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Interaction between some Oxides and Cordierite

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Abstract

Today, cordierite plays a very important role in the reduction of noxious substances emitted from internal combustion engines. Honeycomb structures with parallel channels offer a good solution as supports for catalysts at an acceptable counterpressure. Porous ceramic materials permit an efficient mechanical filtration of carbonaceous particles contained in the exhaust gases of diesel engines, which are forced to flow through the walls. Interest in these components is increasing due to their potential effectiveness; it is therefore important to study the problems sometimes encountered during actual applications. This research considers the interaction between some oxides encountered in practical use and the material itself in order to understand the behaviour of cordierite as a basis for better utilisation; some observations and comments are reported.

Heute spielt Cordierit eine bedeutende Rolle bei der Reduktion von schädlichen Substanzen, die von Verbrennungsmotoren ausgestoßen werden. Honigwabenstrukturen mit parallelen Kanälen bieten sich als Träger für Katalysatoren bei vertretbarem Gegendruck an. Poröse Keramiken erlauben eine effiziente mechanische Filterung von kohlenstoffhaltigen Partikeln, die z.B. in den Abgasen von Dieselmotoren vorkommen, indem das Abgas durch die Wände geleitet wird. Das Interesse an diesen Komponenten nimmt aufgrund ihrer möglichen Wirksamkeit zu. Es ist deshalb von Bedeutung, die Schwierigkeiten, die während des Einsatzes auftreten können, zu analysieren. Die vorliegende Arbeit betrachtet die Wechselwirkung zwischen einigen Oxiden, wie sie in der tatsächlichen Anwendung vorkommen, und dem Material selbst, um das Verhalten des Cordierit in der Anwendung besser zu verstehen. Im folgenden werden einige Beobachtungen und Erläuterungen wiedergegeben.

Aujourd'hui, la cordiérite joue un rôle important dans la réduction des substances nocives émises par les moteurs à combustion interne. Les structures en nid d'abeilles comportant des canaux parallèles présentent une chute de pression acceptable. Les matériaux céramiques poreux autorisent une filtration mécanique efficace des particules carbonates contenues dans les gaz d'échappement des moteurs diesel. L'intérêt manifesté pour ces composants grandit en raison de leur efficacité potentielle; il s'avère dès lors important d'étudier les problèmes que l'on rencontre parfois en application réelle. Cette recherche examine l'interaction entre quelques oxydes utilisés dans la pratique et le matériau lui-même, pour comprendre le comportement de la cordiérite comme base d'une meilleure utilisation; quelques observations et commentaires sont repris.

1 Introduction

α-Cordierite ($Mg_2Al_4Si_5O_{18}$) is a hexagonal framework silicate having $a_0 = 9{\cdot}770$ Å and $c_0 = 9{\cdot}352$ Å, with zeolite-like channels parallel to the c axis.

The list of industrial and commercial applications for cordierite-based ceramics is extensive. Some of the most important uses have been as insulators in

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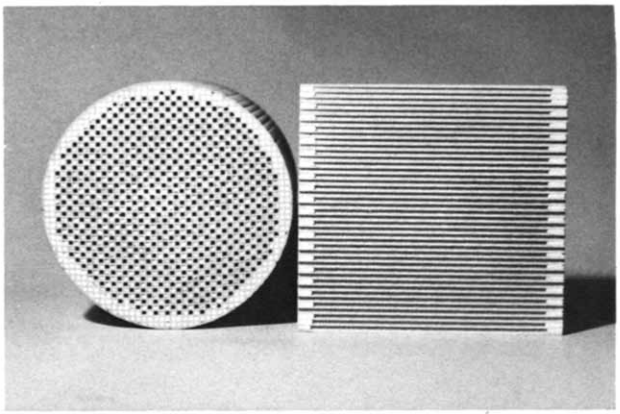


Fig. 1. Cordierite extruded trap.

spark plugs, refractory coatings on metal substrates, selected parts in gas turbine engines such as rotor vanes and heat exchangers and as automotive catalytic converters.[1]

Extruded cordierite honeycomb monoliths, coated with catalyst are now widely used for controlling automotive exhaust emissions from gasoline fuelled engines.[2]

Filtration of particulates, emitted from diesel engines, occurs in stepped honeycomb structures, by way of the porous walls of the channels where exhaust gases are forced to flow (Fig. 1).

