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Durability of cordierite honeycomb structure for automotive emissions control[1]

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Abstract

Ceramic (cordierite) honeycomb structures are employed in the automotive industry for trapping and incineration of particulate material from the exhaust gases of diesel-powered cars. The most diffuse pollutants present in the particulates are sodium, lead, iron, calcium, zinc and vanadium: they can react with cordierite during regeneration of the filter.

In this paper, the short-term interaction of these pollutants as oxides with cordierite filter was studied to examine the consequences on the ceramic characteristics, using differential dilatometry, coupled to X-ray diffraction (XRD) and scanning electron microscopy (SEM).

These investigations demonstrate that pollutant ions diffuse into the cordierite lattice, modifying its thermal expansion behaviour, often leading to surface etching and formation of new phases. Some of these new phases present a thermal expansion coefficient that is higher than that of pure cordierite one: different local dimensional variations in the ceramic structure lead to the appearance of microcracks. Sodium and lead oxide are the pollutants that most affect the lifetime of cordierite filters.

INTRODUCTION

Ceramic honeycomb structures have been employed in the automotive industry for the last 15 years for the trapping and incineration of particulate material from the exhaust gases of diesel-powered cars [1]. The ceramic material of which these structures are made is cordierite ($Mg_2Al_4Si_5O_{18}$), a hexagonal framework silicate with zeolite-like channels parallel to the *c*-axis.

The structure walls are porous, with porosity ranging from 30% to 50%, and the mean pore size ranging from 2 to 100 μm. The particulate-laden diesel exhaust must flow through the porous walls and in so doing the particulate material is trapped in the pores and the surfaces of open channels.

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Many papers have discussed the nature and dependence of both the mechanical and thermal stresses in the ceramic on its geometry, properties and operating conditions. However, information concerning the problems arising during the regeneration of the filter, when carbon particles have to be burned out to avoid unacceptable counterpressure in the engine, are lacking. Thermal stresses due to the local exothermicity (it is possible to reach temperatures of about 1000°C) of the oxidative reactions may generate cracks in the filter; in addition some problems derive from pollutants emitted from the engine that may react with cordierite, making holes in the channel walls and leading to modifications in its properties.

In this paper, the short-term interaction of some pollutants with cordierite filters is studied in order to examine the effects on the ceramic characteristics.

EXPERIMENTAL

Cordierite honeycomb filter made by Corning Glass Works, USA was studied; this trap has a square-shaped cell geometry with a wall thickness of 0.63 mm and a porosity of about 50%, with a mean pore size of 32 μm. Cordierite powder provided by Baikowsky, Germany was also studied for reference, because it is more pure.

Na_2CO_3 (as Na_2O source), CaO, ZnO, PbO, Fe_2O_3 and V_2O_5 (C. Erba, Italy) were used to simulate the pollutants present in the particulate: sodium and lead derive from accidentally contaminated fuel, iron is released from the engine or exhaust pipes as abraded particles or rust, calcium and zinc derive from lubricant oil, vanadium from the fuel or possibly added as a catalyst assisting particulate combustion.

To investigate the interaction between cordierite and pollutants, samples of the filter (6 mm × 6 mm × 25 mm) were cut in a radial direction. The samples were placed in alcoholic suspensions of the different oxides to obtain a weight increase of 10% ± 1 after drying at 100°C. The purpose of this was to deposit oxide particles on the surface and into the filter pores to simulate operational conditions.

Differential dilatometry (Netzsch 402 ED apparatus), using an undoped filter sample as reference and with a heating rate of 10°C min^{-1}, was performed up to 1000°C on the samples doped with the oxides to verify the influence of the pollutants on the thermal expansion of cordierite.

After dilatometric measurements and after a thermal treatment at 1000°C for 60 min, the morphologies of the etched samples were investigated by scanning electron microscope (Hitachi S-2300 apparatus).

