Pressureless sintering of cordierite ceramics with optimized strength and thermal expansion

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Abstract. In this study, cordierite ceramic samples with very low thermal expansion are prepared by the pressureless sintering technique. The effects of sintering temperature and holding time on their sintering density and elastic modulus are investigated, while their optimal values are assessed as 1420°C and 1 h, respectively. These parameters ensure the elastic modulus of 121 GPa, the relative sintering density corresponding to 95% of the theoretical value, and the coefficient of thermal expansion of |4.4|×10⁻⁷ °C.

1. Introduction

Polycrystalline oxide ceramics with a cordierite matrix are very promising advanced materials due to their very low (near zero) thermal expansion coefficient, superior thermal shock resistance, excellent chemical resistance, and high elastic modulus. In particular, high stiffness, light weight, and precise machining geometry of cordierite matrix ceramics enhance its wide application in many fields, including high-precision lithography equipment, large space telescopes, and new optical systems [1-3]. However, a limited reserve of natural cordierite necessitates the alternative of man-made cordierite ceramics production via sintering of cordierite powders, which are usually synthesized from natural materials or oxide chemical reagents.

There are several methods to synthesize cordierite, such as the spark plasma sintering [4-6], hot-pressed sintering [7-9], and pressureless sintering [10-12]. The disadvantages of the first two sintering techniques include low yields, complicated processing procedures, and uncontrollable sintering processes, which inhibit their large-scale and application. From the perspective of low-cost production, the third method, namely the pressureless sintering, allows one to produce cordierite ceramics directly from high-purity powders. However, a very narrow sintering temperature range of cordierite ceramic makes it quite problematic to control crystalline growth and introduce the second phase into the cordierite phase [13-15], which leads to the significant scatter in the thermal expansion coefficients of the prepared composites even under minimal adjustment of the sintering formula during the cordierite ceramics preparation by this method.

In this study, cordierite ceramic samples were successfully synthesized by the solid-state reaction method using raw materials, including high-purity powders of MgO, Al₂O₃, and SiO₂, mixed according to the stoichiometric ratio of cordierite. The effects of pressureless sintering parameters, such as forming
pressure, sintering temperature, and holding time, on the relative sintering density and mechanical properties are investigated and discussed in detail.

2. Experimental

The theoretical composition of cordierite ceramic is known to have MgO, Al$_2$O$_3$, and SiO$_2$ mass fractions of 14.0, 35.0, and 51.0%, respectively. This study used the mass fractions of MgO (13.7%), Al$_2$O$_3$ (34.9%), and SiO$_2$ (51.4%) powders, which characteristics and manufacturers are listed in Table 1.

| No. | Name     | Mean grain size | Purity     | Wt.% | Manufacturer                |
|-----|----------|-----------------|------------|------|-----------------------------|
| 1   | MgO      | 1μm             | ≥98.5%     | 13.7 | Xuan Cheng Jing Rui New Materials Co., Ltd., China |
| 2   | Al$_2$O$_3$ | 0.5μm       | ≥99.9%     | 34.9 |                             |
| 3   | SiO$_2$  | 30nm            | ≥99%       | 51.4 |                             |

Insofar as a thorough grinding and mixing of the ingredients requires a long-term milling, all mixtures were ball-milled via MITR-YXQM-2L by the MITR Instrument and Equipment. Co., Changsha, China, for 8 h in acetone with a high-purity zirconia (99.5%) grinding media using a pure alcohol dispersant, subsequently dried at 60°C for 2 h (in a DY881-3 drying oven by the Wujiang Electric Heating Equipment Co. Ltd, Jiang Su, China), granulated manually, and filtered through 60mesh. The powders were pressed (in a YQ32-63t powder press by the Dazheng Engineered Equipment Co., Ltd., Shandong, China) to form green bodies. The amount of 30g of powders was used to produce each sample by pressing via 15mm-diameter steel dies with the forming pressure of 190MPa. Next, samples were sintered in a conventional high-temperature resistance furnace (an HY021 by the Zhu Zhou Electric Heating Equipment Co., Ltd, Hunan, China). The heating of samples started at 25°C, and then samples were sintered in the air up to 1380, 1390, 1400, 1410, 1420, 1430, and 1440°C, respectively. The heating rate was 5°C/min, and the peak temperature holding time was 1 h. Then, samples were naturally cooled down in the furnace to room temperature.

The density of specimens was measured by the Archimedes method. The shrinkage rate of samples was calculated using measurements of their diameter, thickness, and mass. The optimum sintering temperature was identified.

The sintered samples containing the same amount (30g) of powders were prepared at the optimum sintering temperature with different holding times (0.5, 1, 1.5, and 2 h). Their density, shrinkage rate, and optimum holding time were assessed, similar to the above case.

The sintered samples were subjected to the XRD analysis via a D/Max-γβ X-ray diffractometer (at 40mA, 40kV, CuKr radiation) to analyze their phase transformation patterns. The morphology of sintered samples was observed using a JSM-6700F scanning electron microscope at the accelerating voltage of 15kV. The elastic modulus of sintered samples was tested via an MTS810 equipment using finished bars and discs with polished surfaces, in compliance with the GB/T 10700-2006 standard specifications. The coefficient of thermal expansion (CTE) was measured using a Netzsch 402C device in the temperature range between -40 and 250°C. The microstructure was examined via a QUANTA FEG250 (FEI Co.) scanning electron microscope.