The shape and size of the unit cell of the ceramic monolith are designed to provide the best characteristics which enhance filtration efficiency, durability and vehicle driveability. With adequate surface area, controlled porosity, good mechanical properties, the efficiency of abatement of particulates can become very high and the ratio of filtering area over volume can be considered convenient for the application.

Problems arise during the regeneration of filters when carbon particles, with absorbed hydrocarbons, must be burned out to avoid unacceptable counterpressure in the engine. Thermal stress, due to the local exothermicity of the oxidative reactions (it is possible to reach temperatures of about 1000°C), may generate cracks and fractures in the structure of the monolith. In addition to the thermal stresses, some problems derive from pollutants emitted from the engine that may react with the cordierite thus engendering holes in the channel walls (Fig. 2) and leading to modification of its properties.

The efficiency and durability of the abatement of the diesel particulate, using a cordierite trap, are strictly dependent on the integrity of the ceramic component and hence on the evaluation of thermal stress and on the behaviour of the cordierite towards the pollutants; knowledge about these problems which can lead to critical failure is still lacking.

The aim of this work is to study the interaction of cordierite honeycombs with single pollutants: the interaction of mixtures of several pollutants will be analysed in the following researches.

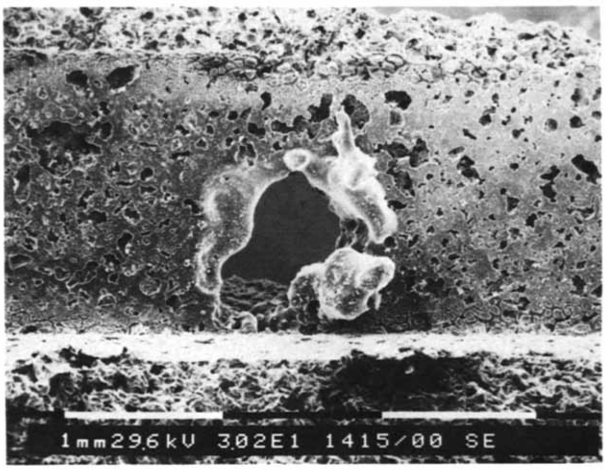


Fig. 2. Hole and fused zone on the trap wall.

2 Experimental

2.1 Materials

The cordierite honeycomb trap (type EX66-100/25) made by Corning Glass Works (USA) and cordierite powder prepared by Baikowski (France) were considered. The latter was used as a reference material because it was more pure: it is known that impurities modify cordierite behaviour.[2]

Table 1 details the composition of these two cordierites.

Sodium carbonate, calcium, zinc, lead, iron and vanadium oxides all obtained from C. Erba (Italy) were used to simulate the pollutants which are or may be present in the particulate. Sodium and lead derive from accidentally contaminated fuel; iron is released from the engine or the exhaust pipes as abraded particles or rust; calcium and zinc come from lubricant oil; vanadium comes from fuel or is added as a catalyst coating to assist particulate combustion.

2.2 Microstructural characterisation

To investigate the reaction between cordierite and pollutants, thin tablets (5 mm in diameter and 0·5 mm thick) of different oxides (carbonate for sodium) were put on specimens (10 mm × 10 mm × 2 mm) of the trap and heated to 1000°C. This temperature was selected because it is probably reached on the trap walls during filter regeneration. The morphologies of the etched porous cordierite surface were investigated by scanning electron microscope (Hitachi S-2300 apparatus).

