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Short communication

Ce^{4+}-modified cordierite ceramics

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Abstract

A dense, low thermal expansion cordierite ceramic was prepared by the co-precipitation method and Ce^{4+} addition. Ce^{4+} addition can inhibit μ-cordierite crystallization and improve α-cordierite crystallization. Adding 3.2 wt.% Ce^{4+} enables density and mechanical strength to reach maximum values with a minor increase in thermal expansion coefficient.

Keywords: A. Sintering; C. Mechanical properties; C. Thermal expansion; D. Cordierite

1. Introduction

Cordierite ceramic is a good candidate for the honeycomb structure of catalyst converters and diesel particulate trappers due to its low thermal expansion coefficient [1]. In order to increase the catalytic and trapping efficiency, it is necessary to decrease the thickness of walls of the honeycomb and to increase cell density. Because the durability of the honeycomb depends on its strength and thermal stability [2], the ceramic should possess enough high strength and a low thermal expansion coefficient to avoid wall failing.

Stoichiometric cordierite ceramic fabricated by oxide-powder sintering possesses very low density and strength [3,4]. Therefore, many processes have been adopted to improve its mechanical and thermal expansion properties. One of the processes is adding a low-melting flux such as K_2O, Na_2O, Li_2O, CaO, B_2O_3, NaF and LiF [3,5–9]. The flux is helpful for obtaining dense cordierite ceramic and improving cordierite transformation, but it will deteriorate the thermal expansion coefficient once a glass phase occurs. The sol-gel method is another route to prepare high-performance cordierite ceramics [10–12]. Suzuki [13] observed that the densification of cordierite ceramics prepared by this process appeared at 800–900 °C without any sintering aid. Sintering at 1300 °C for 12 h provided a dense α-cordierite ceramic with a flexural strength of 120 MPa. Addition of rare earths to cordierite ceramics can decrease sintering temperature and porosity, facilitate cordierite transformation and result in less increase of the thermal expansion coefficient [14–17]. Okamura [18] found that a dense cordierite glass-ceramic was obtained by adding La_2O_3 at sintering temperatures between 1355 and 1420 °C. Moreover, cordierite ceramics can be reinforced by graphite, SiC and stainless-steel fibers or mullite and zirconia secondary phases [19–23].

An additive, for cordierite ceramic to be effective, not only should increase the mechanical properties but also limit the thermal expansion coefficient. The present work aims at preparing high density and low thermal expansion coefficient cordierite ceramic by the co-precipitation method and Ce^{4+} addition.

2. Experimental procedures

Tetraethyl silicate (TEOS), aluminum isopropoxide ($Al(OC_3H_7^{I})_3$), magnesium isopropoxide ($Mg(OC_2H_5)_2$) and cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) were used as precursory materials. The sheer hydrolyzed alkoxides and nitrate were mixed into solutions with stoichiometric

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cordierite composition and different amounts of Ce^{4+}, and strongly stirred to form sols. NaOH solution was added into the sols to precipitate amorphous powders. Such powders were cleaned with deionized water, dried at 100 °C, calcined at 450 °C, ball-milled for 3 h, mechanically pressed at 50 MPa, and ultimately sintered at different temperatures in air atmosphere.

The phase analysis was conducted by XRD (D/max-2400X, Rigaku, with Cu Kα radiation, 40 kV, 120 mA and scanning speed of 4°/min). Backscattered electron images of surface-polished samples covered with carbon by ion-sputtering were observed by SEM (CSM950, Opton). The apparent porosity of samples was measured by the water displacement technique. The three-point flexural strength of 3 mm × 4 mm × 40 mm samples was measured by using a testing machine (AGS-10KNG, Shimadzu) with 30 mm span and loading rate of 0.5 mm/min. The thermal expansion coefficient was measured with a TMA92, Setaram apparatus at a heating rate of 10 °C/min and in Ar protective atmosphere.

3. Results and discussions

3.1. Crystallization

Fig. 1 shows the XRD patterns of ceramics sintered at different temperatures, and Fig. 2, the morphology of CeO_2 particles in the ceramics with different Ce^{4+} additions. CeO_2 easily precipitates from the Ce^{4+}-modified amorphous at low temperatures, and the content of CeO_2 particles increase with the increase of the Ce^{4+} addition. When sintered at 1200 °C for 3 h, the Ce^{4+}-modified ceramics are composed of α-cordierite and CeO_2, while the Ce^{4+}-free ceramic is composed of larger amounts of μ-cordierite and small amounts of α-cordierite phases. This proves Ce^{4+} addition to promote the transformation of μ-cordierite to α-cordierite.