To investigate new phases produced by the ceramic–oxide reaction, compacts of carefully dry-mixed Baikowsky cordierite and the different oxides (50% by weight) were made. One part of these compacts was submitted to the same thermal cycle as the samples examined by the dilatometer; another part was heated at 1000°C for 60 min. After heat treatments, all the compacts were milled and analysed by X-ray diffractometry (Philips PW 1710 apparatus, Cu Kα radiation).

RESULTS AND DISCUSSION

When the cordierite filter is doped with sodium carbonate (Fig. 1), a large expansion takes place at about 860°C. Changing the dopant (for example, using sodium acetate), yielded the same effect: the anion has no influence on the expansion. After heat treatment, the sample appears expanded. Lachman et al. [2] also found a damaging effect on the thermal expansion of extruded cordierite doped with alkalis.

In contrast, the heating of the samples containing calcium, zinc, lead and vanadium oxides, leads to slight shrinkage beginning at about 300°C; at room temperature, the samples remain shrunk.

The behaviour of cordierite is only slightly influenced by iron: a shrinkage takes place at about 700°C, but a small expansion during cooling compensates the shrinkage.

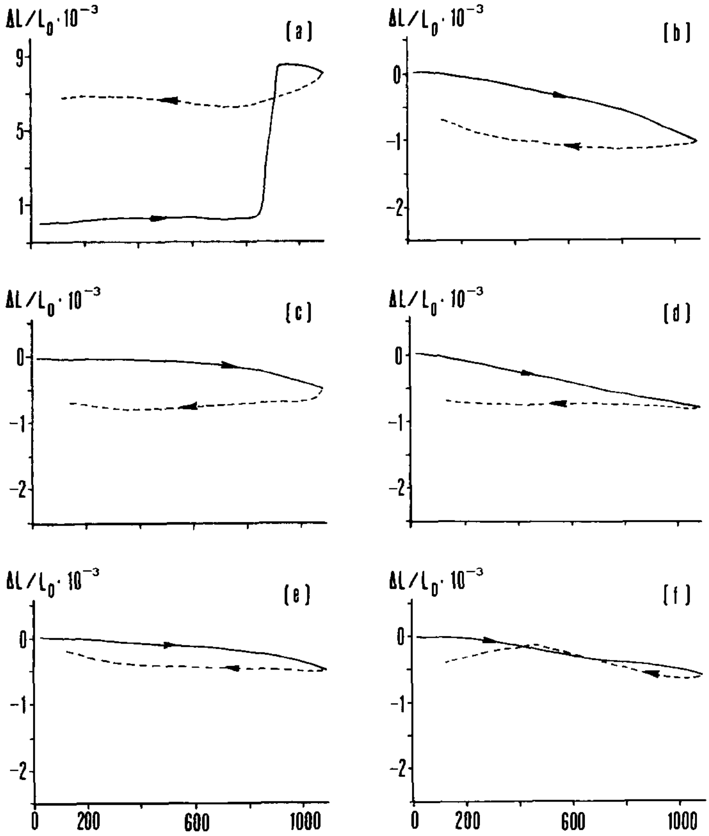

Fig. 1. Differential dilatometric curves of cordierite filter polluted by (a) Na_2CO_3; (b) CaO; (c) ZnO; (d) PbO; (e) Fe_2O_3; (f) V_2O_5. Temperatures are in °C.

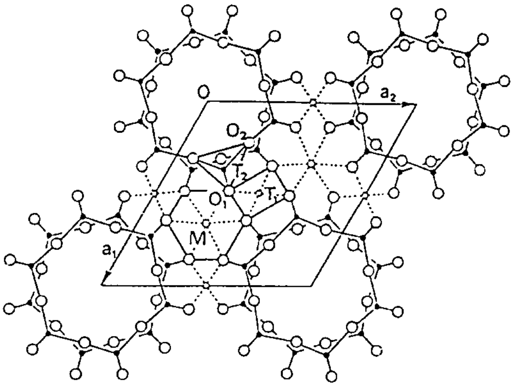

Fig. 2. Projection along the *c*-axis of the hexagonal cordierite. The five atoms in the asymmetric unit — T_1, T_2, M, O_1 and O_2 — are shown together with the three basic polyhedra, T_2, T_1 and M, from which the structure is built. Each tetrahedron T_1 shares two edges with adjacent M octahedra. Each M shares three edges with adjacent T_1s. Origin is at O. (Predecki et al. [4].)

