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Journal of the European Ceramic Society 23 (2003) 2983–2986

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Development of porous corundum layers on cordierite ceramics

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Abstract

The surface of cordierite ceramics is transformed into porous corundum (α-Al_2O_3) by heating the ceramic at 1350–1450 °C in a controlled reducing atmosphere with a partial CO pressure below 10^{-8} atm. The least stable oxides in the cordierite (SiO_2 and MgO) are selectively reduced and volatilized, leaving the most stable Al_2O_3 as a surface layer up to 15 μm thick, with a specific surface area of up to 15 m^2/g. The characteristics of this layer and the chemical and thermal stability of corundum make ceramics treated in this way well suited for use as catalyst supports for high-temperature catalysis.

Keywords: Al_2O_3; Cordierite; Films; Functional applications

1. Introduction

Recent developments in the field of ceramics have included a spectacular increase in the use of surface coatings for protection from wear and heat, and for their various electrical and optical properties.[1,2] One rapidly expanding area in applications requiring high chemical and thermal resistance is ceramic catalyst supports, which are necessary both for catalytic combustion and for catalytic reduction of gas emissions by vehicles or industrial plant.[3,4] In both cases, the active catalyst (often a noble metal) is borne by a mechanically sturdy support that, in order to maximize the quantity of catalyst exposed to the reactive gas per unit volume, has a large specific surface area that is stable under working conditions.[3–5] This surface is often itself achieved by coating a bulk support with a layer of a suitable material. Existing industrial processes for coating ceramics include chemical or physical vapor deposition (CVD, PVD) and successive immersion in dilute suspensions of the coating material.[1,6,7] These processes are laborious and relatively expensive, and although they allow substrates with a variety of compositions and microstructures to be coated, they impose lower limits on the diameter of gas-flow channels running through the support.

Cordierite ($2Al_2O_3 \cdot 2MgO \cdot 5SiO_2$) is a ceramic material with numerous important industrial applications that make use of its low coefficient of thermal expansion, low dielectric constant and high resistance to thermal shock.[2,8] In this paper we describe the transformation of the surface layer of a sintered cordierite ceramic into porous corundum (α-Al_2O_3) by heating the ceramic at high temperature in a controlled reducing atmosphere. Under appropriate conditions, SiO_2 and MgO are selectively reduced and volatilized from the ceramic surface, leaving a surface layer of corundum of high specific surface area. This is a one-step process that leaves the dimensions and geometry of the ceramic unaltered.

The conditions required for the above process were inferred from the volatility diagrams of the various chemical species involved, which were likewise used to interpret experimental results. Volatility diagrams are isothermal plots of solid-gas equilibrium thermochemical data; they show the partial pressures of two gaseous species in equilibrium with the condensed phases in a system.[9–11]

2. Experimental procedure

Al_2O_3 (mean particle size 5 μm, purity 99.6%; from Alcoa, San Ciprian, Lugo, Spain), MgO (mean particle size 8 μm, purity 97%; from Merck) and SiO_2 (mean particle size 3 μm, purity 99%; from Sigma), in proportions corresponding to the stoichiometry of cordierite, were mixed in water with Y-TZP balls for 6 h. The

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doi:10.1016/S0955-2219(03)00314-5

mean particle size of the resulting mixture, determined by scanning electron microscopy (SEM) using a JEOL JSM-6400 apparatus, was smaller than 3 μm. This mixture was compressed to form discs 20 mm in diameter and 5 mm thick, which were then heated in air for 4 h at 1450 °C. Analysis of the calcinated discs was by x-ray diffraction (XRD) using a Siemens D5000 apparatus, operating with Cu Kα radiation at 25 kV and 35 mA, with a scan rate of 2°/min. XRD analysis showed that the only crystalline phase was cordierite. The specific surface area, as determined by the BET nitrogen adsorption method in a Micromeritics Gemini 2360 apparatus, was less than $0.01 m^2/g$.

