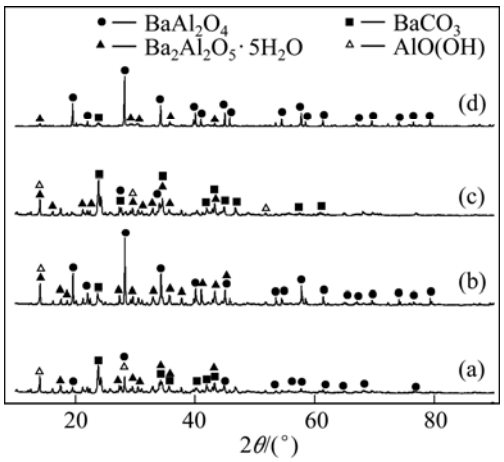

Fig.3 XRD analysis results: (a) Microwave sintered at 800 °C for 20 min; (b) Microwave sintered at 900 °C for 5 min; (c) Convention sintered at 1 200 °C for 60 min; (d) Convention sintered at 1 300 °C for 90 min

spectrum of mixed Al_2O_3 and BaO powder with mole ratio of 1.1 by microwave sintering (MS) at 800 °C for 20 min. It is found that the main phase is $Ba_2Al_2O_5{\cdot}5H_2O$ and the minor phases are the raw materials of $BaCO_3$ and the residue of AlO(OH). By increasing sintering temperature to 900 °C, it is found that the BALO is the main phase (Fig.3(b)), and the other peaks are formed

due to the raw materials of $BaCO_3$ and the reaction residue of $Ba_2Al_2O_5{\cdot}5H_2O$ and AlO(OH). For comparing phase formation, the conventional sintering powders were examined by XRD and the results are shown in Fig.3(c) and Fig.3(d). Fig.3(c) shows that the main phases are $Ba_2Al_2O_5{\cdot}5H_2O$ and $BaCO_3$. BALO is not formed completely because of only one small peak corresponding to BALO. By increasing the conventional sintering temperature to 1 300 °C and prolonging exposure time to 90 min, it is found that the BALO is the main phase, and the other peaks are the reaction residue of $Ba_2Al_2O_5{\cdot}5H_2O$ and $BaCO_3$.

3.3 Micro-morphological characteristics

Digital polarization microscope images of microwave sintered samples at 800 °C and 900 °C and conventionally sintered samples at 1 200 °C and 1 300 °C are given in Fig.4. It can be seen from Figs.4(a) and (b) that there is a great difference in grain size between $BaCO_3$ and $Al(OH)_3$. The conventionally sintered samples at 1 300 °C have smaller size and rougher surface than that at 1 200 °C, which may be caused by the decomposition of $Ba_2Al_2O_5{\cdot}5H_2O$. Floccus grains have already appeared in microwave-sintered sample at 800 °C, but there is still a large number of non-reacted barium carbonate. From the results mentioned above, it is obvious that the reaction has begun, but the reaction tendency is small. When the samples are sintered at 900 °C for 5 min, there are a large number of small translucent grains of BALO generated. This shows that the reaction has begun with a great composition dynamics. At the same time, the phenomenon of grain aggregates exists, and shortening sintering time can lower aggregation tendency. It is concluded that microwave irradiation has a significant influence on the microstructure on account of its high energy[14].