To explain the thermal behaviour of doped cordierites, it is necessary to remember that this framework silicate presents a highly anisotropic expansion when heated. This anisotropy results in an expansion along the *a*-axis and an initial contraction along the *c*-axis; thus cordierite bodies can achieve near-zero bulk expansion up to 400°C [3].

According to Hochella and Brown [3] and Predecki et al. [4], the thermal behaviour of pure cordierite crystals is due to either expansion of bond length or to changes in bond angle. The positive *a*-axis expansion results from M–O bond expansion and an associated decreasing torsional distortion of the T_1 tetrahedra, with increasing temperature; the shrinkage along the *c*-axis results from increasing distortion of the T_2 tetrahedra and from coupled distortion of T_1/M tetrahedra/octahedra with increasing temperature (Fig. 2).

From X-ray diffraction patterns of the mixtures of cordierite and oxides submitted to the same thermal cycle as the samples examined by dilatometer, it appears that the (100) and (002) peaks of the doped cordierites are displaced relative to those of pure cordierite, and that their intensities are changed. Changes in diffracted intensities and in expansion coefficients reflect, in general, the adaptation of the structure to compositional change. Following Hochella and Brown [3] and Predecki et al. [4], we assume that the doping ions increase distortion of the T_2 tetrahedra and of the T_1/M tetrahedra/octaedra along the *c*-axis and/or limit expansion of the M–O bonds and increase torsional distortion of the T_1 tetrahedra along the *a*-axis.

To explain the large expansion of Na-doped cordierite, it is also necessary to note not only that its pattern presents the displacement of (100) and (002) peaks of the cordierite, but also that the composition of this

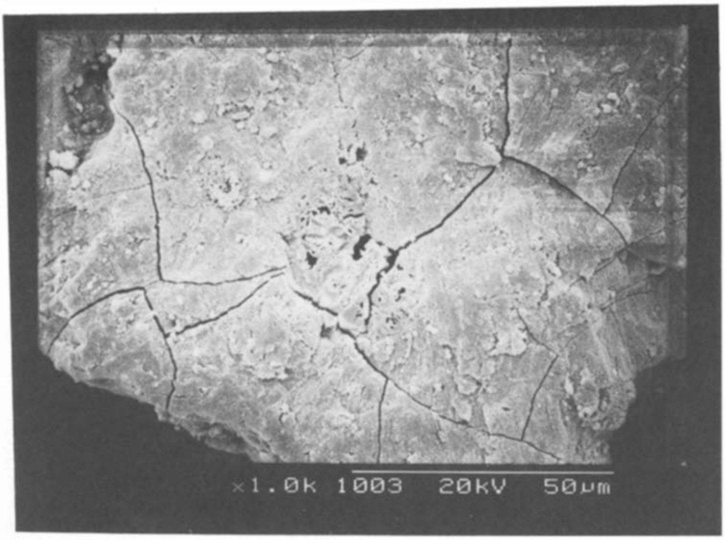

Fig. 3. Scanning electron micrograph of filter microstructure after dilatometry: Na-cordierite.

silicate approaches the silicoaluminate $NaAlSiO_4$. The high expansion presented by this sample, at about 860°C, is due to the formation of this second phase.

If the dilatometric test is repeated on the same sample, it is possible to observe a large expansion, once again at 860°C: this confirms that this new phase is responsible for the expansion.