The cordierite discs prepared as described above were placed in corundum crucibles and loaded into a Pyrox HI-16L/17 graphite-lined furnace equipped with W5%Re/W26%Re thermocouples and a vacuum pump. Once loaded, the furnace was closed, and the pressure inside was pumped down to 10^{-4} atm. It was then filled to atmospheric pressure with nitrogen (N50 from Air Liquide; $P_{O_2} < 2 \times 10^{-6}$ atm, $P_{CO} < 0.5 \times 10^{-6}$ atm, $P_{H_2O} < 1 \times 10^{-6}$ atm) before being pumped down to 10^{-4} atm again. At this point, with a $P_{O_2} < 2 \times 10^{-9}$ atm, heating was begun. Temperature was maintained constant between 1350 and 1450 °C, usually for $\leqslant 5$ h. The vacuum pump was operated throughout to ensure a constant total furnace pressure of about 10^{-4} atm. Assuming a complete reaction between residual O_2 and the graphite furnace lining at the working temperatures, the value of P_{CO} when surface transformation of the cordierite discs began would have been about 4×10^{-9} atm.

3. Results and discussion

XRD analysis of the surfaces of discs treated for 1h at 1450 °C shows the appearance of considerable quantities of corundum, along with spinel ($Al_2O_3{\cdot}MgO$) and sapphirine ($2Al_2O_3{\cdot}2MgO{\cdot}SiO_2$) (Fig. 1A). The degradation of cordierite subsequently slows down (Fig. 1B,C), the composition attained after about 5h being practically unchanged by heating for longer periods (results not shown). The alteration of cordierite and the formation of corundum are significantly greater after 5h treatment at 1450 °C than after 5 h treatment at 1350 °C (Fig. 2). SEM images of the surfaces of treated discs, together with the results of surface analysis by energy-dispersive spectrometry (EDS) using a Link Analytical eXL system with the SEM, show these surfaces to consist of small corundum particles sintered together at their points of contact to form a highly porous layer (Fig. 3). SEM-EDS images of cross sections and fracture surfaces of discs treated for various times at various temperatures in the range 1350 °C-1450 °C showed all to have acquired similar corundum layers (Fig. 4). These layers reach a maximum thickness of ~15μm after 5 h at 1450 °C. Examination of these sections at greater magnification, and their analysis at various depths, showed that the spinel illustrated in Fig. 1 lay immediately below the corundum layer, and that the sapphirine lay between the spinel and the unaltered cordierite. For the specific surface area of the corundum layer of discs treated at 1450 °C, values of up to 15 m^2/g were estimated using BET/N_2 measurements of the total post-treatment specific surface area of the disc, together with SEM measurements of the thickness of the layer.

These results may be explained by starting from the relative stabilities of the oxides into which cordierite decomposes under high-temperature reducing conditions. Since both relevant reactions [$SiO_2 \rightarrow SiO(g) + 1/2O_2(g)$ and $MgO \rightarrow Mg(g) + 1/2O_2(g)$] produce oxygen, the reaction for which the partial pressure of oxygen at equilibrium is greatest, which the volatility diagrams show to be the reduction of SiO_2, suppresses the others. Thus the overall reaction that initially occurs in the cordierite discs under the working conditions is:

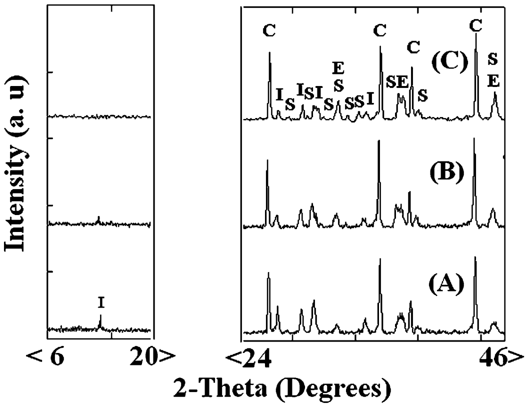

Fig. 1. Diffractograms of the surfaces of cordierite discs after treatment in a reducing atmosphere for 1 h (A), 2 h (B) or 5 h (C) at 1450 °C. Peak identification labels: I, cordierite; S, sapphirine; E, spinel; C, corundum.

