Effect of powder reactivity on microwave sintering of alumina

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Abstract

Effect of the reactivity of starting alumina powder of varying crystallinity on the sintering behavior in microwave process was studied. From X-ray amorphous to highly crystalline alumina, powders were obtained by conventional heating of compacts made of the precursor amorphous powder by heating it at different temperatures from 800 to 1500 °C. These samples were then sintered in a multimode microwave field of 2.45 GHz for 10 min at 1500 °C. The microwave effect on densification of the various alumina powders was evaluated by comparing the microwave and conventional sintering data. The results show significant microwave enhancement in the densification of the samples without any pretreatment. This enhancement became less significant as the temperature of the pretreatment increased and finally diminished. Since the pretreatment at elevated temperatures made the powder more stable thermodynamically, this study indicates that the sintering enhancement of a ceramic material in microwave is a metastability-related phenomenon.

Keywords: Microwave sintering; Alumina; Reactivity; Ceramics; Densification

1. Introduction

Microwave heating of ceramics goes back to the post-World War II era when old radar equipment was used for drying large whiteware. Early work on the use of microwave sintering was concentrated on dark ceramics [1]. Extraordinarily rapid heating and high temperatures were reported by Haas [2] in urania gels. Several excellent reviews by Clark and Sutton [3], Schiffman [4], Katz [5], Sutton [6,7], and Agrawal [8] adequately give the interested readers a broader picture of the status of microwave processing research. According to these reviews, considerable research was focused on white ceramics, especially on traditional ceramic materials in 1980s, to obtain rapid sintering of materials. These are reported in several proceedings volumes starting in 1988 [9]. By controlling the starting material microstructure, transparent ceramics have been produced [10], and this has been extended later to alumina and other ceramics [11]. This paper examines the possible influence of the structural state (crystallinity) of the Al2O3 on its microwave sinterability.

Phenomena of microwave-enhanced sintering or densification of some ceramic materials have been observed by researchers in the past [12–16]. Recently, Roy et al. [17] have observed anisothermal situations on the enhancement of reaction kinetics in the synthesis of all ceramic multi-phase powder containing 3d or 4f oxides [18]. The most remarkable changes in sintering of WC and the improved properties obtained have been explained by Cheng et al. [19]. Next, the reaction and sinterability of various materials in single-mode microwave cavities have been reported [20]. It is well known that grain boundary diffusion is a primary mechanism responsible for the densification of ceramics during sintering. Ionic mobility along a grain boundary can be three to four orders of magnitude greater than in the bulk [21] because of the higher defect concentration at grain boundaries as compared to the bulk. A grain boundary is the interface bonding two grains, while the surface usually implies the interface between solid and vapor phases. The structural state of both grain boundaries and surfaces of fine ceramic powders is close to the amorphous state. If the influence of reactivity or specific surface area of the materials in a microwave field can be experimentally verified, the effect of grain boundary on the microwave sintering enhancement would be confirmed. Fang et al. [22] found that microwaves couple with diphasic mullite gel very efficiently because of the presence of the amorphous silica in the gel. This can also be explained in terms selective microwave absorption since amorphous silica has higher microwave absorption than mullite, causing anisothermal situation and hence enhancement in the reaction and diffu-
sion kinetics. It was also observed [23] that microwave enhancement in the sintering of alumina is very significant when using amorphous alumina as starting material. However, when using crystalline alumina as starting material, the microwave effect became negligible. Here we report the results of our preliminary study on the influence of structural state of starting materials on the sintering of alumina in a microwave field.

2. Experimental

2.1. Material

An X-ray amorphous, reactive alumina powder from a commercial source (RP–Al₂O₃, Rhone-Poulenc, France) was used as the precursor material. This alumina has been characterized in detail by Agrawal et al. [24]. The material is chemically pure with less than 100 ppm of impurities of Ca and Mg. It is mostly X-ray amorphous with the presence of poorly crystalline α-Al₂O₃ as a minor phase. The amorphous powder was sifted to 325 mesh (45 μm). Circular pellets of 6.35 mm in diameter and 2.5 mm in thickness were compacted by uniaxial pressing at 350 MPa using the sifted alumina powder. To obtain samples of alumina with different degrees of crystallinity, the pellets were thermally annealed in a conventional furnace for 1 h at 800, 1000, 1200, 1300, and 1500 °C, respectively.