Figures 3 and 4 present the change in microstructure resulting from the interaction between the oxides and samples of cordierite filter. As shown in

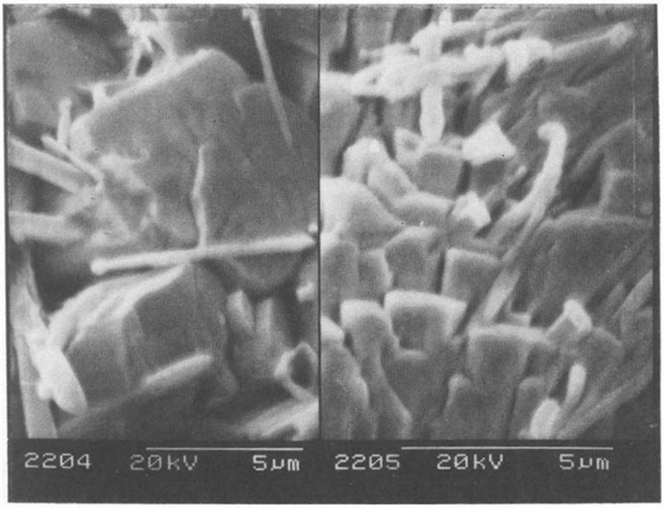

Fig. 4. Scanning electron micrograph of filter microstructure after 60 min at 1000°C: V-cordierite.

TABLE 1

Phases yielded by the reaction between cordierite + oxides after 1 h at 1000°C

Oxide	Reaction products
Na_2O	$2Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ (h); $Na_2O \cdot MgO \cdot SiO_2$ (h)
CaO	$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ (m); $2CaO \cdot Al_2O_3 \cdot SiO_2$ (m); $CaO \cdot MgO \cdot SiO_2$ (s); CaO (m)
ZnO	$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ (h); $2ZnO \cdot SiO_2$ (h); $MgO \cdot Al_2O_3$ (h); ZnO (h)
PbO	$PbO \cdot Al_2O_3 \cdot 2SiO_2$ (h); $MgO \cdot Al_2O_3 \cdot 3SiO_2$ (m)
Fe_2O_3	$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ (h); Fe_2O_3 (h)
V_2O_5	$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ (m); $3Al_2O_3 \cdot 2SiO_2$ (s); α-SiO_2 (crystobalite) (h); $MgO \cdot V_2O_5$ (s); V_2O_5 (m)

Key: (h) = high, (m) = medium, (s) = small content.

Fig. 3, sodium interacts with cordierite giving cracks as a consequence of the formation of Na-silicoaluminate and of the different thermal expansion behaviour of this new phase and the cordierite matrix. The presence of lead leads to surface etching; the other oxides do not give any visible modification.

If the thermal treatment at 1000°C is prolonged for 60 min, sodium produces bigger cracks, and zinc, lead and vanadium (Fig. 4) etch the cordierite leading to the formation of new phases; no visible modifications appear for samples doped with the remaining oxides.

X-ray analysis of the compacts treated at 1000°C for 60 min confirmed the presence of new phases (Table 1). Table 1 indicates that sodium and lead are the most harmful pollutants because they completely destroy the cordierite. Iron, at the allowed level of operating conditions, seems to give only a solid solution; the other pollutants react partially with cordierite to produce new phases. Some of the new phases formed, e.g. sodium silicoaluminate [3], willemite [5], spinel [5], mullite [6] and α-cristobalite [7], have expansion coefficients that are higher than that of cordierite.

The durability of cordierite ceramics may be strongly affected by this difference in expansion coefficients. In fact, during filter regeneration (when the temperature can reach about 1000°C), if a pollutant particle is present on the trap wall, zones of low expansion coefficient (pure cordierite) may be formed close to zones of higher expansion coefficient (polluted cordierite), leading to the appearance of microcracks due to the dimensional variations.

CONCLUSIONS

Investigations of the short-term interaction between cordierite and single pollutant oxides have demonstrated the following points.

Pollutant ions diffuse in the cordierite lattice modifying its thermal expansion behaviour.

In general, pollutants also lead to surface etching and the formation of new phases, some of which have thermal expansion coefficients that are higher than that of pure cordierite. Thus during filter regeneration, when the temperature may reach about 1000°C, different dimensional variations in the ceramic body may be produced locally and microcracks appear.

Sodium and lead oxides seem to be the most damaging pollutants, because they can completely destroy the cordierite structure.

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