Thermal diffusivity of porous cordierite ceramic burners

E. García, M. I. Osendi, and P. Miranzo

Instituto de Cerámica y Vidrio, CSIC, 28500 Arganda del Rey, Madrid, Spain

(Received 22 January 2002; accepted for publication 28 May 2002)

The applicability of the laser flash method for measuring the thermal diffusivity of highly porous cordierite materials is investigated. Due to the surface roughness of the samples, some indetermination in the sample thickness measurement is produced, which induces errors in the thermal diffusivity calculation. This problem was partially overcome by attaching two thin Cu layers to both surfaces of the samples. The thermal diffusivity and conductivity values of two porous cordierite materials (40 and 50 vol % of porosity) are reported using this procedure and results are discussed comparing with data for three-layer models. © 2002 American Institute of Physics. [DOI: 10.1063/1.1495071]

I. INTRODUCTION

Infrared radiant burners seem to be an efficient and clean way to obtain radiant energy from natural gas.¹ In typical ceramic plate burners, the gas flows through multiple channels or pores² produced intentionally in the material and combustion takes place on the top surface of the plate. When working in radiant mode, the combustion occurs near to the surface of the burner and a steep thermal gradient is usually generated between top ($\sim 800^\circ\text{C}$) and bottom surfaces ($\sim 50^\circ\text{C}$).³ Therefore, the thermal conductivity of the plate material is a key parameter for this type of application. In fact, low values are required to avoid problems of flashback when the thickness of the plate is small. Cordierite-based materials seem to be suitable for these purposes due to their nominally low thermal conductivity.^{4,5}

Different techniques have been employed to measure thermal diffusivity and conductivity of commercial cordierite materials^{4,5} with porosity levels ranging between 10 and 24 vol %. Deviations of 15% were found among the data obtained with the different techniques, which were partly attributed to the testing method but also to the material reproducibility. In particular, the room temperature thermal diffusivities measured by the laser flash method were 0.014 and 0.010 cm^2/s for the 10 and 24 vol % porous cordierites, respectively. These values gave thermal conductivities in the range of 1.5–2.5 W/m K. There is no data in the literature for thermal diffusivity/conductivity of highly porous (more than 30 vol %) cordierite materials.

The laser flash method is a versatile and useful technique to measure thermal diffusivity of materials.⁶ This technique is especially suitable for dense opaque materials, nevertheless, measurements are not totally reliable when materials are transparent to infrared (IR) radiation or have pores, which allow laser radiation to penetrate into the sample. Some authors have addressed this problem assuming a certain penetration of the radiation and numerically correcting heat conduction equations.^{7,8} Here, an alternative method is described to avoid laser radiation penetration into the porous samples, which was applied to samples of porous cordierite ceramic burners. In this way, thin copper layers were attached to

cordierite samples and the thermal diffusivity of the Cu/Cordierite/Cu sandwich structure was appraised using a three-layer model.⁹ The average pore size was an important parameter that was used to correct the experimental data.

II. EXPERIMENT

Two different porous cordierite materials used in honeycomb-type ceramic burners (Morgan Matroc S.A., Spain) were studied. The main characteristics of both materials are shown in Table I. The crystalline phases in material A were mainly cordierite and cristobalite, while in material B, the main phase was cordierite. The density of cordierite B is slightly higher than that of cordierite A. The average pore diameter for both materials is $\sim 100\ \mu\text{m}$ (Fig. 1) and the porosity of material A (50 vol %) is higher than that of cordierite B (40 vol %).

Cylinders of 12.5-mm diameter and 1- and 2-mm thick were machined from both materials using diamond core drills. Two different sample thicknesses were used to verify the reliability of the measurement. The Cu/cordierite/Cu sandwich structures were assembled by placing two opaque-to-light high-purity copper disks (99.9% pure, Goodfellow Ltd.) at both sides of the samples. These disks were 0.05-mm thick and had the same diameter as the cordierite samples. These sandwich structures were heated at 1000°C for 1 h in a vacuum of 1.6×10^{-6} mbar while applying a small pressure, which ensured good contact between the layers. In Fig. 1, a cross-sectional view of this type of structure can be observed.

