Journal of the European Ceramic Society **13** (1994) 129-134

Deterioration of Cordierite Honeycomb Structure for Diesel Emissions Control

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(Received 25 June 1993; revised version received 13 October 1993; accepted 2 November 1993)

Abstract

The durability of cordierite honeycomb structure for automotive emissions control is strongly affected by the presence of some pollutants on the trap walls during the high temperature step of filter regeneration.

The short term interaction between cordierite and some single pollutant oxides (Na_2O*,* CaO*,* ZnO*,* PbO*,* Fe_2O_3*,* V_2O_5*) has been investigated by differential dilatometry, XRD, IR spectroscopy and SEM.*

There is evidence that the pollutant ions diffuse into the cordierite lattice. The formation of new phases and surface etching have often been observed; the appearance of new phases having a thermal expansion coefficient different to that of the pure cordierite is responsible of a diffuse microcracking, particularly in the sample polluted by sodium oxide.

At 900°C all the pollutants except Fe_2O_3 *strongly etch the cordierite; particularly dangerous is the presence of sodium or lead oxides which are able to completely destroy the cordierite structure.*

Die Bestandigkeit der zellenförmigen Struktur von Cordierit Filtern, die fur die Kontrolle der Abgase von Vergasermotoren verwendet werden, ist von der Gegenwart verschiedener Verunreinigungen beeinflußt, welche sich an den Wanden des Filters absetzen und mit ihnen bei den hohen Temperaturen der Regenerierung des Filters reagiren.

Die kurzfristige Wechselwirkung zwischen Cordierit und einphasigen Verunreinigungen (Na_2O*,* CaO*,* ZnO*,* PbO*,* Fe_2O_3*,* V_2O_5*) wurde durch Differenzialdehnungsmessung, Infrarotspektroskopie und Rasterelektronenmikroskopie untersucht.*

Die Untersuchung zeigt vor allem die Oberflächen Angriffserscheinungen des Filters, aber auch die Diffusion der Verunreinigungsione in das Gitter des reinen Cordierit und die Bildung neuer Kristallinphasen. Nachdem die letzteren einen anderen Warmeausdehnungskoeffizent haben als der Cordierit sind sie fur die verbreiteten Mikrorisse verantwortlich, dies wird ganz besonders deutlich bei Na_2O *verunreinigten Strukturen.*

Es wurde beobachtet, daß alle Verunreiniger außer Fe_2O_3 *von 900°C an den Cordierit mit Sicherheit angreifen. Die gefahrlichsten Verunreiniger sind jedoch* Na_2O *und* PbO*, weil sie zu vollkommenen Zerstorung der Cordieritstruktur führen.*

La durabilité de la structure à nid d'abeille à base de cordiérite utilisée pour le contrôle des émissions automobiles est affectée par la présence sur les parois du filtre des différents polluants, pendant les cycles thérmiques de régénération à haute température.

L'interaction à court terme entre la cordiérite et chaque polluant (Na_2O*,* CaO*,* ZnO*,* PbO*,* Fe_2O_3*,* V_2O_5*) a été étudiée par dilatomètrie differentielle, diffraction des rayons X, spectroscopie IR et MEB.*

La diffusion des ions polluants dans le réseau de la cordiérite a été mise en évidence; la formation de phases nouvelles et phénomènes d'attaque superficielle ont été observés. Les nouvelles phases ayant un coefficient de dilatation thermique different de la cordiérite pure sont responsable de la microfissuration diffuse, surtout evidente dans l'échantillon pollué par l'oxyde de sodium.

A l'exception du Fe_2O_3*, à partir de 900°C, tous les polluants attaquent fortement la cordiérite; particulièrement dangereux sont l'oxyde de sodium et l'oxyde de plomb, qui détruisent completement la structure de la cordierite.*

1 Introduction

Cordierite honeycomb structures have been widely employed in the automotive industry in the last 15 years.[1,2] They have performed as catalytic converters for hydrocarbons, carbon monoxide and nitrous oxides emissions of gasoline-powered cars and also as traps and incinerators for particulate material from the exhaust gases of diesel-powered cars.[1-5]

In this last application, the durability and efficiency of the ceramic structure may be strongly affected by the interaction with the pollutants emitted from the engine: at the high temperatures sometimes reached during filter regeneration (about 1000°C),[6] the pollutants may react with the cordierite, leading to noxious modification of the filter properties.