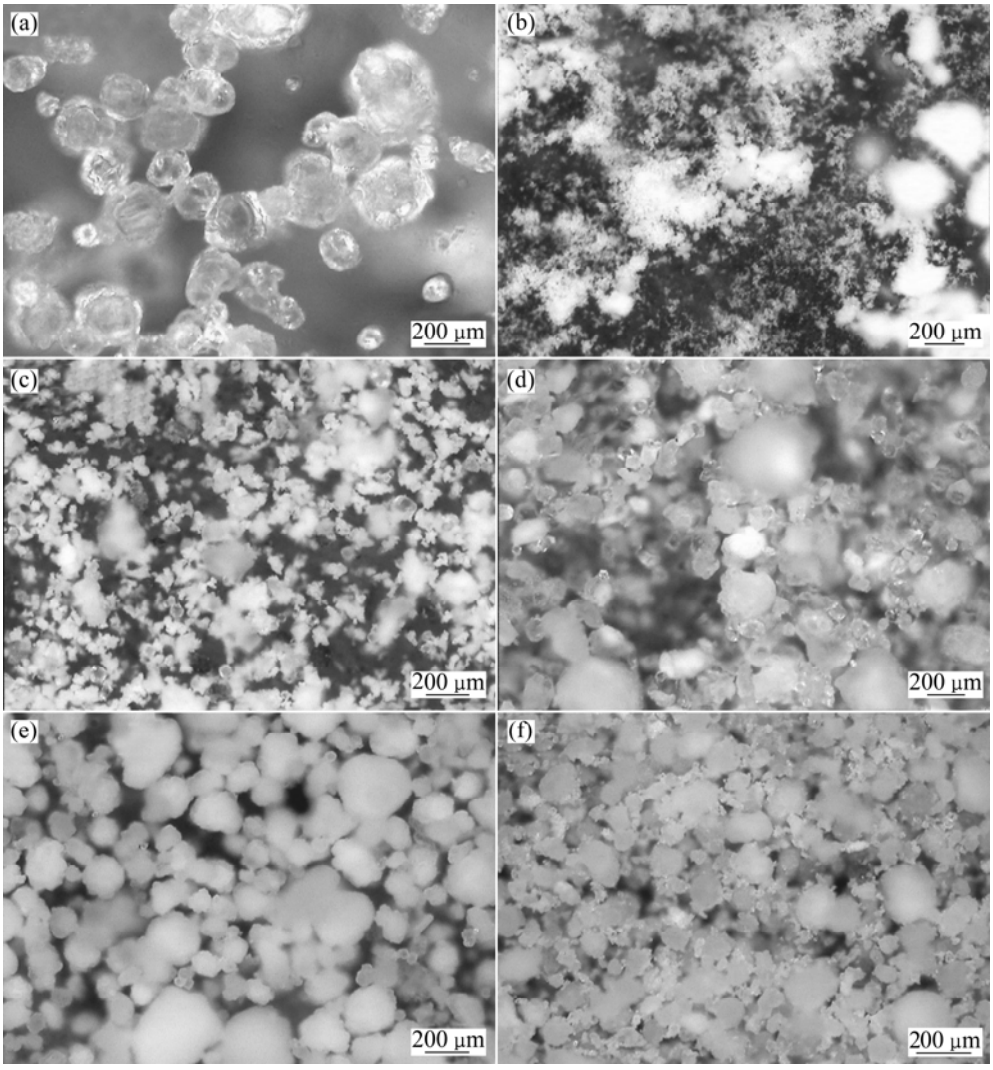

Fig.4 Microscope images (dark field) of sintered powders by different sintering methods: (a) $Al(OH)_3$ powders; (b) $BaCO_3$ powders; (c) Microwave sintering at 800 °C for 20 min; (d) Microwave sintering at 900 °C for 5 min; (e) Convention sintering at 1 200 °C for 60 min; (f) Convention sintering at 1 200 °C for 90 min

3.4 Synthesis mechanisms

Fig.5 shows the schematic plan of the synthesis mechanisms of $BaAl_2O_4$. It is assumed that $BaCO_3$ and $Al(OH)_3$ are spherical. From Fig.5 we can see that the reaction mechanism can be explained by un-reacted core model. $Al(OH)_3$ particles wrapped by a layer of small barium carbonate particles are composed of different-size crystals, crystals gap filled with small crystals and closely combined inter-grain. $Al(OH)_3$ particles can rapidly dehydrate and have nanometer cracks on the original grain surface at 200−400 °C[16]. These cracks result in the phenomenon that the crystal surface area increases, which benefits the reaction.

With the temperature rising, the reaction scheme can be presented as follows:

$$BaCO_3 \rightarrow BaO + CO_2 \uparrow \quad (1)$$

$$2BaO + 2Al(OH)_3 \rightarrow 2BaO \cdot Al_2O_3 \cdot 5H_2O + H_2O \uparrow \quad (2)$$

$$2BaO \cdot Al_2O_3 \cdot 5H_2O + 2Al(OH)_3 \rightarrow 2(BaO \cdot Al_2O_3) + 8H_2O \uparrow \quad (3)$$

$$Al(OH)_3 \rightarrow AlO(OH) + H_2O \uparrow \quad (4)$$

Reaction (2) has lower reaction temperature than reaction (3). As shown in Fig.3, the reaction (2) has happened under the microwave sintering conditions or under the conventional sintering conditions at 800 °C or 1 200 °C, respectively, but the tendency is small. When the temperature are 900 °C (microwave sintering) or 1 300 °C (conventional sintering), reaction (3) obviously occurs.