Diffusivity measurements were carried out by the laser flash method in both monolithic cordierites and the Cu/cordierite/Cu sandwiches. Experiments were done in an Argon atmosphere up to 800°C , using ThermoFlash 2200 equipment (Holometrix-Micromet Inc. Bedford, USA). To prevent direct transmission of the laser radiation through the samples, they were thermally evaporated with a thin gold layer of approximately $0.1\ \mu\text{m}$. The efficiency in radiation absorption and heat emission was increased by coating the sample surfaces with a layer of $\approx 10\ \mu\text{m}$ of colloidal graphite. The experimental data were analyzed by the Clark–

TABLE I. Characteristics of the cordierite materials

		Cordierite A	Cordierite B
Chemical	SiO ₂	65	52
Composition	Al ₂ O ₃	20	35
(wt %)	MgO	15	13
Density (g/cm ³)		0.92	1.04
Open Porosity		50	40
(vol %)			
Pore size range		10–300	10–300
(μm)			

Taylor model and the Koski procedure,^{10,11} both implemented in the equipment software.

Thickness indetermination was estimated on optical micrographs of polished cross sections and the error associated to it was analyzed for type A cordierite using two different thicknesses. This error was also considered for the sandwich structures. The thermal diffusivities of both cordierites were deduced from the effective diffusivity of the sandwich structures by applying a mathematical model implemented in the software by Holometrix.⁹ Data for each condition have been comparatively discussed.

The specific heat (C_p) as a function of temperature was calculated using the polynomial fit proposed by Cabannes and Minges within an international CODATA program aimed to qualify a cordierite-based ceramic as a standard reference material⁴

$$C_p = 0.7327 + 1.946 \times 10^{-3} \times T - 4.261 \times 10^{-6} \times T^2 + 5.889 \times 10^{-9} \times T^3 - 3.459 \times 10^{-12} \times T^4. \quad (1)$$

The thermal conductivity at each temperature was calculated by the expression

$$\lambda = \rho C_p \alpha, \quad (2)$$

where “ ρ ” and “ α ” are the density and the thermal diffusivity of the material, respectively.

FIG. 1. Optical micrograph of the polished cross section of a Cu/cordierite/Cu multilayer structure. P indicates pores, C indicates cordierite, and Cu indicates copper layer.

FIG. 2. Thermal diffusivity from room temperature to 800 °C for cordierite A: (a) monolithic specimens and (b) three-layer structures. Full symbols correspond to the values obtained from the optically corrected thickness.

III. RESULTS AND DISCUSSION

The thermal diffusivity results for the monolithic samples of cordierite A are shown as a function of temperature in Fig. 2(a). Thermal diffusivity differed by more than 40% for the different thicknesses, which is well above the accuracy of the technique (5%) that approximately corresponds to the size of the symbols in the plots (Fig. 2). Therefore, these differences in diffusivity may be attributed to penetration of the laser radiation inside the porous sample, which induces large experimental errors. As the measured sample thickness is higher than the actual value, the diffusivity is overestimated because it depends on the square of the power of the sample thickness.¹² This error should be higher for the thinner sample because the penetration/thickness ratio is larger, which explains the overestimated diffusivity value measured in the thin sample compared with the thick one. This error can be estimated by observing the microstructure of Fig. 1. The larger pores in the sample have an average diameter of $\sim 100 \mu\text{m}$, therefore, the actual thickness must be reduced in $\sim 200 \mu\text{m}$, taking into consideration both surfaces. The values attained correcting for this effect are shown in Fig. 2(a). We note that the values are very similar for the two thicknesses, assuring a greater reliability in the measurements.

