

Microstructural investigation and thermal shock behaviour of mullite-cordierite refractory materials

C. Leonelli, D. N. Boccaccini, M. Romagnoli, P. Veronesi, I. Dlouhy*, A. R. Boccaccini**

*Dipartimento di Ingegneria dei Materiali e dell'Ambiente,
Università di Modena e Reggio Emilia, Italy*

**Institute of Physics of Materials, ASCR, Brno, Czech Republic*

***Department of Materials, Imperial College London, UK*

ABSTRACT

The influence of the mineralogical composition and phase distribution on crack initiation and propagation in cordierite-mullite refractory materials used in fast firing of porcelain whiteware is investigated. Two different refractory compositions, characterised by different silica to alumina ratios, were studied. Propagation of cracks introduced by Vickers' indentations was observed by scanning electron microscopy. Chemical analysis by EDS was used for phase identification together with X-ray diffraction analysis. Thermal and mechanical properties were determined by means of standard laboratory techniques. The fracture toughness of selected samples was measured by the chevron notched specimen technique. Preliminary assessment of thermal shock resistance was obtained by water-quenching tests from 1250°C. Microstructural features and crack propagation behaviour were correlated and used to draw conclusions on the behaviour of the two different refractory compositions under thermal shock.

1. INTRODUCTION

Cordierite-mullite composites find increasing applications as refractories in the context of recent developments in fast-firing techniques of ceramic products [1]. These refractories exhibit in general a complex microstructure characterised by crystalline phases of different thermal expansion coefficients and elastic moduli and a residual silicate glassy phase. There is a current lack of understanding about the effect of microstructural features, including residual thermal stresses, on the overall performance of the materials at high temperature and under thermal shock conditions.

Many authors have proposed thermal resistance parameters to characterise the thermal shock behaviour of refractory materials [2-5]. These parameters can be calculated using thermal and mechanical properties of refractories measured at room temperature. It has been demonstrated [6] that the sensitivity to thermal shock damage of many refractory materials decreases as temperature increases. This suggests that the evaluation of thermal shock parameters based on properties measured at room temperature is probably an efficient (cost effective) procedure in determining the smallest difference between different refractory materials under thermal shock.

The aim of this work is to investigate the microstructure and microcrack propagation behaviour at room temperature and to correlate them with the observed thermal shock behaviour when refractory plates are subjected to actual duty cycles. Two different types of refractory plates were chosen, one exhibiting a fast microcrack propagation behaviour and the second showing early microcrack formation, but delayed microcrack propagation. Thermal shock tests by the water quenching method were carried out and the relevant mechanical properties measured on samples after each number of thermal shock cycles.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and microstructural characterisation

The two commercial plates (hereafter indicated as REFO and CONC) used for this work are made of cordierite-mullite refractory mixtures, REFO material being richer in SiO₂ by 5 wt% with respect to CONC material. X-ray diffraction (XRD) analyses were carried out on powdered samples to determine the mineralogical composition of the two materials: the cordierite to mullite weight ratio is equal to 50:45 in REFO and 50:50 in CONC material. Microstructure and crack propagation observation were determined by means of scanning electron microscopy (SEM) (PHILIPS XL 40) equipped with Energy Dispersion X-ray fluorescence Spectroscopy, EDS, (X_EDS INCA, Oxford Inst.) on polished sections after gold coating. Microcracks were created by means of high load (500-1000 g) Vickers' indentations (REMET HX 1000) on polished surfaces.

2.2. Testing procedure

Seven samples, 20x5x40 mm³, were cut from the plates of each refractory material and heated at 10 °C min⁻¹ up to the on-duty temperature of the refractories (1250°C) and maintained at 1250°C for 30 min to attain thermal equilibrium. After each water quenching test, Young's modulus, shear modulus and Poisson' ratio of the samples were determined by the impulse excitation technique (Grindosonic MK5, J.W. Lemmens, Belgium). Then they were subjected to three point bending test for flexural strength determination. The thermal expansion coefficients of the two refractories were determined using a high temperature dilatometer (Netzsch 402 EP, Selb, Germany). The fracture strength of the samples was determined at room temperature after samples had been subjected to a given number of thermal shock cycles. Tests were carried out in three-point bending using a 25 mm span and a cross-head speed of 1 mm/min.

Fracture toughness was determined by the chevron notch technique at room temperature. Specimens in the form of bars were cut from non thermally shocked plates in the dimensions 4x3x16 mm³. Chevron notches with angles of 90° were cut using a thin diamond wheel. The specimens were loaded in three-point bending (span of 16 mm) at a constant cross-head speed of 0.01 mm/min. Each bar with notches was then placed in the three-point bend fixture and loaded up to fracture initiation.

Graphs of load versus deflection were recorded and the fracture toughness was calculated from the maximum load (F_{max}) and the corresponding minimum value of geometrical compliance function (Y_{min}^*) using the equation [7]:

$$K_{Ic} = \frac{F_{max}}{BW^{1/2}} Y_{min}^* \quad (1)$$

where B and W are the width and height of the specimens, respectively. The calculation of the function Y_{min}^* for chevron notched bending bars was based on Bluhm's slice model [8]. SEM was used to characterise fracture surfaces of materials after the fracture strength tests and after chevron notched specimens tests.