In a previous work[7] some preliminary results on the interaction between single pollutants and cordierite were reported. In this paper the deterioration of the cordierite honeycomb structure due to the new phases formation and local differential dimensional variations was investigated. The low temperature limits at which the damage becomes evident were specified.

2 Experimental

Cordierite (indialite) honeycomb filter (type EX 60 100/25, Corning Glass Works, USA) was used; this trap has a square shape 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 (indialite) powder (Baikowsky, Germany) was also investigated as reference as it is purer. Na_2CO_3 (as Na_2O source), CaO, ZnO, PbO, Fe_2O_3 and V_2O_5 (C. Erba, Italy) were used to simulate pollutants present in the particulate.[7]

To investigate the interaction between cordierite and pollutants and its influence on the thermal expansion, mixtures of cordierite powder and oxides (ratio 1:1 by weight) were pressed at 400 MPa to obtain bars of 6 mm × 6 mm × 10 mm. This weight ratio (1:1) was chosen to simulate the real conditions in use when a local superficial contact between a pollutant particle and the filter wall takes place.

Samples of the filter (6 mm × 6 mm × 25 mm) were also cut in the axial direction. The samples were plunged in alcoholic suspensions of different oxides to obtain a weight increase of 10% ± 1 after drying at 100°C. In this way oxide particles were deposited on the surface and into the pores of the cordierite filter to simulate operative conditions. The value of 10% by weight of pollutants was chosen on the ground of statistics (Giachello, A., pers. commun., 1991) of the pollutant level in filters after long-term use.

Differential dilatometry experiments (Netzsch 402 ED apparatus, using alumina standard bar as reference for the mixtures cordierite–oxide and an undoped filter sample as reference for doped filter samples) up to 1000°C with a heating rate of 10°C/min were performed. To investigate new phases produced by ceramic-oxide reaction, compacts of carefully dry-mixed Baikowsky cordierite and different oxides (ratio 1:1 by weight) were made. These compacts were treated in air at temperatures ranging from 500°C to 1000°C and held at each temperature for 5 min (heating rate of 10°C/min). After heat treatment, all the compacts were milled and studied by X ray diffractometry (Philips PW 1710 apparatus, CuK_α radiation) and by IR analysis (Jasco DS-702 G apparatus). The morphologies of

