Photothermal characterization of refractories for the steel industry

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Abstract

The companion paper ("Non-destructive Characterisation of Refractories by Mirage Effect and Photothermal Microscopy", by G. Savignat, P. Boch, L. Pottier, D. Vandembroucq, and D. Fournier, in the same EUROMAT meeting) has explained the potential of photothermal techniques for the non-destructive evaluation of refractories. The present study gives photothermal data for three sorts of refractories: carbon bonded alumina, aluminium nitride / boron nitride bonded alumina, and carbon-bonded magnesita. The mirage effect and the photothermal microscopy are shown to be complementary methods, able to bring information about both macroscopic and microscopic thermal diffusivity.

Introduction

For an optimal use, refractories should be characterised with great precision. However, most of the characterisation studies are difficult for those porous, multiphase, and heterogeneous materials, in particular when the properties under investigation are thermal properties.

At a macroscopic scale, materials parameters such as the bulk thermal diffusivity and average thermal expansion of the refractory control the temperature map in the lining and determine the level of thermal stresses. At a microscopic scale, parameters such as the local thermal conductivity and anisotropic, heterogeneous thermal expansion of the constituent phases control the thermal mismatch along interfaces and determine the extent of microcracking along grain boundaries. It is a reason why thermal parameters, in particular thermal diffusivity, should be measured at both the macroscopic scale and the microscopic scale.

As indicated in the companion paper in ref. [1], photothermal techniques offer great potential to characterise refractories in a non destructive manner. The mirage effect and the photothermal microscopy are complementary techniques because they apply to different scales for the investigated area. Three sorts of refractories for the iron and steel industry have been studied : carbon bonded alumina, aluminium nitride / boron nitride bonded alumina, and carbon bonded magnesita.

1 Refractories

1-1 Carbon bonded alumina

Oxide aggregates are mainly alumina (≈ 65 wt% of the total), with also silica (≈ 10 wt%), mullite, and zirconia. The dimensions of aggregates vary from 1 to 700 μm . The bonding consists of amorphous

carbon (≈ 5 wt%) produced from pyrolysis of an organic resin, with addition of graphite flakes (≈ 20 wt%) to improve thermal properties. The flakes are typically $15\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$ wide and $100\text{ }\mu\text{m}$ to $1000\text{ }\mu\text{m}$ long. The apparent density of the refractory is $\approx 2600\text{ kg/m}^3$ and porosity is $\approx 16\%$.

1-2 Aluminium nitride / boron nitride bonded alumina

The material contains ≈ 75 wt% of alumina and ≈ 16 wt% of aluminium nitride and ≈ 8 wt% of boron nitride. The dimensions of alumina aggregates vary from a few μm to a few mm. The nitride bonding increases global thermal conductivity. Apparent density is $\approx 3000\text{ kg/m}^3$ and porosity is $\approx 13\%$.

1-3 Carbon bonded magnesia

Carbon bonded magnesia contains ≈ 85 wt% of magnesia as aggregates whose size ranges from $100\text{ }\mu\text{m}$ to a few mm. The bonding consists of amorphous carbon (≈ 5 wt%) resulting from pyrolysis of an organic resin. A graphitisation treatment (≈ 10 wt% of graphite) improves thermal behaviour. Density is $\approx 3000\text{ kg/m}^3$ and porosity is $\approx 3\%$.

2 - Determination of thermal diffusivity

Thermal diffusivity (α) is involved for heat diffusion in non steady state conditions. It is related to thermal conductivity k (W/m.K), density ρ (kg/m^3), and specific heat C_p (J/kg.K) by the following relation:

$$\alpha = k/(\rho \cdot C_p)$$

Thermal diffusivity is sensitive to the presence of microstructural defects such as pores, inclusions, or microcracking, which implies that its determination at the microscopic scale can bring information on microstructure.

Some thermal diffusivity data found in literature are given in Table 1.

Aggregate	Diffusivity (20°C) ($10^{-4}\text{ m}^2/\text{s}$)	Bonding	Diffusivity (20°C) ($10^{-4}\text{ m}^2/\text{s}$)
Al_2O_3	0.17 [2] / 0.10 - 0.06 [3]	AlN	0.16 [2] / 0.63 [3]
MgO	0.19 [2] / 0.12 - 0.06 [3]	BN	0.44 [2] / 0.9 [3]
Other oxides	< 0.05 [2]	Graphite ($\perp$ to c axis)	1.33 [2] / 2.5 [3]

Table 1 : Thermal diffusivity at 20°C of constituent materials.

