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Cordierite ceramics from silicone resins containing nano-sized oxide particle fillers[☆]

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Abstract

Many silicates and alumino-silicates feature remarkable mechanical properties at high temperatures, low thermal expansion and high thermal shock resistance, optimum dielectric properties, etc. The poor interdiffusion, due to their characteristic partially covalent bonding however, greatly complicates the obtainment of dense and/or phase pure articles, by conventional sintering. The present paper concerns the realization of high-purity cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) components by direct thermal treatment in air of preceramic polymers embedding suitable nano-sized oxide particles. More precisely, a selection of silicone resins allowed the obtainment of both dense and highly porous bodies.

Keywords: A. Shaping; A. Powders: solid state reaction; B. Porosity; D. Cordierite

1. Introduction

Cordierite is a Mg-aluminosilicate with the general formula $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$. Its very low CTE (coefficient of thermal expansion, equal to $\sim 1.5 \times 10^{-6}$/K), good thermal stability, corrosion resistance and generally low price make this material one of the most used refractory materials for applications subjected to severe thermal gradients (for a maximum temperature generally not exceeding 1250 °C) [1]. Cordierite has also been so far the main ceramic for the realization of particulate filters for diesel engines [2], and finds also application in the catalytic converters field.

The most important synthesis route for cordierite ceramics is the high temperature reactive sintering of various combinations of different inorganic powders, such as oxides, hydroxides, clays, etc. [3]. Homogeneous and highly pure cordierite powders could be also synthesized by the sol–gel route [3,4], but the relatively high prices of the reagents and the solvents needed during the sol–gel process are generally not compatible with the inexpensive nature of the final ceramics.

The main aim of the present paper is to show the possibility of obtaining both dense and porous cordierite ceramics by the PDC (polymer derived ceramics) route. More precisely, oxide nano-sized particles were added to preceramic polymers, in the form of silicone resins, in analogy to recent experiments concerning silicates, alumino-silicates and SiAlONs [5]. Song et al. [6] previously followed a similar strategy, but used different fillers (i.e. talcum and alumina powder) and did not present data concerning the phase purity of the resulting ceramics. Unlike the paper by Song et al., our approach allowed to achieve remarkable phase purity, after optimization of the firing conditions. Moreover, we confirmed the distinctive potential of processing using preceramic polymers, i.e. the possibility of shaping in the polymeric state, with the development of particularly strong and homogeneous foams.

2. Experimental procedure

2.1. Preparation of nano-composite powders

The experiments were based on the use of two different polysiloxanes, MK and H62C (Silres MK and Silres H62C,

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Wacker–Chemie GmbH, Muchen, Germany), characterized by different physical and chemical properties. Silres MK is a solid methyl polysilsesquioxane resin, characterized by a 84 wt% SiO_2 yield after pyrolysis in air [7]. It can be thermally cross-linked through condensation reactions involving OH functional groups present inside its chemical structure. Silres H62C instead is a liquid polysiloxane, thermally cross-linkable without the formation of gaseous by-products, thanks to the presence of vinyl groups, characterized by a lower SiO_2 yield (approximately 58 wt%) [8].

Al_2O_3 nanopowder (Aeroxide Alu C, Evonik Industries AG, Essen, Germany, 13 nm average dimension, 100 m^2/g specific surface area) and MgO nanopowder (Inframat Advanced Materials, Manchester, CT, 30 nm average dimension, 30 m^2/g specific surface area) were used as nano-sized filler powders. The preceramic polymers were first dissolved in isopropyl alcohol by magnetic stirring, then Al_2O_3 and MgO powders were added, for an overall solid content of about 20%. The nanopowders were dispersed into the solvent/silicone solution in the stoichiometric proportions to yield pure cordierite. For calculation purposes, preceramic polymers were assumed to fully convert into amorphous SiO_2 upon thermal treatment in air. When both MK and H62C were used, their amount was calculated in order to obtain the same SiO_2 quantity from each polymer after pyrolysis, taking into account their ceramic yield (0.84 and 058 wt%, respectively). Resulting formulations are reported in Table 1. After magnetic stirring for 10 min, ultrasonication was applied for additional 10 min to reduce the size of the residual particles agglomerates, thus obtaining homogeneous and stable dispersions, later dried in oven at 60 °C overnight. The solid residue was finely pulverized in a mortar obtaining powders a few microns in size in which the silicone resin embedded the nano-sized fillers. The powders were heat treated in alumina crucibles in the 1000–1400 °C range for 1 h (10°/min heating rate) in air.