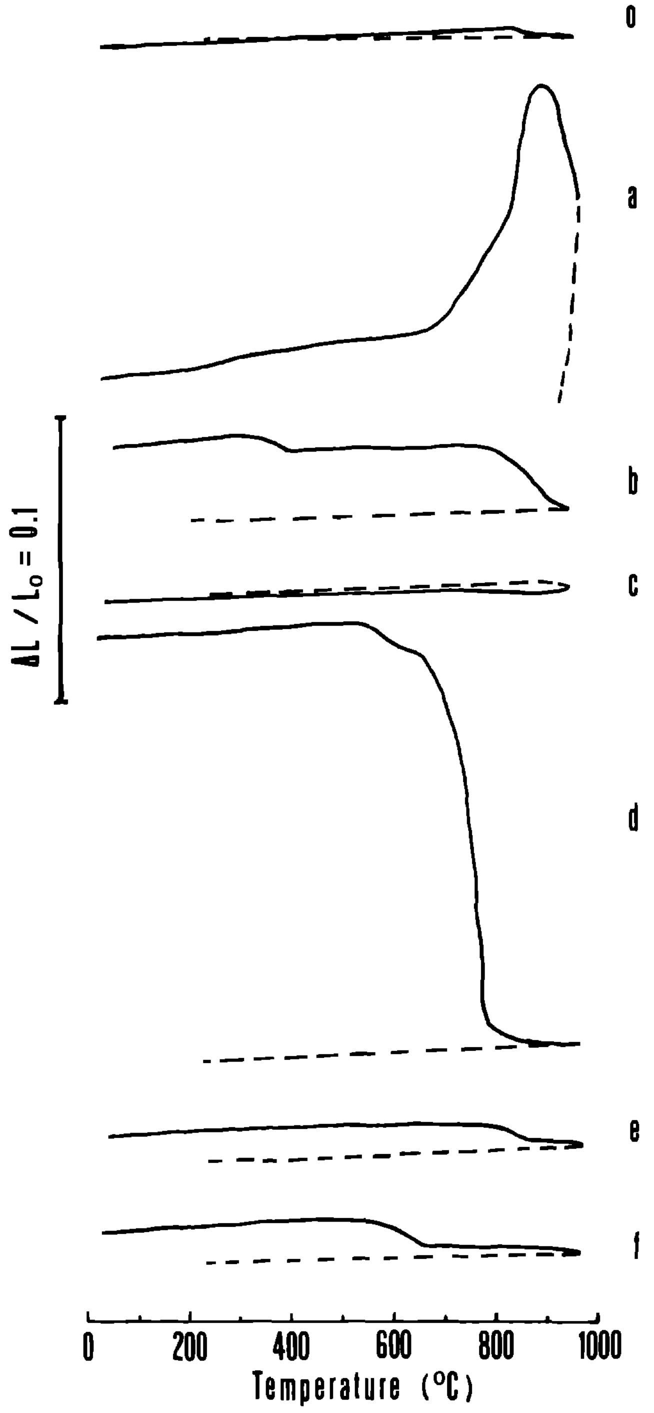


Fig. 1. Differential dilatometric curves of pure cordierite and cordierite oxide bars (o) Pure cordierite, (a) Na_2CO_3, (b) CaO (c) ZnO, (d) PbO, (e) Fe_2O_3, (f) V_2O_5 (——) Heating and (- - - -) cooling curves

the etched samples were investigated by scanning electron microscopy (Hitachi S2300 apparatus).

3 Results and Discussion

The dilatometric behaviour of cordierite-oxide bars compared to that of pure cordierite is presented in Fig. 1. The cordierite-$NaCO_3$ sample (Fig. 1(a)) showed a large expansion, starting at about 700°C and with a maximum at 900°C, at higher temperatures and during cooling, a large shrinkage was detected. This behaviour can be ascribed to new phase formation. The cooling curve stops at about 900°C because the detection limit is overcome. The sample containing cordierite and CaO (Fig. 1(b)) shrank at 400°C and 800°C probably because of the presence of $Ca(OH)_2$ and $CaCO_3$, detected by XRD. The cordierite-ZnO bar (Fig. 1(c)) did not present any evident dimensional change. The cordierite-PbO specimen (Fig. 1(d)) showed a large shrinkage starting at about 600°C, after cooling the bar was shrunk. The cordierite-Fe_2O_3 (Fig. 1(e)) and cordierite V_2O_5 (Fig. 1(f)) samples presented only little shrinkages beginning at about 800°C and 600°C, respectively.

The dilatometric curve of pure cordierite (Fig. 1(g)) shows a little shrinkage at 840°C due to the starting of sintering phenomena. In the case of the mixtures with V_2O_5 or PbO, the sintering starts at lower temperatures and shrinkage becomes more evident, probably because of their low melting temperatures and the new phase formation. When Fe_2O_3 is present, only the shrinkage is modified and becomes more noticeable.

The dilatometric behaviour of cordierite filter bars doped with the different oxides is presented in Fig. 2. When a cordierite filter is doped with sodium carbonate (Fig. 2(a)), a large expansion takes place at about 860°C, changing the dopant (for example, using sodium acetate as precursor of Na_2O), a similar effect was obtained, the influence of the anion appears to be negligible. After heat treatment the sample remained expanded: also Lachman *et al*[4] reported a deleterious effect on thermal expansion of extruded cordierite when doped with alkalis.

In contrast, during heating, the samples containing calcium, zinc, lead and iron oxides (Fig. 2(b)–(e), respectively) present a little shrinkage and, at room temperature, the samples appear shrunk.