Table 1. Cordierites impurities (wt%)

	Corning	*Baikowski*
Na_2O	0·081	0·056
K_2O	0·053	100 ppm
CaO	0·31	0·14
TiO_2	0·42	0·013
Fe_2O_3	0·78	0·018

Table 2. Mixtures of Baikowski cordierite-pollutants

Mixture number	*Metal added*
1	5% Na
2	10% Ca
3	10% Zn
4	5% Pb
5	10% Fe
6	5% V

To study any new phases produced by the ceramic monolith–oxide reactions, carefully dry-mixed mixtures of Baikowski cordierite and several single oxides were made. The weight percents of the added oxides, given as metal, are presented in Table 2. From these mixtures, compacts were prepared by pressing the powders at 200 MPa in order to obtain a good contact between the reactants. These compacts were heated at 1300°C for 30 min. After heat treatment, the sintered bodies were milled and analysed by X-ray diffractometry (XRD) (Philips apparatus PW 1710, CuKα radiation). Dilatometry (Netsch 402 E/3 apparatus), with heating and cooling rate of 10°C/min, was performed on mixed compacts (25 mm × 10 mm × 10 mm) pressed at 500 MPa to verify the pollutants influence on the thermal expansion of unsintered cordierite.

3 Results and Discussion

Figure 3 shows the microstructure of cordierite as fired at 1000°C; elongated grains and their preferred orientation in cordierite sample are due to the extrusion process employed to produce the monoliths. This surface may be compared with the surfaces of cordierite monolith etched by oxides (Fig. 4). The micrograph of Fig. 4(a) shows typical morphology of the cordierite surface etched by sodium: the surface is very cracked, fused areas and small acicular crystals are present. Figure 4(b) illustrates the calcium etching: it shows the presence of a large fused-area. The cordierite surface etched by zinc (Fig. 4(c)) exhibits many tetragonal-like crystals with corroded faces and a fused area from which some crystals seem to grow. Finally, iron, lead and vanadium (Figs 4(d)–(f), respectively) modify cordierite grain morphology and create porosity.