2.2. Preparation of dense samples

After manual grinding, composite powders were sieved through a 75 μm mesh. Stoichiometric formulations comprising MK and fillers (Table 1, Formulation A), or alternatively MK, H62C and fillers (Table 1, Formulation B), were used. When both MK and H62C were used, a partial cross-linking at 250 °C for 30 min was performed before the subsequent grinding step, because the mixture had a plastic behavior after drying, due to the fact that H62C is liquid at room temperature. Powders were then cold-pressed at 40 MPa in a cylindrical steel die, without using any binder, thus obtaining specimens with a diameter of 20 mm and thickness of approximately 2 mm. Pressed samples were finally heat treated in the 1100–1400 °C range for 1 h in air (10°/min heating rate).

Table 1
Composition of formulations used for the experiments.

Component	Formulation A (wt%)	Formulation B (wt%)
Al_2O_3	31.8	28.2
MgO	12.6	11.2
Silres MK	55.6	24.7
Silres H62C	–	35.9

2.3. Preparation of highly porous samples

PMMA microbeads were added as sacrificial fillers, in order produce highly porous components. Unlike in previous experiments with wollastonite-based materials [5] the microbeads were introduced directly in the polymer-based dispersion, after the addition of oxide nanoparticles. PMMA-containing powders, obtained by manual grinding of the residue from drying operation, were warm-pressed uniaxially at 40 MPa at 170 °C for 5 min, thus producing samples with a diameter of 40 mm and a thickness of approximately 5 mm. Before the final pyrolysis treatment, PMMA sacrificial micro-beads were removed at 300 °C for 2 h in air (1°/min heating rate).

2.4. Characterization

Differential thermal and thermo-gravimetric analysis (DTA/TG) were done up to 1500 °C in air (DTA/TGA, STA409, Netzsch GmbH, Selb, Germany).

Microstructural characterization of the samples was carried out by scanning electron microscopy (SEM; FEI Quanta 200 FEG, FEI Company, Eindhoven, The Netherlands) and density measurements by the Archimedes' method following the ASTM C 373 norm. The phase evolution was investigated by means of X-ray diffraction (XRD; Bruker AXS, D8 Advance, Karlsruhe, Germany) operating with CuKα radiation (0.15418 nm). The diffraction patterns were analyzed by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from the PDF-2 database (International Centre for Diffraction Data - ICDD, Newtown Square, PA, USA).

For dense samples, mechanical strength measurements were carried out using the ball on three balls (B3B) configuration (biaxial bending test – samples with a diameter of 17–18 mm; thickness of 1.1–1.2 mm; support radius of 4.6 mm) with the support of a Zwick/Roell Z005 machine (Zwick GmbH, Ulm Germany); highly porous samples were cut down to small components (approximately 5 mm × 5 mm × 5 mm) and subjected to uniaxial compression, with the support of an Instron 1121 UTM machine (Instron, Danvers, MA, USA).

3. Results and discussion

3.1. Cordierite synthesis

Mixtures of Silres MK, Al_2O_3 and MgO nanopowders were pyrolyzed in air in the 1000–1400 °C. In Fig. 1, the XRD analysis of the samples after heat treatment in the 1000–1400 °C temperature range are reported.