The cordierite dilatometric behaviour is weakly influenced by vanadium oxide (Fig. 2(f)) the

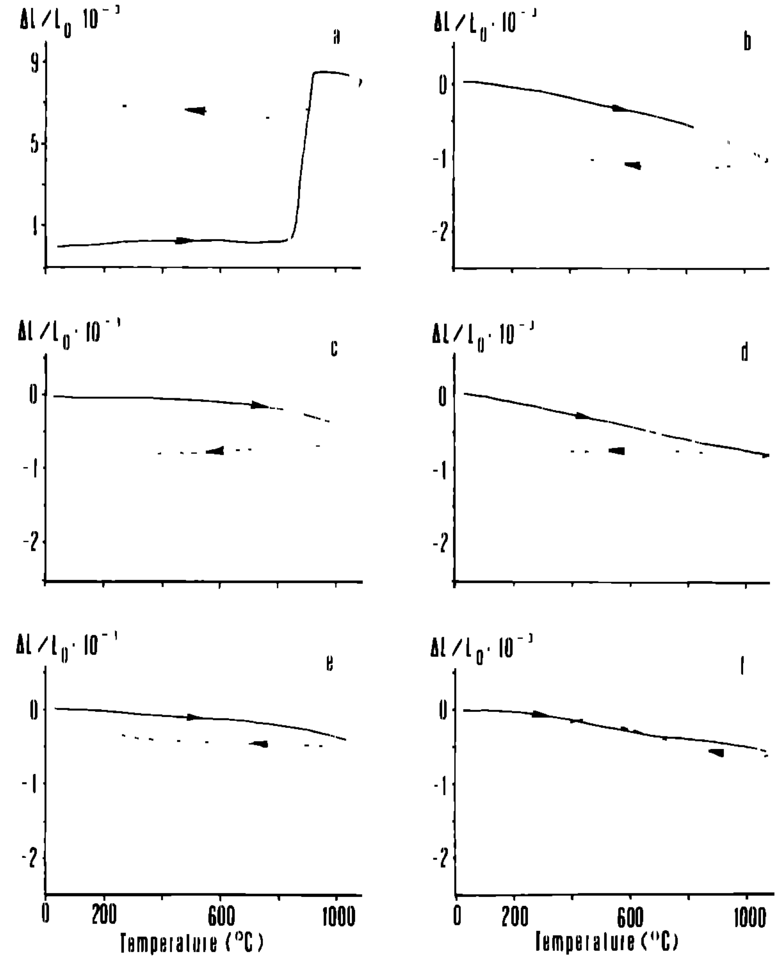


Fig. 2. Differential dilatometric curves of cordierite filter polluted by (a) Na_2CO_3, (b) CaO, (c) ZnO (d) PbO (e) Fe_2O_3 (f) V_2O_5, (——) Heating and (- - - -) cooling curves

Table 1. X Ray diffraction results, principal phases formed by the reaction between cordierite and oxides as a function of temperature (held at each temperature for 5 min)

Oxide	*Temperature (°C)*				
	600	*700*	*800*	*900*	*1000*
Na_2O	Cordierite (h) Na_2CO_3 (h) $Na_2Al_2SiO_6$ (l)	Cordierite (l) Na_2CO_3 (h) $Na_2Al_2SiO_6$ (l) Mg_2SiO_4 (l)	Na_2CO_3 (l) $Na_4Mg_2Si_3O_{10}$ (h)	$Na_4Mg_2Si_3O_{10}$ (h)	$Na_4Mg_2Si_3O_{10}$ (h) $NaAlO_2$ (l)
CaO	Cordierite (h) CaO (h) $CaCO_3$ (l)	Cordierite (h) CaO (h) $CaCO_3$ (l)	Cordierite (h) CaO (h) $CaCO_3$ (l)	Cordierite (l) CaO (h) Melilite (l)	Cordierite (l) CaO (h) Melilite (m)
ZnO	Cordierite (h) ZnO (h)	Cordierite (h) ZnO (h)	Cordierite (h) ZnO (h)	Cordierite (h) ZnO (h)	Cordierite (m) ZnO (h) Zn_2SiO_4 (m) $MgAl_2O_4$ (l)
PbO	Cordierite (h) PbO (h) Pb_2SiO_4 (l)	Cordierite (m) Pb_2SiO_4 (h) $PbAl_2SiO_6$ (m)	Cordierite (m) $PbAl_2SiO_6$ (m)	$PbAl_2SiO_6$ (h) $PbAl_2Si_2O_8$ (h)	$PbAl_2SiO_6$ (h) $PbAl_2Si_2O_8$ (h)
Fe_2O_3	Cordierite (h) Fe_2O_3 (h)	Cordierite (h) Fe_2O_3 (h)	Cordierite (h) Fe_2O_3 (h)	Cordierite (h) Fe_2O_3 (h)	Cordierite (h) Fe_2O_3 (h)
V_2O_5	Cordierite (h) V_2O_5 (h)	Cordierite (h) V_2O_5 (h)	Cordierite (m) V_2O_5 (h) SiO_2 (l) MgV_2O_6 (l)	Cordierite (m) V_2O_5 (h) SiO_2 (m) MgV_2O_6 (l)	Cordierite (m) V_2O_5 (m) SiO_2 (m) MgV_2O_6 (h)

Content (h) = high, (m) = medium, (l) = low

shrinkage starts at about 300°C but a small expansion, during cooling, partially counterbalances the shrinkage.