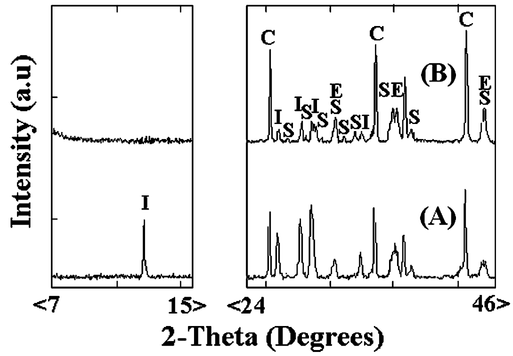

Fig. 2. Diffractograms of the surfaces of cordierite discs after treatment in a reducing atmosphere for 5 h at 1350 °C (A) or 1450 °C (B). Peak identification labels: I, cordierite; S, sapphirine; E, spinel; C, corundum.

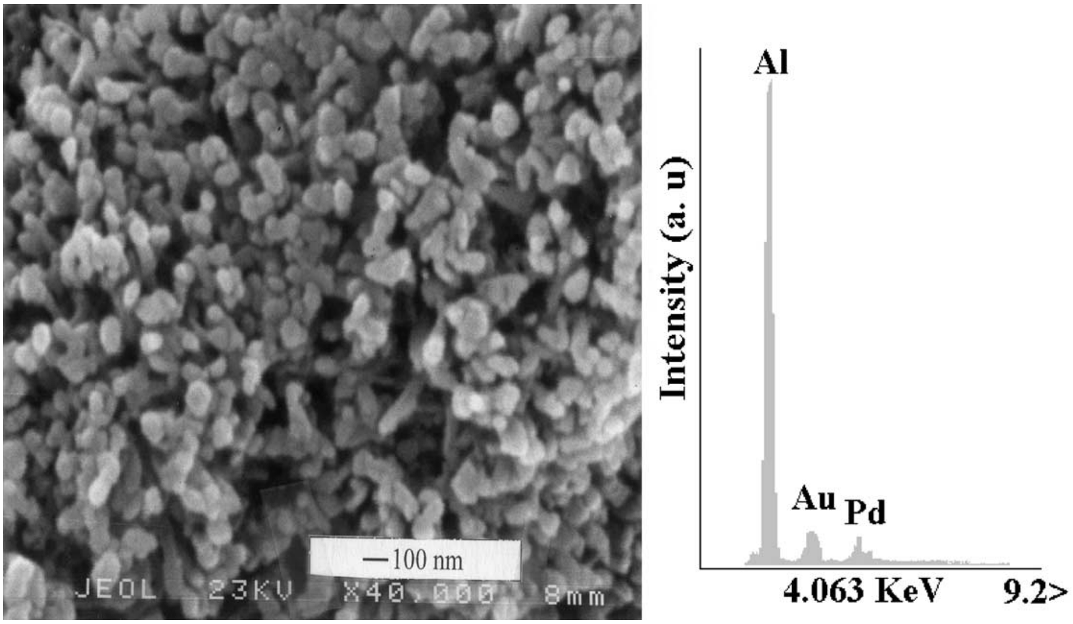

Fig. 3. SEM photomicrograph of the surface of a cordierite disc after 5 h at 1450 °C in a reducing atmosphere, and the results of its analysis by EDS.

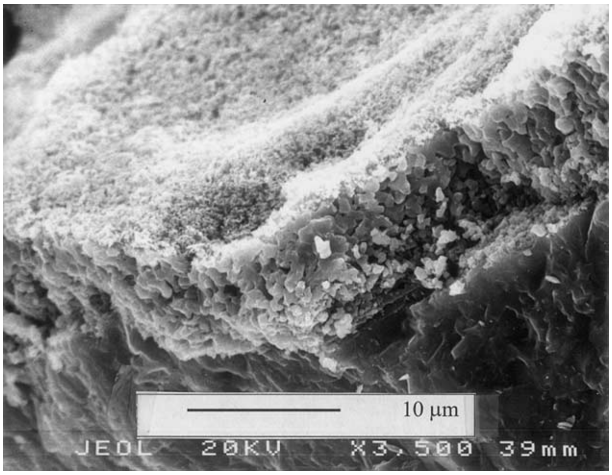

Fig. 4. SEM photomicrograph of the fracture surface of a cordierite disc treated for 1 h at 1450 °C in a reducing atmosphere, showing the corundum layer acquired during treatment.