At lower temperature (1000 °C), the ceramic material is mostly XRD amorphous: the broad peak in the 18–26° range is mainly associated with the amorphous ceramic residue

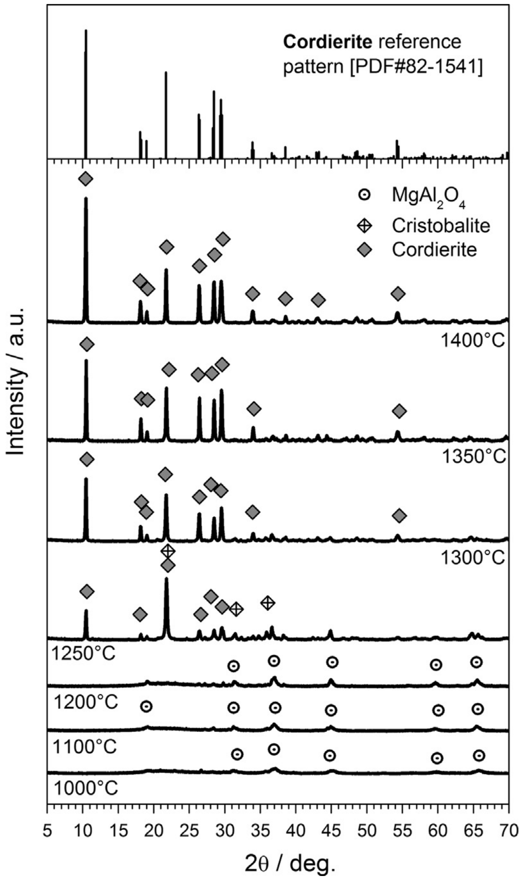

Fig. 1. XRD patterns of Silres MK filled with Al_2O_3 and MgO nanopowders and fired in the 1000–1400 °C range for 1 h (10°/min heating rate).

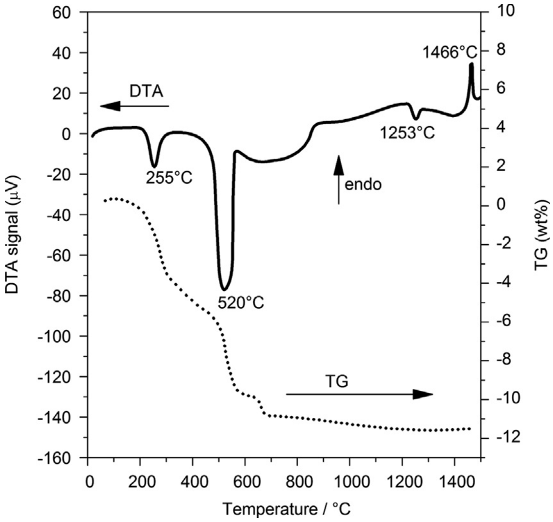

Fig. 2. DTA/TG curves for an $MK/Al_2O_3/MgO$ mixture fired in air.

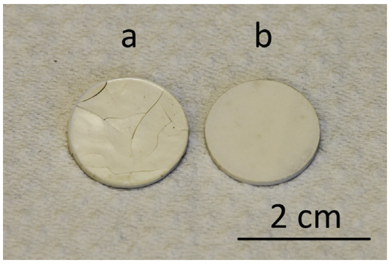

Fig. 3. (a) MK+fillers and (b) MK+H62C+fillers samples after pyrolysis at 1300 °C for 1 h.

deriving from the preceramic polymer; the presence of spinel crystals ($MgAl_2O_4$, PDF#86-2258) could also be observed. This phase likely forms because of the presence, in the final precursor powders, of local agglomerations of magnesia and alumina nanoparticles providing direct contact between them. In the 1100–1200 °C range, small quantities of Mg-silicates and Mg-aluminosilicates have also been observed, but the very low intensity of the peaks make their identification and the evaluation of their evolution not trivial. The presence of cordierite is clearly observed at 1250 °C, together with cristobalite from the amorphous silica residue present at lower temperature. The main diffraction peak of cristobalite (PDF#82-0512) is located at 21.8°, and it is superimposed to one of the main cordierite peaks. The nucleation of these two phases is in relation with the occurrence of an exothermic effect in the DTA curve, located at 1253 °C (see Fig. 2).