2.2. Sintering

Microwave sintering was conducted in a 900-W, 2.45-GHz multimode microwave cavity (Panasonic, Model NN-6371WM) with a turntable to rotate a sintering packet in which the samples were loaded. Details of the configuration of the sintering packet are shown in Fig. 1. Multi-pellet sintering was conducted. In each run, six samples made of powders pretreated at various temperatures were placed at the same level in the center of the cavity, forming a circle, to subject to the same microwave radiation. A porous (density = 0.48 g/cm³) zirconia cylinder (Type ZYFB 3, Zircar Products, Florida, NY) containing 8% Y₂O₃ was used as susceptor. The susceptor was thermally insulated with Fiberfrax™ (Unifrax, Niagara Falls, NY 14302), a highly porous thermal insulator composed of mullite fibers. All samples were sintered at 1500 °C for 10 min in the microwave field. Duplicate samples were sintered in a conventional furnace for comparison. The heating rate in both conventional and the microwave processes was kept at ~100 °C per min. The temperature was measured with an S-type thermocouple. In the microwave sintering, the thermocouple was shielded with platinum foil and grounded to the wall of the microwave cavity to avoid interference of the microwave field. The tip of the thermocouple was in touch with one sample and close to rest of the samples.

2.3. Characterization

The BET-specific surface area of the thermally annealed samples was measured using a Quanta Chrome MS-12 Monosorb (Quanta Chrome, Syosset, NY). Powder X-ray diffraction (XRD) of the powders was conducted for phase composition on a Scintag diffractometer (Scintag, Sunnyvale, CA) using CuKₐ radiation. Density of the sintered alumina was measured by weighing and dimensional measurements. Microwave effect on densification of alumina was evaluated by the enhancement in the sintered density achieved by microwave and conventional processes.

3. Results and discussion

3.1. Characteristics of the samples

The XRD patterns of the alumina powders preheated at various temperatures are shown in Fig. 2. The as-received powder was X-ray amorphous. When annealed at 800 and 1000 °C, the powder was poorly crystalline, corresponding
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Fig. 2. XRD patterns showing the phase composition of the powder samples before microwave sintering. The phases are untreated, amorphous; 800 °C, γ-Al₂O₃; 1000 °C, θ-Al₂O₃; 1200 °C and above, α-Al₂O₃.

to γ-alumina, with trace amount of α-alumina at 1000 °C. The powders pretreated at 1200 °C and above, as well as all the sintered samples, were identified as single-phase α-Al₂O₃. The crystallinity increased as temperature increased as was evident from the increasing sharpness and intensity of the main peaks of α-Al₂O₃. As expected, the specific surface area decreased as the temperature increased (Table 1). The precursor powder had a specific surface area of 114 m²/g. At 1000 °C, the surface area was only 65, and at 1500 °C, it reduced to only 1.1 m²/g. The thermal treatment made the powders less reactive. In other words, the pretreatment made the alumina powder more stable thermodynamically.

3.2. Microwave effect

The relative density data of the samples before and after sintering are listed in Table 1, where \( \rho_0 \), \( \rho_c \), and \( \rho_m \) are green density, conventionally sintered density, and microwave-sintered density, respectively (in terms of percent of theoretical); \( \Delta \rho_c \) and \( \Delta \rho_m \) are the change in densification, i.e., relative density increase in conventional and microwave sintering, respectively. The microwave effect is expressed as the enhanced densification in the microwave sintering over the conventional process, 100[\( \Delta \rho_m / \Delta \rho_c \)]\%. The results clearly show a correlation of specific surface area and the microwave enhancement in densification. It is seen that the alumina without any thermal pretreatment showed 60% microwave-enhanced densification. Once preheat treated at elevated temperatures, the microwave enhancement decreased substantially. The microwave effect completely diminished as the temperature of the pretreatment increased to 1500 °C.