The thermal behaviour of doped filter bars is similar to that of the cordierite–oxide mixtures when the pollutant is in contact with the filter wall, it reacts with cordierite and modifies its thermal expansion because of a solid solution or a new phase formation.

The influence of the pollutant–filter interaction can be found not only in local variation of the thermal expansion behaviour of the filter but in a dimensional change spread over the whole ceramic structure during the thermal cycles: the filter porosity, even if ranging around 50%, is not able to completely take up the local dimensional variations.

In Table 1 the principal new phases formed by the reaction between cordierite and single oxides as a function of the heat treatment temperature are reported. The XRD patterns are complex and in some samples (doped with Na, Zn, Pb, V oxides) the backgrounds are high, supporting the hypothesis of the presence of variable amount of amorphous phases. Up to 500°C no interaction between cordierite and pollutants has been observed.

Starting from 600°C, sodium oxide reacts with cordierite to give $Na_2Al_2SiO_6$, a carnegieite-like phase, since Na_2CO_3 melts at 850°C, this reaction occurs in the solid state. Considering the results of Evans *et al.*[8] and the XRD patterns of the mixtures having increasing Na_2O content (1, 5, 10, 25 wt%), it can be deduced that a large amount of Na_2O can enter into the zeolite like channels[9] of the cordierite without any evident structural change. When a critical amount is reached, the attack and deterioration of the lattice take place starting from the T_2 tetrahedra[9] with new crystalline phase formation. Residual products of the attack are SiO_2 and MgO which form crystalline Mg_2SiO_4 after heat treatment at 700°C. This is in agreement with the MgO-Al_2O_3-SiO_2 phase diagram:[10] the subtraction of silica and alumina from cordierite, to give $Na_2Al_2SiO_6$, generates forsterite.

Remembering that sodium silicoaluminates have a thermal expansion coefficient ten times higher than cordierite[11] and high background present in the XRD patterns, the large expansion of the cordierite-Na_2CO_3 mixture can be imputed to sodium silicoaluminate and glass formation. Cordierite disappears and $Na_4Mg_2Si_3O_{10}$ is synthesised after heat treatment at 800°C, at 1000°C, near Mg–Na silicate, $NaAlO_2$ appears. Cordierite is more stable in presence of calcium oxide: only a small quantity of melilite ($Ca_2Al_2SiO_7$-$Ca_2MgSi_2O_7$) appears at 900°C. Cordierite is unaffected by ZnO until 1000°C: at this temperature Zn_2SiO_4 and $MgAl_2O_4$ are formed.

At 600°C cordierite reacts with PbO to give Pb_2SiO_4; since the melting point of PbO is 890°C the reaction occurs in the solid state. Lead silicate is expansive[12] but sintering phenomena enhanced by the low melting point of both PbO and silicate (740°C) result in a large total shrinkage. At 700°C $PbAl_2SiO_6$ is formed; starting from 900°C, cordierite is completely destroyed to produce two lead silicoaluminates. This is in agreement with the