Cordierite seems to nucleate directly in the high-temperature α-form (PDF#82-1541), and the presence of intermediate μ-cordierite, a metastable high-quartz solid solution [9], was not observed, unlike in other works in literature where the presence of μ-cordierite was detected at lower temperature (approximately 1000 °C) [4,10–13]. A further increase in the treatment temperature (above 1300 °C) finally led to the virtually total elimination of the residual secondary crystalline phases (mainly silica) and cordierite became the only phase detectable for temperatures ≥1300 °C, as testified by the good matching of the experimental pattern with the theoretical one (in terms of position and relative proportion of peaks, see Fig. 1). These results are comparable with some previous observations made on sol–gel-derived cordierite [3], indicating that also with this approach a homogeneous distribution of the reactants at a quasi-molecular level can be obtained, owing to the nano-scale size of the filler powders. As previously observed in other works focusing on preceramic polymer containing fillers of high surface area (because of their small size) [5,14,15], the formation of the desired phase at low temperatures (comparable to what reported for sol–gel systems) was observed also for cordierite, due to the intimate mixing of the starting constituents.

3.2. Dense cordierite components

Monoliths realized with MK as the only silica source were found to be subjected to cracking upon heat treatment. When preceramic polymers are used, reactions such as cross-linking and the polymer-to-ceramic conversion imply the release of gases and a noticeable volume shrinkage, both potential sources of cracks. The substitution of part of MK with H62C was found to be fundamental for the obtainment of crack-free monoliths (see Fig. 3), especially considering the relatively high heating rate during pyrolysis (10°/min).

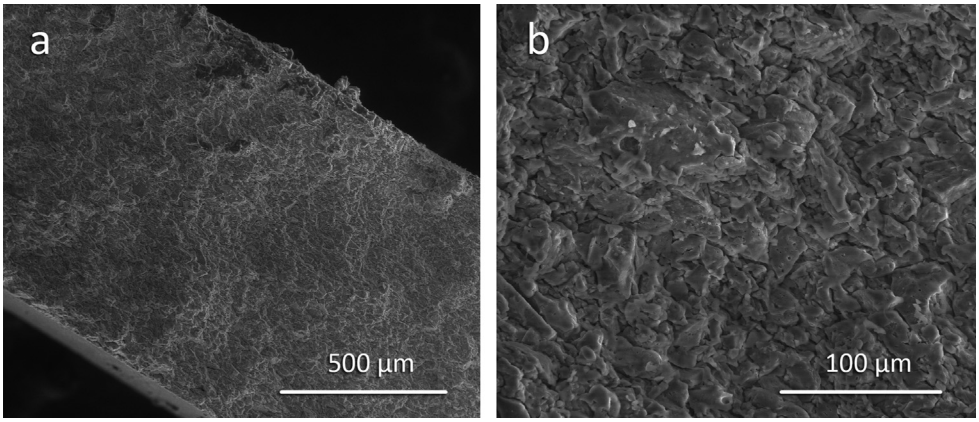

Fig. 4. (a) Low magnification and (b) high magnification SEM images of the fracture surface of a cordierite sample produced from a mixture of MK, H62C, Al_2O_3, and MgO nanopowders, after pyrolysis at 1300 °C for 1 h.

The reasons beneath the increase of mechanical consistency obtained by substituting part of MK by H62C remain unclear, although some contributing factors can be identified: (1) the partial substitution of MK for H62C lowers the gas release during polymer cross-linking (due to different cross-linking reactions occurring in the two polymers), thus decreasing the generation of cracks and pores that could further develop in the subsequent phases of the heat treatment, (2) the pre-curing step before powder compaction, which involves a certain degree of shrinkage that is consequently absent in the subsequent pyrolysis, (3) the different chemical characteristics of the polymeric precursors, which could generate a silica matrix with different features, e.g. network connectivity and number of defects, and thus with a different ability to relax structural rearrangements by viscous flow or diffusion processes, and (4) the residual and quite interconnected porosity (as can be observed in Fig. 4b), which could allow a more efficient and homogeneous elimination of gases during the pyrolysis step, without local pressure accumulation phenomena and the subsequent cracking generation that is typically observed in all PDCs.