Figure 2(b) represents the effective thermal diffusivity for three-layer structures considered as homogenous specimens; data in the plot correspond to two thicknesses of the middle cordierite (type A) layer. Although effective diffusivity in layered structures should depend on the relative thickness of each layer,⁹ this was not observed in our data as they were very similar for the 1- and 2-mm thick cordierite layer specimens. This divergence indicates that the thermal diffusivity data are not representative and that an error in the thickness measurement may still occur. In fact, a bending of the Cu layer into the pores can be observed in Fig. 1. This deflection was estimated in $\sim 44 \mu\text{m}$ and a total decrease in thickness of $88 \mu\text{m}$ should be considered to correct errors in the thickness determination of the sandwich structures. As can be seen from Fig. 2(b), the corrected values were slightly lower than the noncorrected ones and, as expected, depend on the cordierite layer thickness.

In a first attempt, it can be assumed that the Cu layer does not affect the thermal diffusivity of porous samples, but

FIG. 3. Thermal diffusivity between room temperature and 800 °C for cordierites A and B calculated from the three-layer effective thermal diffusivity. Dashed lines correspond to thermal diffusivity data of monolithic samples with the thickness correction due to the pore structure.

would only prevent the laser-beam penetration.¹³ This assumption can be made when the diffusivity of the first and the third layers are very high compared to the middle layer, their thickness is thin compared to the middle layer thickness and when their contribution to the total structure mass is small. In the present case, the first and second assumptions are true but not the third one, due to the low density of both A and B cordierites compared to the density of Cu (8.96 g/cm³). Therefore, a thermal diffusivity model for three-layer configurations⁹ should be considered to analyze the effect of the Cu layers. In this way, the thermal diffusivity of the middle cordierite layer was calculated from the measured effective thermal diffusivity, and data are plotted in Fig. 3. Diffusivity values for cordierite A were similar for the two thicknesses and close to the values for the monolithic samples after applying the thickness correction. Comparing data of Figs. 2 and 3, it can be said that the porosity and surface roughness effects are less critical for the thicker samples.

The three-layer configuration can be used to measure the thermal diffusivity of highly porous samples, ≥ 40 vol %, by the laser flash method using the procedure described above. In the case of samples with high roughness associated with a coarse porosity, a less ductile metal that does not bend into the pores may be used to avoid thickness corrections.

Thermal diffusivity results for cordierite B using the precedent three-layer procedure are also depicted in Fig. 3. The higher diffusivity of this material compared to cordierite A is consistent with its lower porosity (Table I), although its different phase composition should also be taken into account. For both materials, the thermal diffusivity decreased with temperature up to 500 °C while showing a steady increase at higher temperatures. This increase at higher temperatures may be due to the high porosity of these samples (≥ 40 vol %), which leads to heat transfer by gas convection and radiation at high temperatures.¹⁴ This affect was more pronounced for the thicker samples because heat losses also increased by a “flash-by” effect. In this case, the background temperature of the back surface increased because heat flew by the sides of the sample instead of through it. Experimentally, this effect was demonstrated by an initial step in the temperature-time curves that distorted the diffusivity value.

The thermal conductivities calculated from expression (2) using the thermal diffusivity data of Fig. 3 are plotted in

FIG. 4. Thermal conductivity as a function of temperature for cordierites A and B in the range room-temperature 800 °C.

Fig. 4. Thermal conductivity of cordierite A (~ 0.4 W/m K) was 33% lower than that of cordierite B (~ 0.6 W/m K). The difference between both cordierites in porosity alone (≈ 10 vol %) cannot justify this difference in the thermal conductivity values and therefore, the difference in composition (Table I) may be important. To get an idea of the effect of the cristobalite in the composition we can assume that cordierite B is pure and that cordierite A has a 33 vol % of cristobalite.

Santos *et al.*¹⁵ reported a room temperature thermal diffusivity of 0.002 cm²/s for a 95% dense cristobalite material that means a thermal conductivity of 0.34 W/m K considering a specific heat of 0.74 J/g °C.¹⁶ On the other hand, Neuer *et al.*⁵ gave a room temperature thermal conductivity of dense cordierite of 2.5 W/m K. Introducing both conductivity data in the Maxwell equation,¹⁷ the effective thermal conductivity of a dense material composed of 67 vol % of cordierite and 33 vol % of cristobalite as dispersed phase should be around 1.6 W/m K. Therefore, the thermal conductivity at room temperature of dense cordierite-cristobalite composition would be reduced by 36% compared to a dense pure cordierite. As we are dealing with cordierite-based materials with porosities ≥ 40 vol %, the solid phase is hardly continuous and the reduction in thermal conductivity of 36% attributed to the difference in composition of the solid phase should be dimmed. A rough estimation could be given by applying the reduction to the percentage of solid phase (50 vol %) which will give a 18% reduction in the thermal conductivity of cordierite A compared to cordierite B.