3. Results and discussion

3.1. Influence of temperature to the synthesizing cordierite ceramic

The XRD patterns of the synthesized cordierite ceramic at temperatures from 1380 to 1440°C are shown in Figure 1. The distinct characteristic peaks of cordierite, magnesium aluminate spinel, and silicon dioxide at sintering temperature of 1380°C were identified. In the range from 1390 to 1410°C, the intensity of peaks of magnesium aluminate spinel and silicon dioxide dropped with temperature, while...
that of cordierite increased, which indicated that the cordierite purity was improved. When the sintering temperature reached 1420°C, the characteristic peaks of magnesium aluminate spinel and silicon dioxide disappeared, so that only a pure cordierite remained in the synthesized product. Based on these findings, it was concluded that during the synthesizing process, firstly, the magnesium aluminate spinel was formed from MgO and Al₂O₃, which reacted with SiO₂, leading to the formation of cordierite. Due to a narrow sintering temperature range of cordierite ceramics, cordierite decomposed into the mullite, when the temperature reached 1440°C, and the glass phase appeared due to high temperature.

![Figure 1. The XRD patterns of cordierite powders calcined at various temperatures from 1380 to 1440°C.](image)

![Figure 2. SEM images of cordierite powder with granulation at various temperatures.](image)

Microstructures observed by SEM at specific temperatures of 1410, 1420, and 1430°C are depicted in figure 2 (a)-(c), respectively. Each of them exhibits an enhanced growth of cordierite grains, with relatively uniform and dense distribution. The comparison of figure 2 (a) and (b) implies that the cordierite powder with sintering temperature of 1420°C has the optimal structure of grains (including their edges and corners), is tightly compacted, and has flake-stacking grain shape. Figure 2(c) indicates that, with increased temperature, the liquid phase is formed, grains start to generate agglomerations, while grain boundaries become thinner, are amalgamated, and eventually disappear. These results are consistent with macro-observations of the powder morphology, which changed from fluffy to solid block with semitransparent appearance.

3.2. Influence of sintering temperature on the sintering property of cordierite ceramics
Each sample with the forming pressure of 190MPa was sintered in the air up to 1350, 1380, 1410, 1420, and 1430°C, respectively; the heating rate was 5°C/min and holding time was 1 h. Then, samples were naturally cooled down until they reached room temperature. The relative sintering density and shrinkage rate with different sintering temperatures are given in figure 3. Both values are shown to rise with sintering temperature and reached their maxima (95% of the theoretical density value and 12%, respectively) at 1420°C. Meanwhile, the relative sintering density dropped with the further rise in the sintering temperature; and severe deformation occurred in the sintered samples, due to the glass phase development in the matrix at 1430°C. A further temperature increase led to the grain boundary thinning and abnormal grain growth, which could have a negative densification effect on the cordierite ceramic microstructure.

3.3. Influence of sintering temperature holding time on the synthesized cordierite ceramics properties

Samples with the forming pressure of 190MPa were sintered in the air up to 1420°C, with the heating rate of 5°C/min and holding times of 0.5, 1, 1.5, and 2 h, respectively. Then, samples were naturally cooled down to room temperature. The relative sintering densities and shrinkage rates for various holding times are given in figure 4. The relative sintering density and shrinkage rate initially increased versus holding time, reaching their maxima (95 and 12%, respectively) at 1 h. Then, the relative sintering density remained unchanged (saturated) at longer holding times.
3.4. Influence of sintering temperature on mechanical properties of synthesized cordierite ceramics

The values of elastic modulus for different sintering temperatures are given in figure 5: they initially increase with sintering temperature and reach their maximum of 121 GPa at 1420°C with holding time of 1.5h. However, the elastic modulus sharply drops to 67 GPa at sintering temperature of 1430°C. As it was already mentioned, severe deformation occurs in the samples at sintering temperature of 1430°C. The appearance of the glass phase in the matrix at higher temperatures deteriorates the mechanical properties, and samples become over-sintered. Compared with figure 2, the cordierite ceramic sample with a sintering temperature of 1420°C had better grain structure and edges, and its microstructure was more dense and uniform. Moreover, less numerous pores in the former case contributed to higher values of the relative sintering density and elastic modulus.

Table 2 shows bulk densities, shrinkage rates, and CTE values of samples obtained at the sintering temperature of 1420°C with holding times of 0.5, 1, and 2h.

Figure 4. Relative sintering density and shrinkage rate of samples at 1420°C versus holding time.

Figure 5. Elastic modulus of samples versus sintering temperature.
Table 2. Bulk densities, shrinkage rates, and CTE values of samples obtained at the sintering temperature of 1420°C with holding times of 0.5, 1, and 2h.

| Sintering temperature, °C | Holding time, h | Bulk density, g·cm\(^{-3}\) | Shrinkage rate, % | CTE, per °C |
|--------------------------|----------------|-------------------------------|-------------------|-------------|
| 1420                     | 0.5            | 2.38                          | 10                | [8.6]×10\(^{-7}\) |
|                          | 1              | 2.45                          | 12                | [4.4]×10\(^{-7}\) |
|                          | 2              | 2.43                          | 13                | [5.6]×10\(^{-7}\) |

4. Conclusion

The sintering temperature has a strong impact on the mechanical and thermal expansion properties of sintered cordierite ceramics. The relative sintering density, shrinkage rate, and elastic modulus initially rose with the sintering temperature and reached their maximum values (95% of the theoretical density value, 12%, and 121GPa, respectively) at 1420°C. Higher sintering temperatures deteriorated the relative sintering density and elastic modulus and induced severe deformation in tested samples. This phenomenon can be attributed to the appearance of a glass phase in the matrix of cordierite ceramics at a 1430°C sintering temperature. Therefore, the optimal sintering temperature is about 1420°C.

At the forming pressure of 190MPa, sintering temperature of about 1420°C, and holding time of 1h, the cordierite ceramic sintered samples had the optimum properties: the relative sintering density corresponding to 95% of its theoretical value, the elastic modulus of 121GPa, and CTE of [4.4]×10\(^{-7}\)°C.

Acknowledgments

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