SEM images of the fracture surface of a cordierite sample treated at 1350 °C are reported in Fig. 4. At a lower magnification level (Fig. 4a), a quite uniform structure could be observed, with no evidence for the presence of large defects, such as macro-cracks or macro-pores. At higher magnification (Fig. 4b), however, the ceramic material seems to be constituted by very dense and homogenous regions and by some micro-voids. The micro-voids appear both as residual porosity (with a mean pore size of 1 µm) within these regions (see Fig. 5) and as gaps between the dense areas (see detail in Fig. 5). The clear presence of gaps between areas with a dimension compatible to that of the original nano-composite powders, indicates that during warm pressing an insufficient viscous flow was achieved, leading to incomplete compaction at the green stage (as observed by Haug et al. [16]). The high load of nano-sized particle fillers as well as the pre-curing step could have contributed to hinder the viscous flow during the warm pressing.

Density measurements (reported in Table 2) were carried out only on samples heat treated at 1300 and 1400 °C, and a slight increase of density (passing from 2.01–2.15 g/cm^3) was observed changing the temperature from 1300 to 1400 °C. Density of samples treated at lower temperatures was not measured, because of their lower phase purity. Despite the presence of defects and residual porosity, biaxial strength values were in the order of 63 ± 7 MPa for a sample heat treated at 1400 °C. These values are comparable to analogous cordierite commercial products [17], with similar density values and obtained by standard powder processing routes, thus confirming the good potential of the presented methodology.

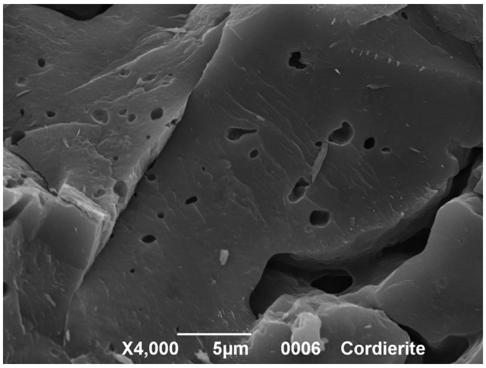

Fig. 5. High magnification detail of a cordierite sample produced from a mixture of MK, H62C, Al_2O_3 and MgO nanopowders, after pyrolysis at 1300 °C for 1 h.

Table 2
Bulk and relative density values for cordierite monoliths fired at 1300 and 1400 °C for 1 h (a theoretical density of cordierite equal to 2.66 g/cm^3 [18] was considered to calculate relative density values).

Treatment temperature (1 h)	Bulk density (g/cm^3)	Relative density (%)
1300 °C	2.01 ± 0.01	76
1400 °C	2.15 ± 0.01	81

3.3. Highly porous cordierite components

Different concentrations of PMMA micro-beads (70, 75 and 80 wt% relative to the weight of the starting, un-pyrolyzed mixture) were used, in order to generate a high volume of pores. We aimed at fabricating samples characterized by a good combination of lightness and thermal insulation, while maintaining a sufficient mechanical strength for potential applications. Contrarily to what observed for low-porosity cordierite samples, the use of Silres MK as the only silica source allowed for the realization of porous cordierite samples with a much more limited presence of cracks. This is in agreement with the general observation that porous PDCs (realized by different methodologies such as the introduction of sacrificial filler, foaming agents or by self-foaming reactions [19,20]) are not affected by extensive cracking after pyrolysis, as instead observed with compact counterparts, since the limited thickness of the walls enables a better release of the gaseous by-products without a local accumulation of pressure that would eventually generate cracks.

In general, a quite homogeneous pores distribution was achieved (as could be observed for two different samples in Fig. 6), with a mean cell size of approximately 50 μm, which is obviously connected to the size of the PMMA sacrificial fillers. A change in the interconnectivity among the cells seems to take place passing from 70 to 80 wt% PMMA, from a basically closed porosity (with 70 wt% PMMA, where no cell windows are present in the pores walls), to a more open porosity (with 80 wt% PMMA, where several windows in the cell walls are clearly noticeable).