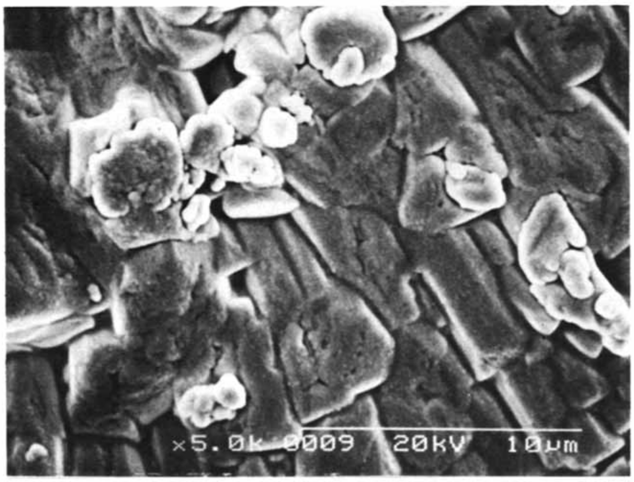
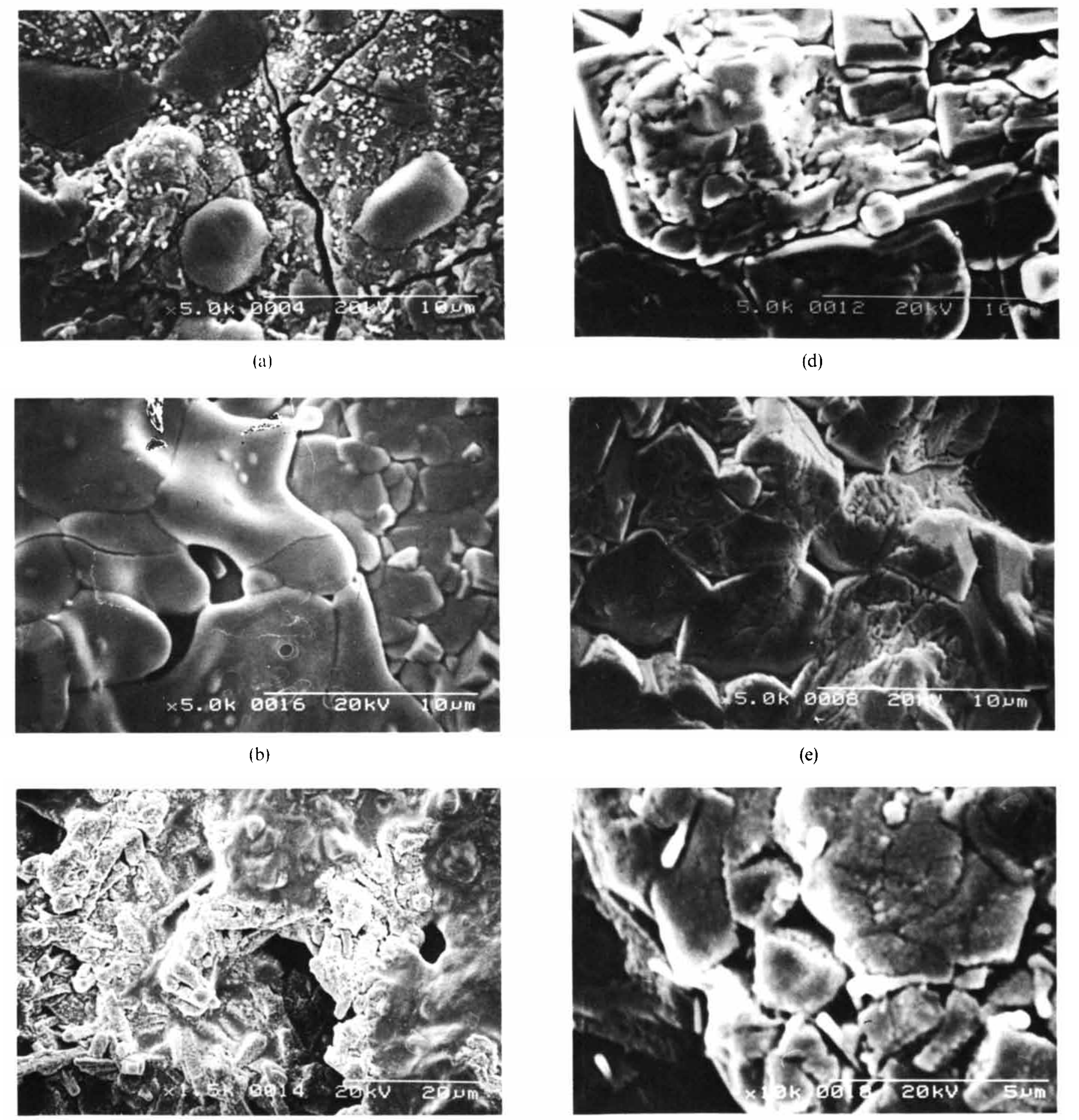


Fig. 3. Microstructure of cordierite treated at 1000°C.

If a cube (2 mm of side) of a mixture of all oxides is put on a small piece of the cordierite trap and heated at 1000°C for 30 min, the filter wall is perforated and a large zone, around the hole, is partially fused; acicular and pseudocubic crystals are also present (Fig. 5). This test, probably more similar to the real work conditions of the monolith, shows the synergic action of the pollutants. The simultaneous action of different oxides on the walls of the trap is, in fact, stronger than that of the single oxides. In this case, the perforation of the filter wall occurs as is sometimes observed in traps assembled on cars.

Figure 6 shows XRD patterns of the cordierite–oxide mixtures (see Table 2) after heat treatment. From the pattern of the mixture containing sodium (N1) it is possible to identify, near cordierite, the spinel ($MgAl_2O_4$) and to suppose, from the high background between 10–40° 2θ, the presence of a glassy phase. Also Kim *et al.*[3] found that cordierite doped with sodium decomposes at high temperature to spinel and amorphous phase.