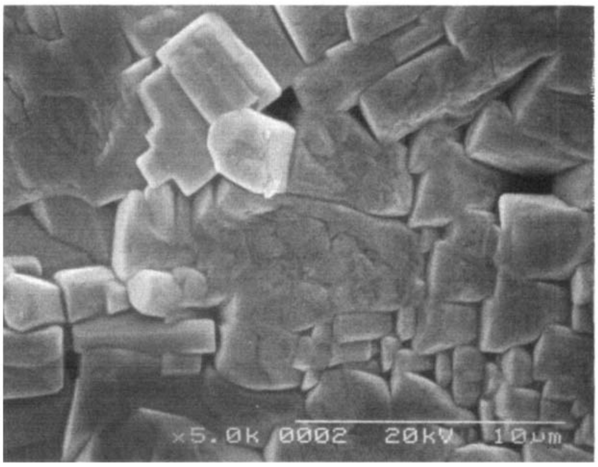
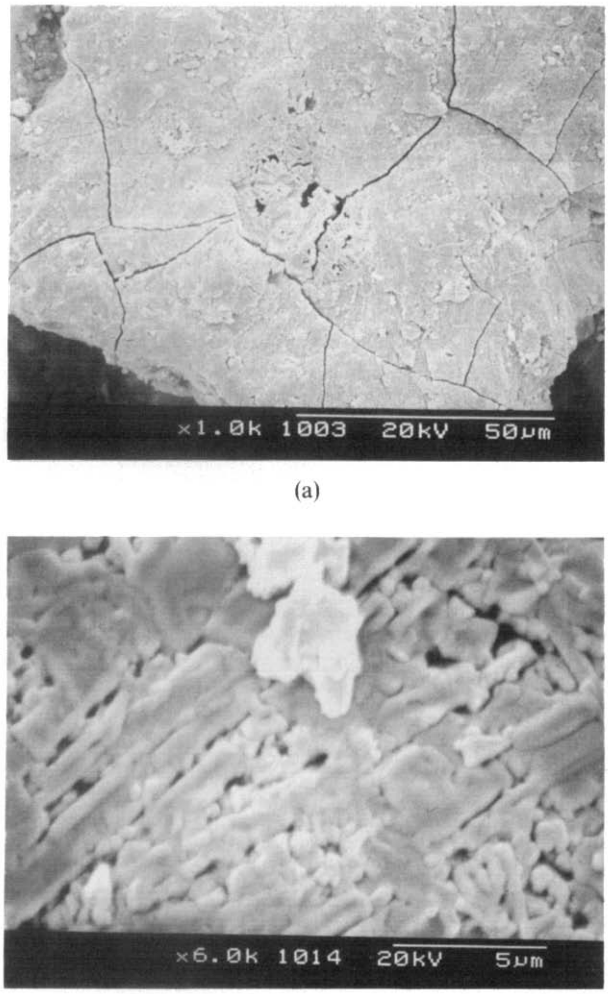


Fig. 3. Microstructure of cordierite as fired at 1000°C

results of Sorrel[13] who obtained lead feldspar by reaction between lead sulphate and kaolin, at about 800°C

Interaction between cordierite and iron oxide does not give any new phases; in contrast, V_2O_5, starting from 800°C, reacts with cordierite to give MgV_2O_6 and cristobalite