3.3. Discussion

As observed above, the densification of alumina in the microwave field was higher at the same temperature than that obtained by conventional process. The maximum enhancement (60%) was observed with the amorphous alumina powder. The enhancement decreased with the increase in the crystallinity and was also highly dependent upon the presence of amorphous phase. This clearly indicates that a microwave enhancing effect on the sintering of alumina depends on the nature of the starting material. The starting material of alumina with higher reactivity has higher microwave absorption than the thermodynamically stable, highly crystalline α-Al₂O₃ obtained by thermal treatment at high temperature. When the powder is amorphous, the microwave coupling is strong and hence the densification is enhanced.

Thermodynamically, an amorphous ceramic powder is always at a higher free energy state than the sintered ceramic made from the powder. Sintering is a process to consolidate powder into a strong ceramic by supplying sufficient thermal energy to overcome the energy barrier between the powder and the ceramics. The driving force for sintering is the difference in Gibbs free energy of the material before and after sintering. The so-called microwave effect is a nonthermal effect that makes the microwave-absorbing materials in the microwave field more reactive. When the nonthermal microwave effect exists, the material in the microwave is activated, thus the energy barrier for sintering decreases so

Table 1

<table>
<thead>
<tr>
<th>Pretreating</th>
<th>SA (m²/g)</th>
<th>Conventional sintering</th>
<th>Microwave sintering</th>
<th>MED (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \rho_0 )</td>
<td>( \rho_c )</td>
<td>( \Delta \rho_c )</td>
<td>( \rho_0 )</td>
</tr>
<tr>
<td>Unfired</td>
<td>114</td>
<td>32.68</td>
<td>46.23</td>
<td>31.75</td>
</tr>
<tr>
<td>800 °C</td>
<td>93</td>
<td>35.12</td>
<td>49.62</td>
<td>41.29</td>
</tr>
<tr>
<td>1000 °C</td>
<td>65</td>
<td>36.86</td>
<td>54.50</td>
<td>47.86</td>
</tr>
<tr>
<td>1200 °C</td>
<td>9.7</td>
<td>46.51</td>
<td>61.42</td>
<td>32.06</td>
</tr>
<tr>
<td>1300 °C</td>
<td>4.7</td>
<td>49.10</td>
<td>66.29</td>
<td>35.01</td>
</tr>
<tr>
<td>1500 °C</td>
<td>1.1</td>
<td>54.31</td>
<td>60.00</td>
<td>10.46</td>
</tr>
</tbody>
</table>

SA, specific surface area.
MED, microwave-enhanced densification, expressed as 100[\( \Delta \rho_m / \Delta \rho_c \)]%.

Fig. 3. A schematic showing the energy states of different powders in the microwave sintering. \( A_1 \) represents the powder with high reactivity that shows higher microwave activating effect during the processing. \( A_2 \) represents a thermally pretreated powder that has lower reactivity and gets less microwave-activating effect during processing. \( E_{a,1} \) and \( E_{a,2} \) represents the energy of activation for sintering for \( A_1 \) and \( A_2 \), respectively.
that less thermal energy is required to initiate the sintering process. This is illustrated in Fig. 3. The apparent microwave effect is related to the relative magnitudes of microwave effect and the activation energy of the process. If the microwave effect is too small compared to the required activation energy, its contribution to the sintering process would be negligible. When excess thermal energy is supplied, microwave effect would also be shielded.

4. Summary

The microwave effect on densification of alumina of different reactivity was characterized by enhanced densification in the microwave field over the conventional sintering. The enhancement in densification up to 60% was observed with the highly reactive amorphous alumina powder. The microwave effect decreased as the reactivity of the alumina powder decreased as a result of thermal pretreatment. The highly crystalline \( \alpha \)-Al\(_2\)O\(_3\) obtained by thermal treatment at 1500 °C did not show any enhancement in its densification in the microwave field. This indicates that the microwave effect is related to the nature of the precursor material. The powder with higher reactivity, or higher thermodynamic metastability (Gibbs free energy), leads to stronger microwave enhancement in densification.

References