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Cordierite composites reinforced with zircon arising from zirconium–vermiculite precursor

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ABSTRACT

The paper aimed with four forms of cordierite and cordierite–zircon ceramic composites prepared via sintering of the pre-ceramics clay mineral mixtures containing vermiculite (V) and zirconium–vermiculite (Zr–V) without the use of long-term grinding procedures. Precursor of zircon in cordierite was Zr–V prepared from V and zirconium salt solution via cation exchange. Cordierite composites containing pure cordierite phase were sintered from the clay mineral mixtures. Cordierite composites composed of spinel and enstatite or forsterite at the expense of cordierite were prepared from the clay mineral mixtures and Al_2O_3 or MgO. The additives contributed to the development of pores that size about 5 μm. Zircon crystals with a size ranging from 150 nm to 1 μm were irregularly distributed on the cordierite matrix surface. Cordierites reinforced with zircon in comparison to their parent cordierites showed a lower porosity and higher hardness values.

1. Introduction

Composites based on the cordierite, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, possess a unique combination of several characteristics as thermal shock resistance due to a low thermal expansion coefficient, porosity and pore size distribution and sufficient refractoriness because the melting point exceeds 1450 °C. Ceramics based on cordierite have wide range of applications as electrical insulators, low-expansion refractory's and packing materials. Cordierite is being used as catalyst carriers in automobile exhaust systems and as a heat exchanger for gas turbine engines.

Toughened composites have been developed to improve the mechanical properties of cordierite ceramics. The interest in zircon ($ZrSiO_4$) as a ceramic and refractory material is due to its excellent thermo-physical properties such as low thermal expansion, low thermal conductivity, as well as a good corrosion resistance. Zircon has thermal expansion (4.1×10^{-6} °C) close to the cordierite mineral (1.5×10^{-6} °C) and possesses high thermal shock resistance and high chemical stability [1]. The oxides Na_2O, PbO, ZnO, Fe_2O_3, V_2O_5 and CeO_2 often present in diesel soot are for cordierite ceramics filter destructive. Hence zircon has been suggested as a suitable material for the production of ceramic diesel engines filters because not all the reactions between zircon and oxides were destructive [2,3]. The addition of $ZrSiO_4$ in the quantities of 2.5, 5, 7.5 and 10 wt.% to the commercial cordierite ceramic powder (the mixtures of talc, kaolinite, quartz and alumina) was monitored in order to determine effects on the densification of cordierite. Researchers found that addition of zircon above 2.5 wt.% had no further effect on the densification of cordierite–zircon composite [4].

The pre-ceramics cordierite mixtures of clay minerals kaolinite and talc were adjusted by adding vermiculite to fire the new forms of cordierite composites [5–7].

This work continues the preparation of various porous cordierite composites from the mixtures of clay minerals with unconventional yet using vermiculite [7]. The goal of the study was characterization of cordierite and cordierite–zircon composites sintered from different pre-ceramic clay mineral mixtures containing vermiculite and zirconium–vermiculite, respectively, with and without additives of MgO or Al_2O_3.

2. Experimental

The clay minerals mixtures, particle size fraction < 0.04 mm, were prepared as pre-ceramics mixtures from the kaolinite (K), talc (T) and vermiculite (V) in the oxide ratio close to the composition of cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$. Precursor of zircon in cordierite was zirconium vermiculite (Zr–V) prepared from V and zirconium salt solution via cation exchange. The structural formula of clay minerals that were used to the pre-ceramics mixtures was calculated from the results of the elemental analysis for K: $Si_2Al_2O_5(OH)_4$, V: $(Si_{3.13}Al_{0.73})(Mg_{2.53}Fe_{0.45}Al_{0.02})O_{10}(OH)_2\,Mg_{0.19}$, both minerals from Czech Republic, and for T: $Mg_3Si_4O_{10}(OH)_2$ from Egypt [5]. The content of