Bulk density, relative density and crushing strength data for the highly porous samples are reported in Table 3. Samples prepared using 80 wt% PMMA exhibited very poor mechanical properties, so practical applications are limited. However, samples prepared using 70 wt% PMMA showed better mechanical properties, whereas samples prepared using the 75 wt% concentration represented an optimal compromise between low relative density, some degree of interconnectivity and sufficient mechanical strength to be of interest for practical applications.

The good mechanical properties can be justified by the homogeneous distribution of the pores (see Fig. 7a) and the characteristics of the struts, which are dense and virtually defect free (see Fig. 7b). Moreover, cordierite grains have a mean dimension of the order of ~1 μm, and in some areas the struts walls appear to be just one-grain thick (see Fig. 7c).

If compared to other experiments previously reported in the literature [6] and relative to the fabrication of cordierite foams with similar density and cell size, the micro-structural homogeneity, continuity and integrity (especially at high-porosity levels) of the foams produced by our approach are quite higher. The higher crushing strength of the 70 wt% PMMA foams (7.1 MPa with relative density = 22.6%, vs. 4.8 MPa with relative density = 26% for the samples of Ref. [6]) could be related to the high crystallinity present in our samples, besides the influence of the foam morphology.

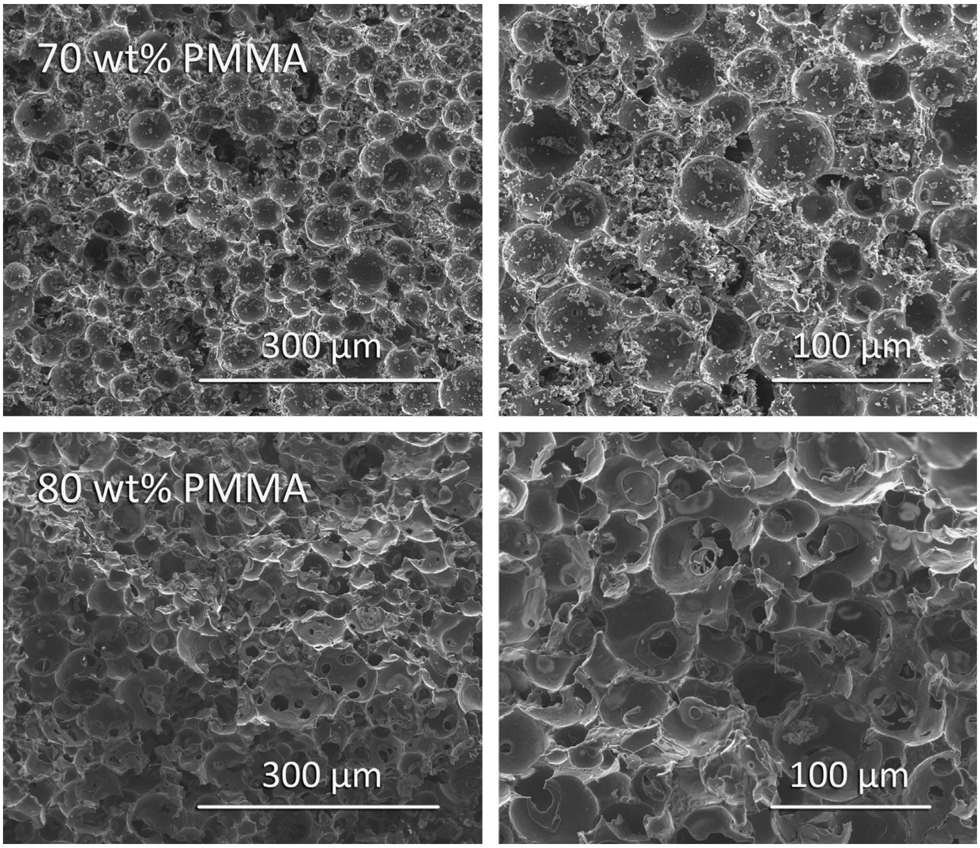

Fig. 6. SEM images of highly porous cordierite samples produced by using PMMA micro-beads as sacrificial fillers, after pyrolysis at 1300 °C for 1 h [70 wt% (top) and 80 wt% (bottom) are referring to the PMMA content in the starting mixture before firing].

