Influence of Mechanical Activation of Al₂O₃ on Synthesis of Magnesium Aluminate Spinel

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Abstract: Magnesium aluminate (MA) spinel is synthesized by reaction sintering from alumina and magnesia. The effects of mechanical activation of Al₂O₃ on reaction sintering were investigated. Non-milled α-Al₂O₃ and α-Al₂O₃ high-energy ball milled for 12h, 24h and 36h were mixed with a MgO analytical reagent according to the stoichiometric MA ratio, respectively and pressed into billets with diameters of 20mm and height of 15mm. The green-body billets were then sintered at high temperature in an air atmosphere. The results show that bulk density, relative content of MA and grain size of MA increase with increasing high-energy ball milling time of Al₂O₃. However prolonged milling time over 24h has a small beneficial effect on the densification of MA. Bulk density and grain size of a sample of α-Al₂O₃ milled for 24h are 3.30g/cm³ and 4-5 μm, respectively.

Keywords: Mechanical activation; Magnesium aluminate spinel; Sintering; Densification

1. Introduction

Magnesium aluminate spinel (MA), which is the only stable compound in the MgO-Al₂O₃ system, possesses a high melting point (2135°C), good mechanical strength and excellent chemical resistance etc. [1-3]. It is becoming more and more important in refractories and ceramics [4]. Especially in recent years, as the hazardous character of chrome bearing materials is exposed, work and use of magnesium aluminate spinel are very important [5]. The major application areas of MA refractories are transition and burning zones of cement rotary kilns, side walls and bottom of steel teeming ladles and checker work of glass tank of furnace regenerators instead of MgO-Cr₂O₃ refractories. However the reaction of MgO and Al₂O₃ to form MA is accompanied by a volume expansion of approximately 7%, making it difficult to obtain a dense reaction sintered body [6]. Hence a two stage firing process is employed, the first one is to synthesize MA. In the second stage the MA synthesized is ground, pressed and sintered in order to be densified, which results in increasing cost of products. To obtain a dense reaction sintered body, researchers have studied several other processes such as freeze drying [7], sol-gel of metal alkoxides or inorganic [8], hydroxide coprecipitation [9] etc. However these chemical processes also have some intrinsic disadvantages. For instance, coprecipitation usually uses aluminum and magnesium chloride or nitrate salts, making repeated washing necessary to remove the anions, which will alter the composition designed and need a lot of water [10].

The effect of fineness of magnesia and alumina on the formation and densification of MA has been studied a lot. There are numerous studies of the influence of raw material
characteristics on the sintering of MA. Ritwik Sarkar et al [11] studied the effect of the calcination temperature of Al₂O₃ on the densification of rich magnesium spinel (MgO 34 wt.%). The results showed that sintered density does not change greatly with the increase in calcination temperature of alumina up to 1200°C, but calcination at 1600°C resulted in reduced sinterability due to greater agglomeration of alumina particles, leading to larger particle size and smaller surface area of alumina particles. Kostic and others [12] found that the grinding energy increases the surface area and structural imperfections and observed MA formation at lower temperature after prolonged grinding of starting materials. We studied the effect of polymorphism of Al₂O₃ on the synthesis and densification in reaction sintering of MA and found that γ-Al₂O₃ as a raw material instead of α-Al₂O₃ can improve synthesis and densification of MA [13].

Mechanical activation processing or high-energy ball milling, which was initially invented for ceramic strengthened alloys [14], can produce grain size down to the nanoscale, together with structure defects. Energetic lattice defects, combined with short diffusion distances, are the driving forces of faster solid-state alloying and chemical reactions at low temperatures [15]. Some authors report that some systems can react during high-energy ball milling [16]. At present, this method has been successfully used to synthesize a wide range of nano-sized ceramic powders and has become one of the most promising methods of promotion of multi-component system reactions. In the present work, we will study the synthesis and densification of MA from MgO and Al₂O₃ that was treated by a high-energy ball milling process for different times.

2. Experimental procedure

The starting materials used in this study were α-Al₂O₃ and an MgO analytical reagent. α-Al₂O₃ was the production of gibbsite heated at 1400°C for 4h. Its X-ray patterns are shown in Fig.1. The composition of the raw material is given in table 1. From Fig.1 we can see that α-Al₂O₃ is the dominant crystal phase and there is no other phase in the XRD pattern, which means gibbsite has already converted to α-Al₂O₃ at 1400°C.

<table>
<thead>
<tr>
<th>Type</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>IL</th>
<th>MgO</th>
<th>Particle size</th>
<th>Surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Al₂O₃</td>
<td>97.86</td>
<td>0.88</td>
<td>0.07</td>
<td>0.02</td>
<td>0.08</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>5.06</td>
<td>43.36</td>
</tr>
<tr>
<td>MgO</td>
<td>0.01</td>
<td>0.14</td>
<td>0.08</td>
<td>0.07</td>
<td>0.09</td>
<td>0.08</td>
<td>-</td>
<td>99.30</td>
<td>5.00</td>
<td>46.03</td>
</tr>
</tbody>
</table>

Note: IL is ignition loss. The operation temperature is 1000-1050°C for 1h.