In the pattern of the mixture N2, cordierite and anorthite ($CaAl_2Si_2O_8$) were detected. A compound anorthite-like was also found in the mixture N3. Near cordierite, ferrian spinel ($Mg(Al, Fe)_2O_4$) was detected in the mixture containing iron: as for the mixture N1, an amorphous phase seems to be present. In the mixtures containing lead or vanadium, only cordierite appears. However, the cordierite peaks present a little shift and a variation of the intensity in comparison to the pure cordierite. A little shift in the peak positions and an important difference in their intensities was also found by Evans *et al.*[4] between cordierite and potassium and cesium doped cordierites. The little shift of the peaks can be explained by considering that zeolite-like channels are known to house various alkalis, alkaline earths and transition metals in natural specimens.[5–7] The open diameter through the channel varies from 0·25 to 0·5 nm. Two crystallographic sites within the channel have been defined: C_1 in the centre of the channel between two adjacent rings and C_2 as the constriction of the channel centring on a six-membered ring. Because of size constraints, large cations, such as K^+, can be located at or close to the C_1 sites, smaller cations, such as Na^+, Ca^{++}, Zn^{++}, Fe^{++} can occupy the C_2 sites.[1] From these results it appears that cordierite forms solid solutions with many oxides. An attempt to incorporate more oxides results in the formation of a secondary phase.



(a) (d)

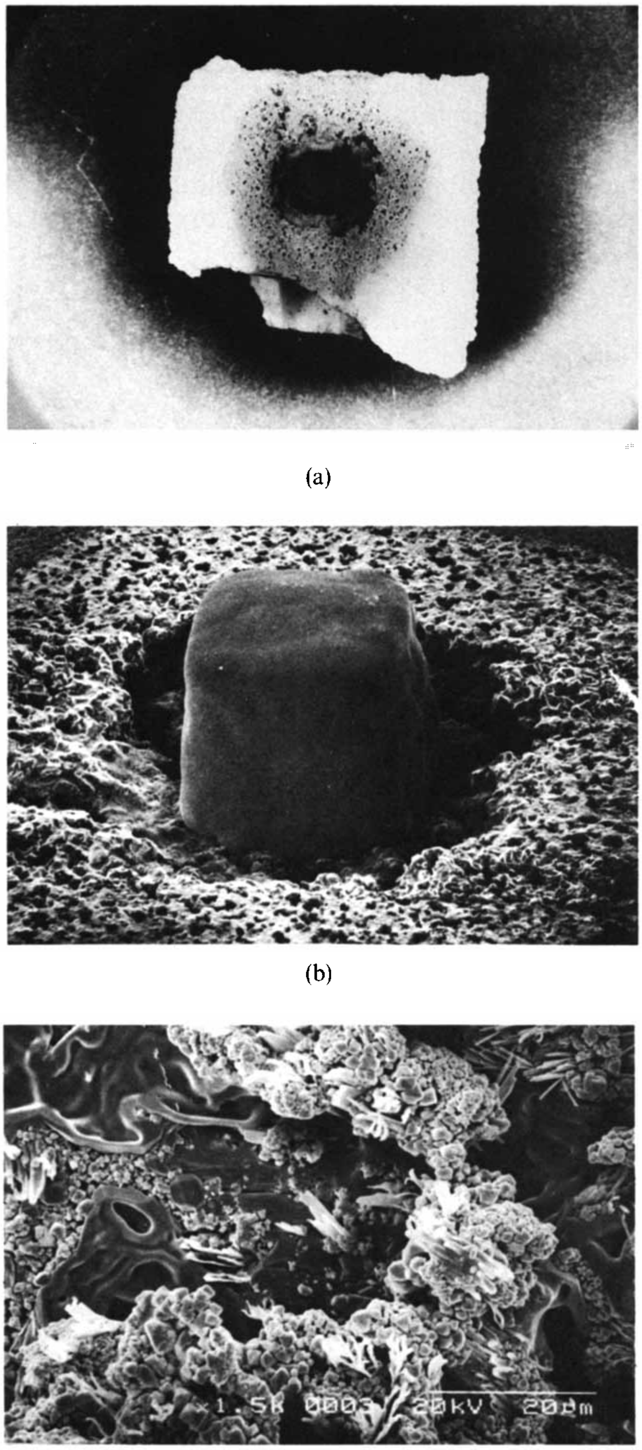
(b) (e)

(c) (f)

Fig. 4. Cordierite monolith etched by (a) Na_2CO_3; (b) CaO; (c) ZnO; (d) Fe_2O_3; (e) PbO; and (f) V_2O_5.