This is related to Ce^{4+} densifying the microstructure of glass or amorphous phase [24] due to its high valence (+4) and large coordination number [25], so the Ce^{4+}-modified amorphous gets more stable than the Ce^{4+}-free amorphous towards μ-cordierite crystallization. Moreover, because of the insignificant solubility of Ce^{4+} in crystalline cordierite, and no reaction between Ce^{4+} and cordierite occurring [26], Ce^{4+}concentration in the amorphous decreases with the precipitation of CeO_2 particles, resulting in a decreasing stability and so an incomplete crystallization of μ-cordierite.

Since the transformation of α-cordierite in the Ce^{4+}-modified ceramics is quite completed when sintered at 1200 °C, we selected this sintering temperature to examine the effect of Ce^{4+} addition on the microstructure and properties for all of the samples.

3.2. Densification and mechanical properties

Fig. 3 shows the variation of linear shrinkage with sintering temperature. Remarkable shrinkage appears at temperatures less than 900 °C below cordierite crystallization. The largest shrinkage occurred at 3.2 wt.% Ce^{4+} addition. Fig. 4 shows porosity and flexural strength versus Ce^{4+} addition. The lowest porosity and the highest flexural strength also appeared at 3.2 wt.% Ce^{4+}.

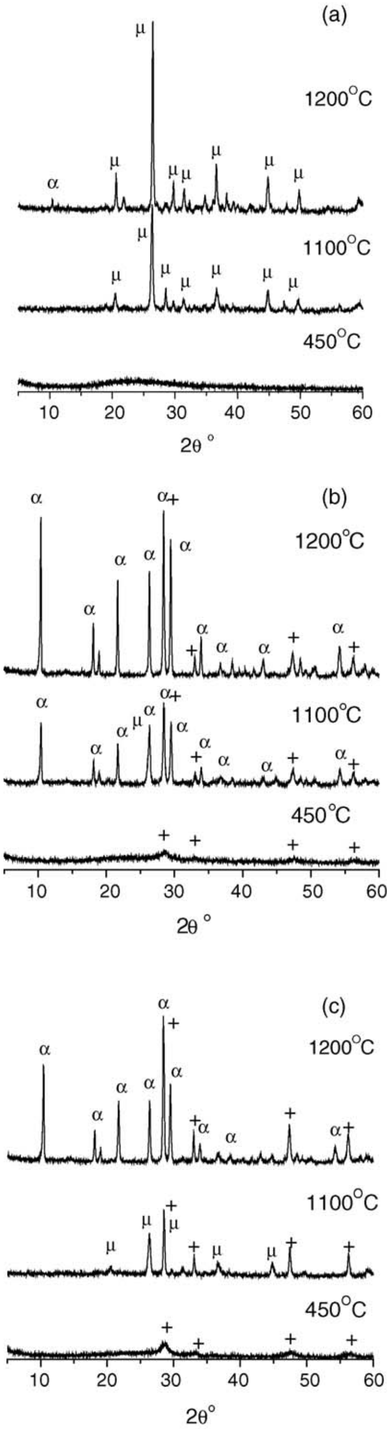

Fig. 1. XRD patterns of ceramics (α: α-cordierite; μ: μ-cordierite; +: CeO_2; soaking time: 3 h). (a) Ce^{4+}-free. (b) 3.2 wt% of Ce^{4+}. (c) 4.8 wt% of Ce^{4+}.

The Ce^{4+} addition may decrease the softening temperature of the amorphous [17], so the density may increase with

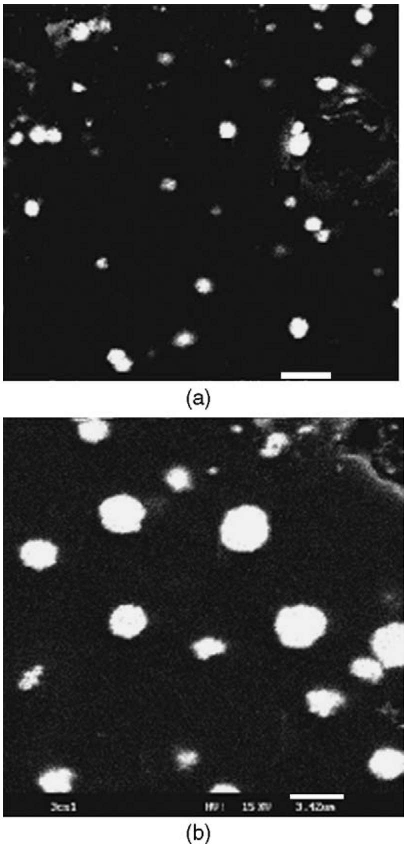

Fig. 2. Backscattered electron images of Ce^{4+}-modified cordierite ceramics. (a) 3.2 wt% of Ce^{4+}. (b) 4.8 wt% of Ce^{4+}.