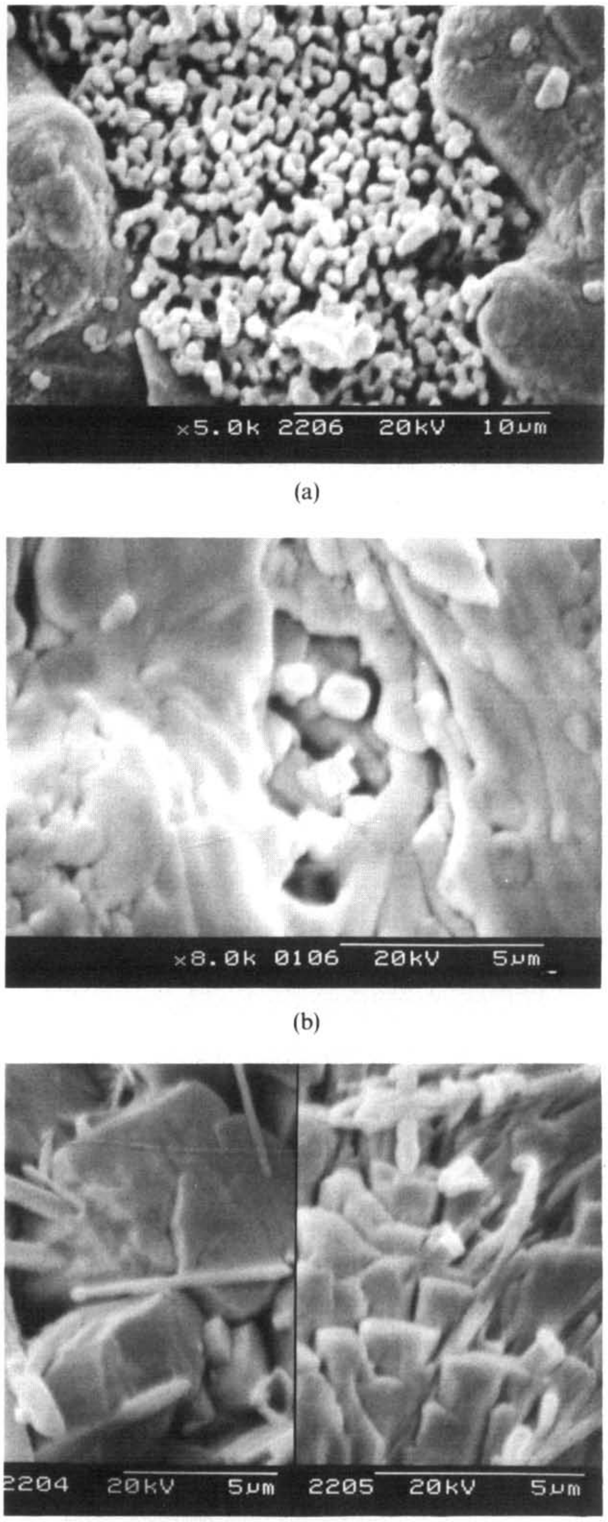


(a)

(b)

Fig. 4. Scanning electron micrographs showing filter microstructure after 5 min at 1000°C (a) Na polluted cordierite (b) Pb polluted cordierite

IR spectroscopy was also performed on the cordierite-oxide mixtures to confirm the XRD results and to check the short range order variations in cordierite structure during heat treatments. Except for the cordierite-Fe_2O_3 mixture, which does not exhibit any significant change of the IR spectra after heat treatment at different temperatures, a slight broadening of the bands was observed for all



(a)

(b)

(c)

Fig. 5. Scanning electron micrographs showing filter microstructure after 60 min at 1000°C (a) Zn polluted cordierite, (b) Pb polluted cordierite, (c) V polluted cordierite

the other mixtures increasing with the heat treatment temperature This phenomenon may be ascribed to the decrease of the short-range order, probably due to the distortion of SiO_4 and AlO_4 tetrahedra caused by ion diffusion into the cordierite structure

In the cordierite–Na_2O mixture, the presence of an amorphous phase is clearly revealed starting from 700°C, as well as the formation of an alkaline silicate containing magnesium in tetrahedral coordination In the cordierite–PbO mixture, after treatment at 900°C, the spectrum shows that the cordierite has completely disappeared, a new crystalline phase is formed and an amorphous phase is also present. For the cordierite–V_2O_5 mixture, the presence of free SiO_2 was detected at temperature $\geq$ 900°C.

In conclusion, the IR data confirm the information from XRD patterns

Figure 3 shows the microstructure of cordierite as fired at 1000°C, the preferred orientation of its elongated grains is due to the extrusion process employed to produce the monolith Figures 4 and 5 present the morphological change due to the interaction between the oxides and cordierite filter after heat treatments at 1000°C.

After 5 min at 1000°C, as shown in Fig 4(a), sodium oxide interacts with cordierite creating cracks as a consequence of the Na silicoaluminate formation and the different thermal expansion behaviour between this new phase and the cordierite matrix; lead oxide (Fig. 4(b)) produces a superficial etching of the cordierite grains, the other oxides do not give any visible modification.

If the thermal treatment at 1000°C is prolonged for 60 min, sodium oxide produces longer and deeper cracks, zinc (Fig 5(a)), lead (Fig. 5(b)) and vanadium (Fig. 5(c)) oxides etch the cordierite giving formation of new phases, no visible modifications are present in the samples doped with the remaining two oxides.

4 Conclusions

The results on the interaction between cordierite and single pollutant oxides have demonstrated that:

- Usually pollutants lead to surface etching and new phase formation. Some of these phases have a thermal expansion coefficient very different from pure cordierite. Thus during filter regeneration, where temperatures of about 1000°C may be reached, different dimensional variations may be produced locally in the ceramic body and microcracks appear.
- Sodium and lead oxides seem to be the most dangerous pollutants, since they are able to completely destroy the cordierite structure at temperatures lower than 900°C. Iron oxide seems to yield only a solid solution; the other pollutants partially react with cordierite to produce new phases.

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