The thermal conductivity values measured for both porous cordierites are much lower, $\sim 80\%$, than those reported for denser cordierite materials (porosity < 25 vol %)^{4,5} and, furthermore, they are almost independent of temperature for the typical working range in burner applications.

IV. CONCLUSIONS

The laser flash technique is adequate for measuring the thermal diffusivity of materials with high porosity (~ 50 vol %) and coarse pores (> 100 μ m) by applying the appropriate corrections and models. Three-layer structures formed by two layers of a high-diffusivity material attached to both sides of the porous specimen have been proved to give reliable values of thermal diffusivity for this type of material.

The thermal conductivity of highly porous (>40 vol %) cordierite-based burners was almost constant and below 1 W/m K in the range of possible working temperatures.

ACKNOWLEDGMENTS

This project has been funded by the EC (Brite-EURAM III Program) under Contract No. BR-CT98-0743 (LIFE-BURN Project) and by Mcyt (ES) Project Nos. MAT99-0168-CE and 2FD97-0345-C02-01. The partners to the LIFE-BURN Project are N.V. Acotech SA, CATIM, CSIC-ICV, EcoCeramics BV, Eindhoven University of Technology, Gaz de France, Ikerlan, INETI, Italgas, Kanthal AB, Morgan Matroc SA, N.V. Nederlandse Gasunie, Politecnico di Torino, Repsol Petroleo SA, and Worgas Bruciatori Srl.

¹L. Ticó, *Global Ceramic Review* **4/98**, 12 (1998/99).

²J. K. Kilham and E. P. Lanigan, *Gas Council Research Communication GC167*, Institution of Gas Engineers Journal, **10**, 700 (1970).

³P. H. Bouma, Ph.D. Thesis, Eindhoven University of Technology, 1997.

⁴F. Cabannes and M. L. Minges, *High Temp.-High Press.* **21**, 69 (1989).

⁵G. Neuer, R. Brandt, K. D. Maglic, N. Milosevic, G. Groboth, and S. Rudtsch, *High Temp.-High Press.* **31**, 517 (1999).

⁶G. S. Sheffield and J. R. Schorr, *Ceram. Bull.* **70**, 102 (1991).

⁷K. Inoue, *Trans. JWRI* **20**, 35 (1991).

⁸M. Golombok and L. C. Shirvill, *J. Appl. Phys.* **63**, 1971 (1988).

⁹T. R. Lee, Ph.D. Thesis, Purdue University, 1977.

¹⁰L. M. Clark and R. E. Taylor, *J. Appl. Phys.* **46**, 714 (1975).

¹¹J. A. Koski, *Proceedings of the Eighth Symposium on Thermophysical Properties*, Gaithersburg, Maryland (ASME, New York, 1982) Vol. II, pp. 94–103.

¹²W. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbot, *J. Appl. Phys.* **32**, 1679 (1961).

¹³E. García, R. Martínez, M. I. Osendi, and P. Miranzo, *Bol. Soc. Esp. Ceram. Vidrio* **40**, 289 (2001).

¹⁴E. Litovsky, M. Shapiro, and A. Shavit, *J. Am. Ceram. Soc.* **79**, 1366 (1995).

¹⁵W. N. Santos, J. B. Baldo, and R. Taylor, *Mater. Res. Bull.* **35**, 2091 (2000).

¹⁶*Engineered Materials Handbook, Vol. 4: Ceramics and Glasses* (ASM International, Metals Park, OH, 1991).

¹⁷J. C. Maxwell, *Treatise on Electricity and Magnetism* (Dover, New York, 1954) Vol. I pp. 435–441.