3.5 Synthesis tests

According to the chemical reaction equation, the synthesis mechanisms can be described briefly using reaction (5)[17]. At the same time, the synthetic rates of BALO can be calculated using reaction (6)[17]:

$$BaCO_3 + 2Al(OH)_3 \rightarrow BaO \cdot Al_2O_3 + CO_2 \uparrow + 3H_2O \uparrow \quad (5)$$

$$\eta_{BALO} = (\frac{39\Delta m}{11m} - \frac{27R}{22}) \times 100\% \quad (6)$$

where R is the molar ratio of Al_2O_3 to BaO, m is the mass of $Al(OH)_3$ before sintering, Δm is the mass difference after sintering. The heating-up curves of synthesis tests are given in Figs.6−8. The BALO synthetic rate under different sintering methods is listed in Table 1. From Table 1, with increasing the conventional sintering temperature from 1 200 to 1 300 °C and the sintering time from 60 to 90 min, the synthetic rate has only increased by 11.27% from 74.60% to 85.87%. However, with increasing the microwave sintering temperature from 800 to 900 °C and decreasing the microwave sintering time from 20 to 5 min, the synthetic rate has increased by 14.47% from 78.26% to 92.73%. It can be concluded from Table 1 that microwave sintering has

Table 1 BALO synthetic rate under different sintering methods

Method	Time/min	Temperature/°C	Sample mass/g	Mass difference/g	Synthetic ratio/%
CS	60	1 200	20	5.5	74.60
	90	1 300	20	5.8	85.87
MS	20	800	20	5.6	78.26
	5	900	20	5.98	92.73

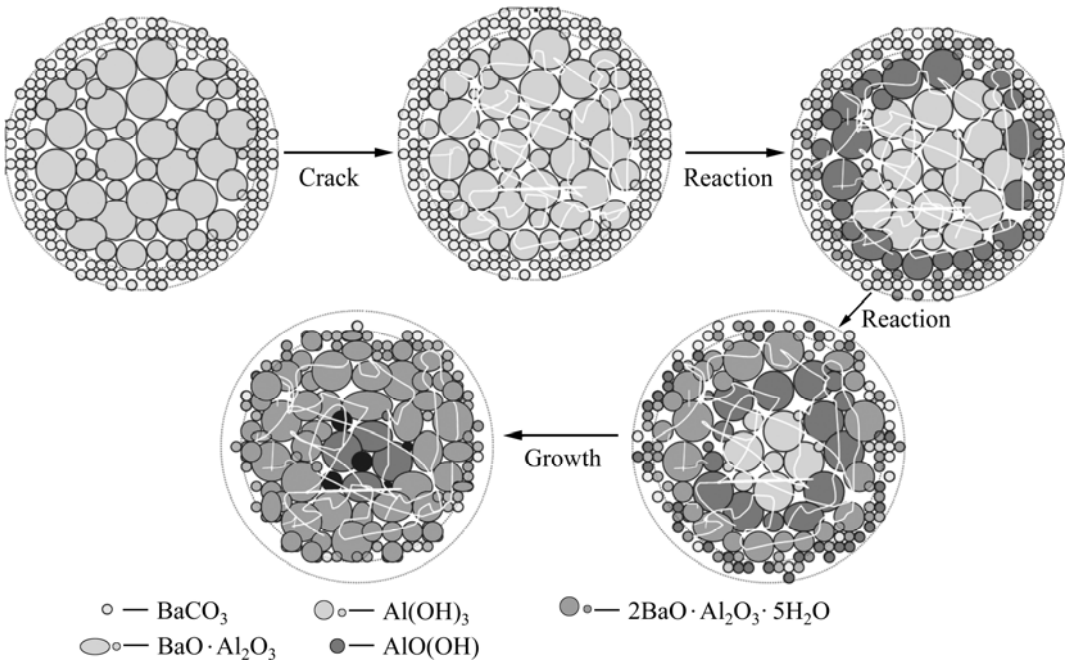

Fig.5 Schematic plan of synthesis mechanisms of $BaAl_2O_4$

lower sintering temperature, shorter sintering time and higher $BaAl_2O_4$ synthetic rate than conventional sintering. The BALO synthetic rate under different microwave sintering time at 900 °C is shown in Fig.9. From Fig.9, the synthetic rate keeps rising with sintering time increasing, so that the synthesis mechanism is verified.