2-1 Mirage effect experiments

Both carbon bonded alumina and nitride bonded alumina were investigated using the mirage effect.

Carbon bonded alumina

Figure 1a shows a typical signal obtained when recording the transverse phase variation induced by modulated heating, as a function of the relative position of the probe beam and the heating beam. Experiments were done for various heating frequencies, as shown in figure 1b. The experimental value found for α depends on frequency. It is of about $1.2 \cdot 10^{-5}\text{ m}^2/\text{s}$ when the heating frequency is of 15 Hz and of about $4.0 \cdot 10^{-5}\text{ m}^2/\text{s}$ when the frequency is of 430 Hz.

Figure 1a: Experimental diffusivity of a refractory C-Al₂O₃ measured at 15 Hz.

Figure 1b: Thermal diffusivity vs. heating frequency (various symbols correspond to various positions on the sample surface).

Nitride bonded alumina

A typical signal shows is similar to that for carbon bonded alumina (Figure 2a). The experimental values of thermal diffusivity vary from $8 \cdot 10^{-6}$ m²/s for a heating frequency of 3 Hz to $4.0 \cdot 10^{-5}$ m²/s for a frequency of 330 Hz.

Figure 2a: Experimental diffusivity of a refractory (AlN,BN)-Al₂O₃ measured at 3 Hz.

Figure 2b: Thermal diffusivity vs. heating frequency (various symbols correspond to various positions on the sample surface).

For an homogeneous materials, thermal diffusivity does not depend on heating frequency. In the present case, the sensitivity of thermal diffusivity to frequency is due to heterogeneity. A low frequency leads to a value which is an average on a large volume whereas a high frequency leads to a value which characterises a small volume. The larger the difference in thermal diffusivity of every constituent phase, the higher the sensitivity to frequency.

2-2 Photothermal microscopy experiments

Experiments were restricted to carbon bonded magnesia materials. In order to obtain a sufficient reflectivity, a gold layer (300 nm thick) was deposited on the sample surface. The photothermal

microscope allows measurement at a microscopic scale and it was, therefore, applied to the determination of the thermal diffusivity of magnesia grains.

Figure 3a shows the result obtained for a scanning of 12 μm . The experimental thermal diffusivity is $9.5 \pm 1.4 \cdot 10^{-6} \text{ m}^2/\text{s}$, which is in good agreement with literature data. To go farther, a scanning was done with the probe beam and the heating beam being kept co-axial. The phase variations and the direct component of the reflected probe beam were recorded versus the beam positions (figure 3b). The geometrical line that was investigated was drawn across the carbon bonding. It was 6.5 μm long and it was chosen in such a way that it intersects a graphite flake.

When imaged using optical microscopy, the two sides of the graphite flake show a similar contrast. However, phase variations of the photothermal signal indicate that those two sides do not behave the same manner (figure 3b) and they allow us to detect the existence of a thermal barrier at the interface.

Figure 3a: Thermal diffusivity of MgO grains.

Figure 3b: Detection of a thermal barrier within the carbon bonding (phase variation and direct component of photoreflected signal).

Conclusion

The mirage effect allows us to investigate areas of $\approx 1 \text{ mm} \times 1 \text{ mm}$. The extent of the zone affected by thermal waves depends on heating frequency and, as a consequence, the experimental diffusivity of an heterogeneous and porous refractory is found to be a function of heating frequency. The photothermal microscopy allows us to investigate areas of $\approx 10 \mu\text{m} \times 10 \mu\text{m}$. It can be used to detect the presence of local thermal barriers. A study is currently going under view to compare photothermal images with other microscopic images (given by optical microscopy and scanning electron microscopy).

References

- [1] G. SAVIGNAT, P. BOCH, L. POTTIER, D. VANDEMBROUCQ, and D. FOURNIER, "Non-destructive Characterisation of Refractories by Mirage Effect and Photothermal Microscopy", EUROMAT-93, Paris, June 1993.
- [2] S.C. CARNIGLIA, G.L. BARNA, *Handbook of Industrial Refractories Technology, Principles, Types, Properties and Applications*, NOYES PUBLICATIONS (1992) 367-404
- [3] R. MORRELL, *Handbook of Properties of Technical & Engineering Ceramics, Part 1* (1989) 90-91
- [4] Ed. R.J. BROOKS, *Concise Encyclopedia of Advanced Ceramic Materials*, PERGAMON PUBL. (1991) 367-400