The thermal expansion of Baikowski cordierite and of doped cordierite compact bodies is shown in Fig. 7. The thermal expansion of pure cordierite powder, compacted at 65% of theoretical density, is at 1000°C ($\Delta L/L = 0{\cdot}35\%$) in agreement with the recent literature data.[8,9] When sodium is added to the cordierite, a large expansion takes place at 900°C followed by a shrinkage due to sintering. At room temperature, after heat treatment, the sample appears expanded. The sample of calcium doped cordierite presents, at 900°C, a shrinkage, but at room temperature the sample regains its original dimension. The zinc cordierite expands at about 1000°C: the shrinkage due to cooling does not allow the sample to return to the original dimension because of secondary phase formation.

The thermal behaviour of the cordierite is weakly influenced by iron: a shrinkage due to sintering at about 1000°C takes place but a small expansion during cooling compensates for the shrinkage. Lead addition to the cordierite produces at 900°C a large shrinkage which lasts during cooling, to 920°C. At this temperature an expansion takes place but at room temperature the sample has a net shrinkage.



(a)

(b)

(c)

Fig. 5. Effects of the total oxides mixture on the trap wall (thermal treatment: 1000°C for 30 min).

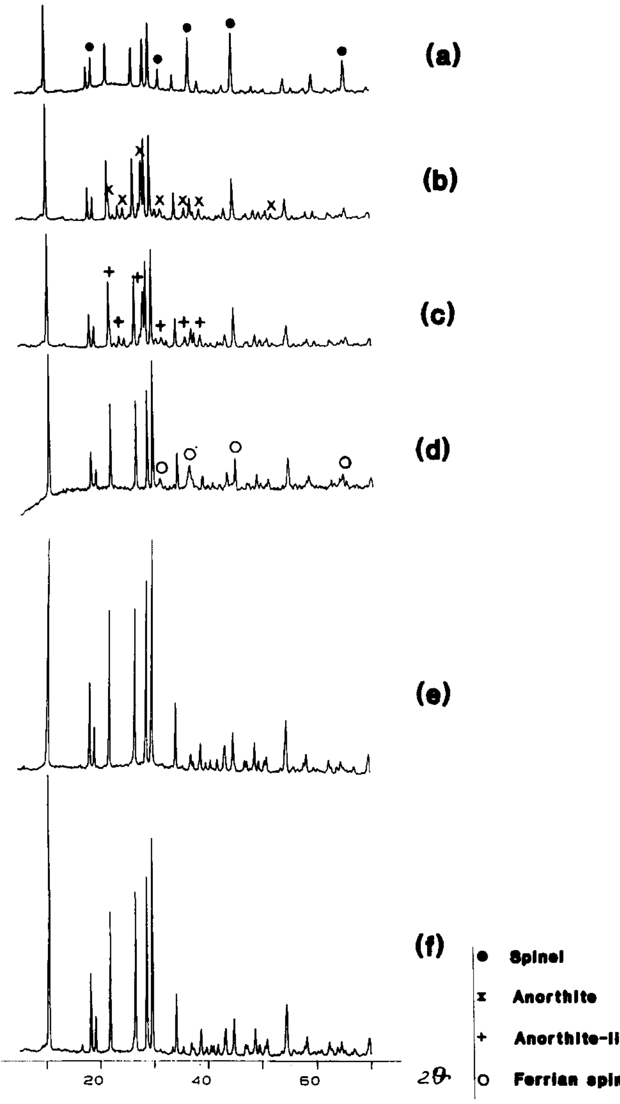


Fig. 6. X-Ray diffraction patterns of oxides–cordierite mixtures: (a) Na_2CO_3; (b) CaO; (c) ZnO; (d) Fe_2O_3; (e) PbO; (f) V_2O_5 (heat treatment: 1300°C for 30 min).