α-Al₂O₃ was milled in a QM-SB type planetary ball milling system with a stainless steel pot in air at room temperature for 12h, 24h and 36h, respectively. The stainless steel ball to powder weight ratio in the pot was 10:1. Every pot was filled with 50g Al₂O₃ and 70g ethanol. The milling speed was 220 rpm. Non-milled α-Al₂O₃ and α-Al₂O₃ milled in a high-energy ball for different times were mixed with a MgO analytical reagent according to the stoichiometric MA ratio, respectively. Green-body billets 20mm in diameter and height of 15mm were prepared by cold-pressing under a pressure of 200MPa, in a stainless-steel die. The billets were then heated at 1400°C and 1600°C for 3h in an air, respectively.

XRD was performed (D/MAXβB) using Ni filtered Cu Kα under the following conditions: scanning speed of 2°min⁻¹ and temperature of 16°C. The density and porosity of
the sintered specimens was measured by the Archimedes method. The microstructure and grain size of sintered samples were examined via SEM (Philip 3lx). In order to study the influence of milling time on the amount of MA formed, the relative content of MA of four samples sintered at 1000°C were measured with a standard-free qualitative method proposed by Zevin [17].

This is not an accurate method to measure the phase content in samples, but it can be used to compare the phase content of Al₂O₃ samples in the same synthesis conditions with different milling times. The phase content can be calculated from the following formula:

\[
\sum_{i=1}^{n} \left( 1 - \frac{I_{ij}}{I_{ik}} \right) x_{ik} u_{mi} = 0
\]

\[
\sum_{i=1}^{n} x_{ik} = 1
\]

In the formula: \( I_{ij} \) and \( I_{ik} \) is the intensity of i phase of sample J and K respectively; \( x_{ik} \) is the content of i phase of sample K. In order to minimize errors, we used polynomial linear regression.

3. Results and discussion

Fig. 2, Fig. 3 and Fig. 4 give the relationships between bulk density, apparent porosity and linear changes of samples and milling time of \( \alpha \)-Al₂O₃ at 1400°C and 1600 °C, respectively. The milling time of \( \alpha \)-Al₂O₃ had a great effect on the densification of MA. Milling sharply increased the bulk density and linear changes and decreased apparent porosity of MA but prolonged milling time over 24h had little effect on the densification of MA.

Fig. 5 gives the relative content of MA in the samples made from \( \alpha \)-Al₂O₃ milled for 0, 12, 24 and 36h, respectively, and heated at 1000 °C. It is found that the MA content increases with increasing milling time of Al₂O₃ but prolonged milling time over 24h had almost no effect on the content of MA.

![Fig. 1 X-ray patterns of Al(OH)₃](image)
Scanning electron photomicrographs of four samples sintered at 1600 °C for 3h are shown in Fig.6. It is noted in Fig.6 that at the same sintering temperature, the grain size of MA in the samples is different. The MA in the sample with non-milled Al₂O₃ has the smallest grain size (≤2µm). The grain size of MA increases with increasing milling time of Al₂O₃ but prolonged milling time over 24h had little beneficial effect on the growth of MA. The sample of Al₂O₃ milled for 24h has the largest grain size (4-5 µm). All grain sizes were measured using the linear intercept method [18].

Formation of magnesium aluminate spinel from its constituent oxides is a counter diffusion process of Al³⁺ and Mg²⁺ ions [19]. In the MA formation based on the Wagner mechanism [20], oxygen ions remain at the initial sites. In order to keep electroneutrality, 3Mg²⁺ diffuse towards the alumina side and 2Al³⁺ diffuses towards the magnesia side, so four MgO change to one MA at the MgO side and four Al₂O₃ change to three MA.

Reduction of particle size can decrease the distance between vacancy sites (or that of grain boundaries) and enhance the vacancy diffusion to external surface and thus help
formation of MA and grain growth. Fig. 7 shows X-ray diffraction patterns of $\alpha - \text{Al}_2\text{O}_3$ milled for 12, 24 and 36h. It can be seen from Fig.7 that the diffraction peak of $\alpha - \text{Al}_2\text{O}_3$ becomes broad and smooth with increasing of high-energy ball milling time.

![Fig. 6 SEM photographs of the samples sintered at 1600$^\circ$C for 3h: (A) 0h, (B) 12h (C)24h (D)36h](image)

![Fig. 7 X-ray diffraction patterns of high-energy ball milled for 12h, 24h and 36h $\alpha - \text{Al}_2\text{O}_3$](image)

That implies an increase of distortion and defects of $\alpha - \text{Al}_2\text{O}_3$ crystals, which improve reactivity and sinterability of $\alpha - \text{Al}_2\text{O}_3$. This is one of the factors resulting in increasing of MA at 1000$^\circ$C and higher bulk density of samples heated at 1400 and 1600 $^\circ$C. When the milling time is longer than 24h it has little effects on sintering.
There may be two reasons for this. One is that the particle size of Al₂O₃ only changes a little when the milling time increases from 24h to 36h. The other may be that a very fine particle size may have a small negative effect on sintering because of agglomeration of fine particles [21].

4. Conclusion

Reaction sintering of MgO and Al₂O₃ is significantly enhanced by mechanical activation of Al₂O₃. Bulk density, relative content of MA and grain size of samples increase with increasing milling time of Al₂O₃. However when prolonged milling time is more than 24h, the effects of milling time on bulk density of samples and grain size of MA in the samples are small.

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