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mineral phases in the prepared mixtures was as follows: mixture named as A1 in wt.% is: K—20, T—30, V—30 and Al_2O_3—20; mixture B1 in wt.% is: K—50, V—50; mixture C1 in wt.% is: K—50, V—30 and MgO—20; mixture D1 in wt.% is: K—50, T—20, V—30. The corresponding mixtures named as A2, B2, C2 and D2 contained Zr–V instead of V. The powders mixtures were homogenized using ball milling for 15 min, then dried at 105 °C for 5 h to the constant weight and pressed into pellets at 30 MPa with a thickness (0.3 cm) to diameter (2 cm) ratio equal to 0.15. The pellets were sintered in an electric furnace with the rate of 5 °C/min up to 1000 °C and 2 °C/min up to sintering temperature 1300 °C, staying at that temperature for 1 h and the cooling rate of 1.5 °C/min.

The X-ray powder diffraction (XRD) patterns were taken on the diffractometer INEL (detector CPSD120, CuKα_1 radiation, Ge-monochromator) from samples in the rotation holder (35 kV, 20 mA). The *d* values and absolute intensities from the XRD patterns were input to the quantitative XRD phase analysis using program XQPA [8]. The models of the identified mineral phases were calculated from the structural data of cordierite [9], protoenstatite [10], $MgAl_2O_4$ spinel [11], forsterite [12] and zircon [13].

Morphology of porous composites was examined using SEM Philips XL 30. The samples were covered with Au/Pd conducting coats. The particle size and morphology of zircon were studied using a SEM (HITACHI SU6600 SEM) at 5.0 keV. The elemental composition was determined via electron dispersive spectroscopy (EDS).

The porosity of sintered composites was determined using the mercury intrusion porosimeter AutoPore IV 9500.

The hardness measurements were recorded using Zwick/Roell 2.5 N equipment hardness meter (Zwick GmbH & Co). The applied load was 98 N during 15 s. Each indent was imaged using laser scanning confocal microscope LEXT OLS 3100 (Olympus) to obtain accurate values of diagonals for calculation of Vicker's hardness.

3. Results and discussion

3.1. XRD analysis

The XRD quantitative mineral phase analysis of cordierite and cordierite–zircon composites in Table 1 demonstrates different contents of cordierite and other minerals, depending on the phase composition of pre-ceramics mixtures. Samples B1 and D1 were prepared from clay minerals in mixtures without the addition of Al_2O_3 or MgO and composite B1 was determined as cordierite with small admixture of enstatite (2 vol.%) as well as composite D1 was cordierite with small admixture of Mg–Al spinel (3 vol.%).

Cordierite samples A1 and C1 were sintered from the clay minerals with the addition of Al_2O_3 and MgO, respectively. XRD phase analysis showed that composites A1 and C1 had content of cordierite reduced to 70 and 67 vol.% in favor of enstatite and forsterite (about 20 vol.%), respectively, and Mg–Al spinel (10 vol.%).

Table 1
Cordierite and cordierite–zircon composites: XRD quantitative mineral phase analysis, porosity and hardness values.

	Minerals (vol.%)[a]					Porosity	Hardness
Samples	Cordierite	Enstatite	Forsterite	Spinel	Zircon	(%)	H_V[a](GPa)
A1	70(3)	20(4)	0	10(1)	0	26	0.98(0.10)
B1	98(1)	2(1)	0	0	0	13	4.41(1.00)
C1	67(5)	0	23(5)	10(5)	0	31	0.88(0.10)
D1	97(2)	0	0	3(1)	0	5	5.50(0.50)
A2	71(4)	12(4)	0	10(2)	7(2)	4	1.23(0.10)
B2	88(3)	0	0	0	12(2)	2	6.38(0.70)
C2	87(5)	0	13(2)	10(3)	10(2)	23	2.16(0.30)
D2	89(6)	0	0	3(2)	8(2)	5	5.60(0.60)

[a] Mean and standard deviation (in parentheses) of 5 measurements.