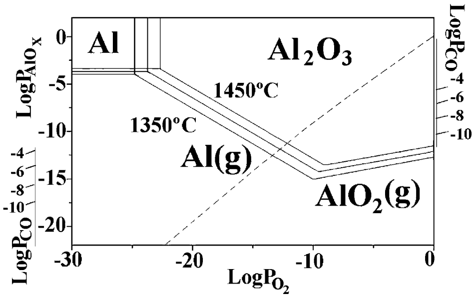

Fig. 5. Volatility diagram for Al– Al_2O_3 system.

$$2Al_2O_3{\cdot}2MgO \cdot 5SiO_2 \;\rightarrow\; 2Al_2O_3 + 2MgO + 5SiO(g) + 5/2O_2(g) \qquad (1)$$

Assuming ideal behavior, the partial pressures of the gaseous products of this reaction at equilibrium at 1450 °C are 7.8×10^{-8} atm for P_{SiO} and 3.9×10^{-8} atm for P_{O_2} ($Kp_{1450\ °C} = 8.705\times10^{-55}$). The observed formation of sapphirine, $2Al_2O_3{\cdot}\ 2MgO \cdot SiO_2$ shows that the Eq. (1) reaction actually occurs in two steps: the initial formation of this phase followed by further loss of silica to leave the final non-gaseous products of Eq. (1). As these products do not decompose at the P_{O_2} values generated locally by the reaction of Eq. (1), the high working temperature leads to their interacting to form spinel, $Al_2O_3{\cdot}\ MgO$.

Degradation of spinel

$$Al_2O_3 \cdot MgO \;\rightarrow\; Al_2O_3 + Mg(g) + 1/2O_2(g) \qquad (2)$$

for which $P_{Mg} = 2.55\times10^{-9}$ atm and $P_{O_2} = 5.1\times10^{-9}$ atm at equilibrium at 1450 °C ($K_{p1450°C} = 2.577\times10^{-13}$), takes place only when the advance of the reaction front into the cordierite disc eventually results in the P_{O_2} gradient set up between the front and the surface of the disc being such that P_{O_2} falls below the above figure at the outer surface of the spinel. When this occurs, the spinel in this zone is transformed into small particles of alumina that crystallize as corundum at the working temperature used.

According to the volatility diagram of Fig. 5, the corundum layer is itself theoretically involved in a reaction with the carbon monoxide present in the atmosphere of the furnace:

$$Al_2O_3 + 3CO(g) \rightarrow 2Al(g) + 3CO_2(g) \quad (3)$$

However, at 1450 °C, with a P_{CO} of 4×10^{-9} atm, the equilibrium partial pressures of aluminium and carbon dioxide are 2.8×10^{-11} and 1.9×10^{-11} atm, respectively ($Kp = 1.928\times10^{-29}$), which means that the reaction of Eq. (3) is in fact negligible.

The observed virtual stopping of the above reactions after 5 h (at 1450 °C) is attributable to the generated corundum layer being by that time so thick that it hinders the withdrawal of gaseous products from the reaction fronts, so that the build-up of these products quenches the corresponding reactions. The observed increase in the thickness of the corundum layer as processing temperature rises is attributable to the increased temperature increasing the equilibrium partial pressures of the gaseous reaction products.

4. Conclusions

Heating cordierite to high temperatures in controlled reducing atmospheres results in the transformation of its surface into a layer of corundum that is separated from the underlying cordierite by thinner layers of sapphirine and spinel. Studying the volatility diagrams for the various species involved in this process suggests that the process consists of sequential reduction and vaporization of the less stable components of cordierite (SiO_2 and MgO, in this order). The Al_2O_3 component was left as a layer of corundum particles that, under the conditions used in our experiments, attained a thickness of up to 15 μm and a specific surface area of up to 15 m^2/g.

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