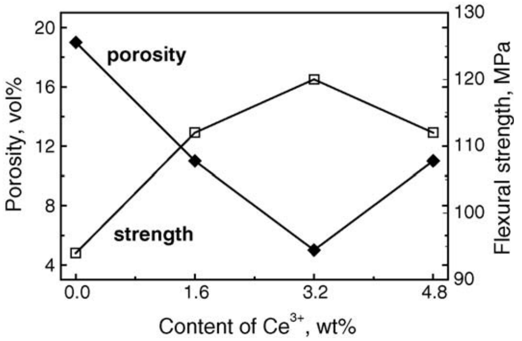

Fig. 4. Variations of porosity and flexural strength with Ce^{4+} content.

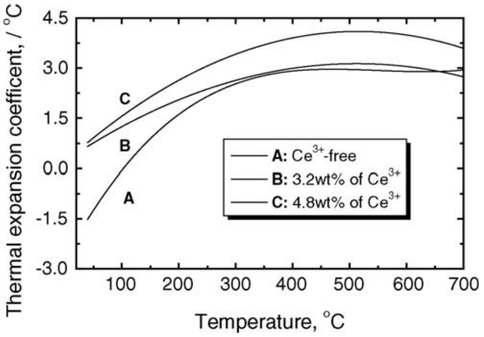

Fig. 5. Variation of thermal expansion coefficient with Ce^{4+} content and temperature.

Ce^{4+} additions. On the other hand, the CeO_2 particles inhibit the densification, the effect becoming stronger with the increase of both particle content and size. This simultaneous action results in the highest density and strength at 3.2 wt.% of Ce^{4+}.

3.3. Thermal expansion coefficient

The thermal expansion coefficient of the ceramics sintered at 1200 °C for 3 h increases with Ce^{4+} content and temperature (Fig. 5). It can be found that the Ce^{4+}-modified cordierite ceramics no longer present the intrinsic character of negative thermal expansion at low temperatures The averages of thermal expansion coefficients are $2.22 \times 10^{-6}/°C$, $2.48 \times 10^{-6}/°C$ and $3.21 \times 10^{-6}/°C$ in 20–700 °C for the ceramics with 0, 3.2 and 4.8 wt.% Ce^{4+} additions, respectively.

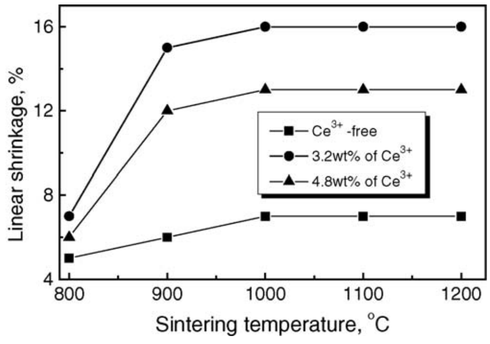

Fig. 3. Linear shrinkage of ceramics sintered at different temperatures for 2 h.

Because of the existence of large amounts of μ-cordierite, the thermal expansion coefficient of the Ce^{4+}-free ceramic is higher than for stoichiometric α-cordierite crystal ($1.5 \times 10^{-6}/°C$). Moreover, because the CeO_2 particles increase the thermal expansion coefficient, the Ce^{4+}-modified ceramic possesses a higher thermal expansion coefficient than the Ce^{4+}-free.

4. Conclusions

The addition of Ce^{4+} effectively depresses the formation of μ-cordierite and stimulates the transformation of α-cordierite. The Ce^{4+}-modified cordierite ceramic, when sintered at 1200 °C for 3 h, is only composed of α-cordierite and CeO_2 particles.

The density and strength of the cordierite ceramics reach the maximum values at 3.2 wt.% Ce^{4+} addition, and the thermal expansion coefficient increases with Ce^{4+} content and temperature.

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