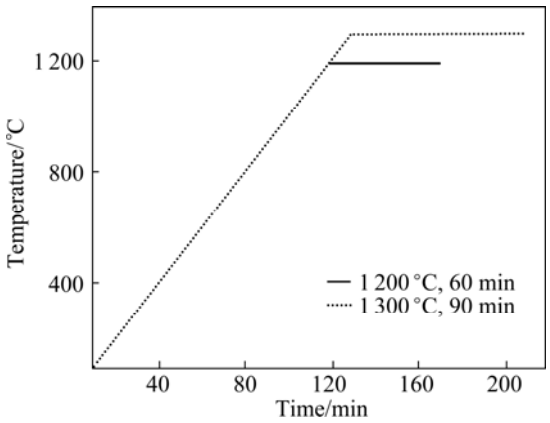

Fig.6 Heating-up curves at different conventional sintering temperatures

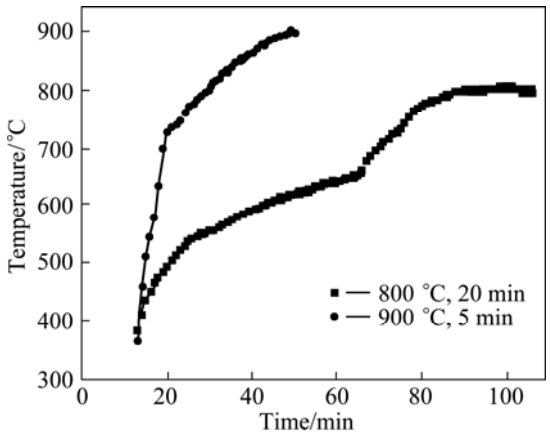

Fig.7 Heating-up curves at different conventional microwave sintering temperatures

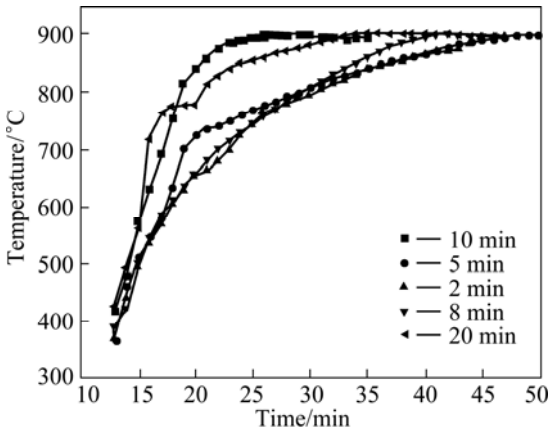

Fig.8 Heating-up curves for different microwave sintering time at 900 °C

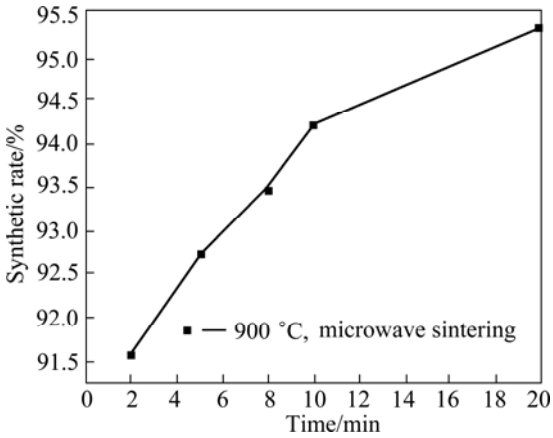

Fig.9 Synthetic rate of sintering powder at different microwave sintering time

4 Conclusions

1) BALO was successfully synthesized by microwave sintering at 900 °C for 5 min other than conventional sintering at temperature 1 300 °C for 90 min. Compared with conventional sintering method, microwave sintering is a better way to synthesize $BaAl_2O_4$ with advantages of low temperature sintering, short time sintering and high synthesis rate.

2) The first major mass loss of $BaCO_3$ and $Al(OH)_3$ are caused by the evaporation of planar water and part of crystallization water release below 600 °C. The decomposition of $BaCO_3$ and dewatering of remaining crystal occur in the temperature range of 900−1 300 °C.

3) The reaction mechanisms can be explained using un-reacted core model, and the intermediate product of $Ba_2Al_2O_5{\cdot}5H_2O$ exists.

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