Table 3
Bulk density, relative density and crushing strength values for highly porous cordierite monoliths 80, 75 and 70 wt% PMMA, fired at 1300 °C for 1 h (a theoretical density of cordierite equal to 2.66 g/cm^3 [18] was considered to calculate relative density).

Sample	80 wt% PMMA	75 wt% PMMA	70 wt% PMMA
Bulk density (g/cm^3)	0.37 ± 0.01	0.49 ± 0.01	0.60 ± 0.01
Relative density (%)	14.0	18.6	22.6
Crushing strength (MPa)	0.38 ± 0.02	2.8 ± 0.4	7.1 ± 1.6

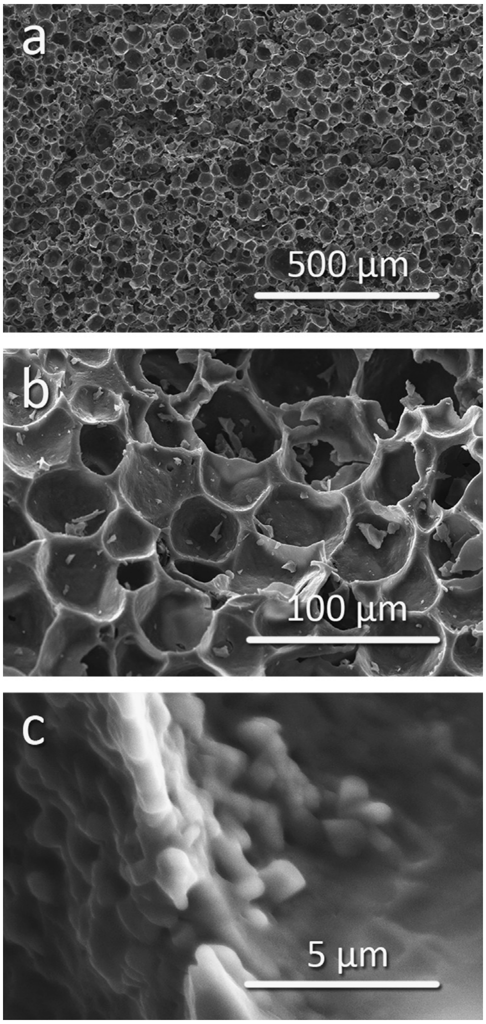

Fig. 7. Microstructural details of a 75 wt% PMMA cordierite foam: (a) low magnification, (b) high magnification, and (c) cell wall detail.

The ceramic components discussed in this paper are only some examples of what can be produced following the proposed processing approach. A wide variety of samples with different combinations of thermal and mechanical properties could be fabricated by common plastic-forming technologies, exploiting the presence of the preceramic polymer. These first studies concerning the synthesis of the desired ceramic phase, the optimization of the heat treatment and simple shaping into low or high porosity components will be followed by the investigation of the use of other forming technologies of industrial interest (such as extrusion, injection molding or fused deposition), in analogy to similar experiments conducted with calcium silicate (wollastonite) ceramics [5,8].

4. Conclusions

The successful synthesis and shaping of cordierite ceramics starting from mixtures of preceramic polymers and nano-sized fillers have been here presented. XRD results confirmed the possibility of producing, at low temperature, highly pure cordierite samples, in which no secondary phases or impurities were present. The nucleation of cordierite was observed for temperatures comparable to those observed for analogous sol–gel derived systems, thus confirming the enhanced nucleation kinetic and reactivity achievable by combining preceramic polymers and fillers with high specific surface area. The realization of monoliths with very different levels of porosity (ranging from 14 to 81 vol%) has been demonstrated. Near-net-shape samples with low residual porosity showed a relative density of approximately 80%, with mechanical properties comparable to analogous commercial products. Highly porous samples were produced by the addition of sacrificial fillers (PMMA micro-beads), which enabled the realization of monoliths with very low relative density (down to 14 vol%) and with a highly controllable size, distribution, amount and type (open or closed) of porosity.

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