The XRD patterns (Fig. 1) of cordierite composites A1 and C1 show good agreement with the patterns calculated for the mixture of cordierite with 20 vol% of enstatite ($Cor_{80}En_{20}$), and 20 vol% of forsterite ($Cor_{80}Fo_{20}$), respectively, (Fig. 1a). The cordierite phase in the parent cordierite–zircon composites increased (Table 1). The highest content of $ZrSiO_4$ was in sample B2 since its pre-ceramic mixture contained the highest content of Zr–V. For evidence of the proper quantitative determination of zircon in cordierite (Table 1) the XRD patterns of cordierite–zircon composites A2, B2, C2 and D2 are compared with the corresponding models of cordierite with 5, 10 and 15 vol.% of zircon (the calculated patterns in Fig. 1b are marked as $Cor_{95}Z_5$, $Cor_{90}Z_{10}$, and $Cor_{85}Z_{15}$, respectively). According to the intensity proportion of diffraction (312) of cordierite and (200) of zircon in real samples the accuracy of quantitative phase calculation can be assumed.

3.2. Morphology of composites and zircon

Fig. 2 shows microstructures of cordierite–zircon samples A2, B2, C2 and D2 which were very similar to their parent cordierite samples A1, B1, C1, D1 (not shown here). Pores shape in A2 and C2 samples prepared from clay mineral mixtures and additives Al_2O_3 and MgO are different with comparison to pores shape in B2 and D2 samples formed from the clay mineral mixtures.

SEM micrographs revealed inhomogeneous distribution of zircon crystals on the cordierite matrix and their different size from 150 nm

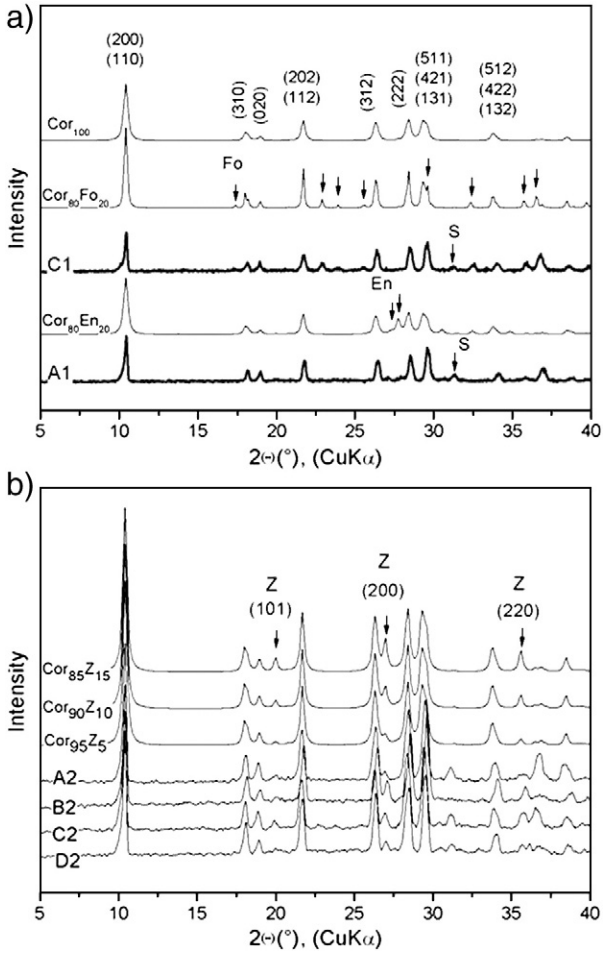

Fig. 1. XRD patterns of a) cordierites A1 and C1 and the calculated cordierite mixtures with 20 vol% of enstatite ($Cor_{80}En_{20}$) and forsterite ($Cor_{80}Fo_{20}$); b) cordierite–zircon composites A2, B2, C2 and D2 and the calculated models (marked as $Cor_{95}Z_5$, $Cor_{90}Z_{10}$, and $Cor_{85}Z_{15}$) of cordierite (Cor) with 5, 10 and 15 vol.% of zircon (Z).