The cordierite doped with vanadium expands during cooling from 1100 to 900°C; at room temperature the sample appears expanded. Finally, considering the pattern of the curves presented in Fig. 7, it appears that the samples of cordierite with the oxides show high dimensional changes between 700 and 1000°C if compared to pure cordierite. It is known that little differences in expansion, observed for cordierites synthesised by different methods or having different impurities, are due to slight variations in chemistry[4] as well as in possible variations in Si, Al ordering.[5] The anomalous dimensional changes of our specimens cannot be explained simply on the basis of the Me–O bond modifications in the cordierite lattice. One may suppose that the important length changes are due to new phases formation: in fact, sodium silicate glass, spinel, anorthite, etc., have higher thermal expansion coefficients than cordierite.[1,10]

4 Conclusions

All pollutants, considered in this work, etch the monolith walls at 1000°C. Their action on cordierite is synergic: the pollutant mixture can perforate the trap walls.

The pollutants react also with cordierite to give new phases (glass, spinel, anorthite, etc.). These compounds, present with cordierite, modify its thermal behaviour. From dilatometric tests it appears also that three samples (cordierite, cor-

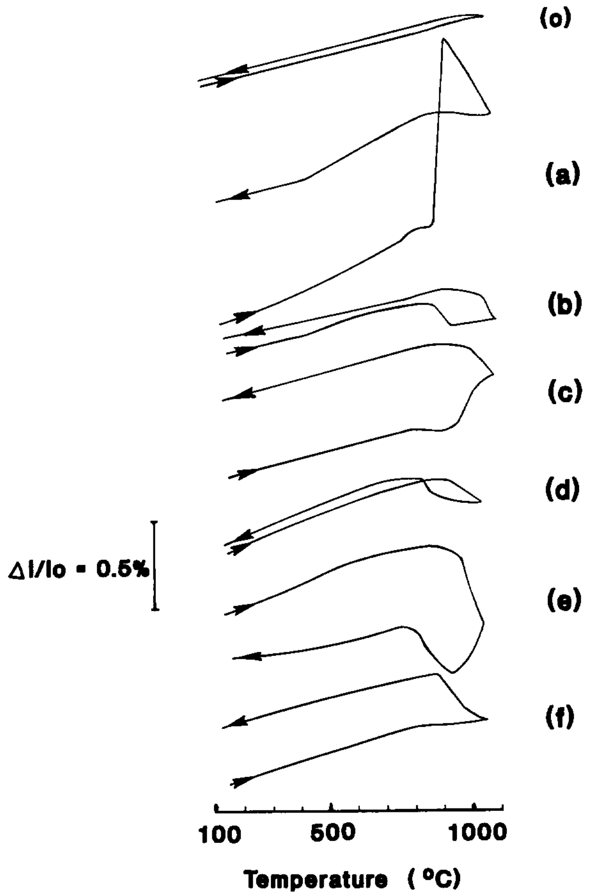


Fig. 7. Dilatometric curves of (○) cordierite and ((a)–(f)) doped cordierite: (a) Na_2CO_3; (b) CaO; (c) ZnO; (d) Fe_2O_3; (e) PbO; (f) V_2O_5.

dierite added with calcium or iron) do not present dimensional variations after heat treatment; three samples (cordierite containing sodium, zinc or vanadium) show expansion after heat treatment; on the contrary, cordierite doped with lead shrinks.

This is very important when cordierite ceramics are used as traps for controlling automotive exhaust emissions: depending on the type of pollutant which arrives on the trap wall, zones having no dimensional changes close to zones showing expansion or shrinkage, with structural modifications, may be present, leading to microcrack formation due to differential dimensional variations.

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