3. RESULTS AND DISCUSSION

3.1 Microstructure and crack propagation behaviour

The microstructures of REFO and CONC materials were observed by SEM on polished cross sections. REFO samples exhibit a less dense microstructure than CONC samples, with large and well defined grains not connected by any amorphous continuous phase. In both materials pores are not spherical, indicating an early stage of sintering, as discussed elsewhere [1,9].

The observed crack propagation behaviour should have direct implications in the different room-temperature mechanical behaviour and different thermal shock resistance exhibited by the REFO and CONC materials. REFO samples show convenient crack propagation behaviour at room temperature because the diffuse microcracking of the α -quartz grains may act as an efficient toughening mechanism [9-11]; whilst CONC samples show easier crack propagation due to the large glassy (structureless) phase present. However, at high temperature, this glassy phase in the CONC refractory microstructure should become viscous, and it could fill or blunt the propagating microcracks (Figures 1 and 2). This mechanism should explain the superior thermal shock behaviour of CONC refractories, as demonstrate by the mechanical and thermal property curves against number of quenches.

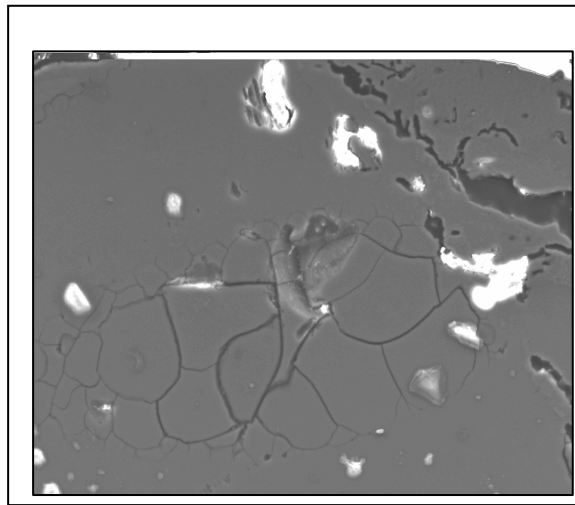


Figure 1: High-magnification SEM image of crack propagation in a REFO sample.

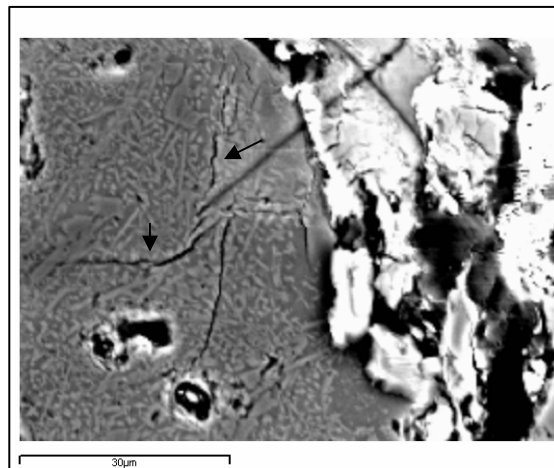


Figure 2: SEM image of a CONC sample with induced microcracks.

3.2 Thermal shock behaviour

It is well-known that the effect of the Young's modulus of elasticity (E), the tensile strength (σ), and Poisson's ratio (ν) are opposite for crack initiation versus crack propagation under thermal shock [12]. Low E and ν with high σ provide high resistance to propagation of existing cracks.

The influence of water quenches on the mechanical and thermal properties of both refractory materials have been investigated in this study. It was found that the values of Young's modulus are slightly reduced by only 7 thermal shock cycles, being REFO the composition more affected (Figures 3 and 4).

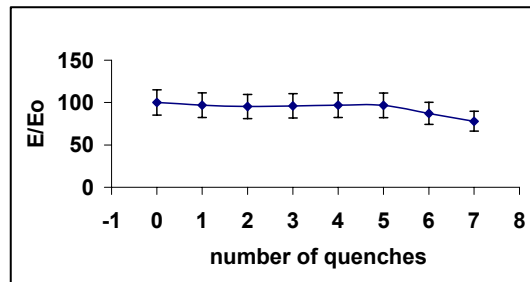


Figure 3: Relative Young's modulus against number of thermal shock cycles for REFO samples (water quenching from 1250°C).

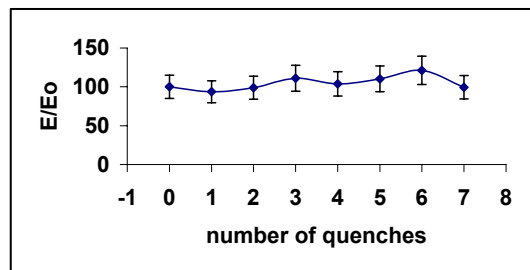


Figure 4: Relative Young's modulus against number of thermal shock cycles for CONC samples (water quenching from 1250°C).

The fracture strength values of the composites before water quenching test were found to be very close: 62 MPa for the REFO material and 60 MPa for the CONC sample. However, the fracture strength of the CONC material is slightly higher after seven thermal shocks: 51 MPa against 42 MPa for the REFO material.

The thermal shock resistance parameter R has been calculated following equation:

$$R = \frac{\sigma \times (1 - \nu)}{\alpha \times E}$$

where α is the thermal expansion coefficient. Values measured of σ , E and ν after each quenching cycle were used whereas α was the as-received value.

Due to the wide variability of the fracture strength values as a result of the heterogeneous microstructure of these materials, and taken into account that both refractories have a very similar microstructure [9], the thermal shock resistance parameter (R) obtained from measured property data is not “sensitive” enough to be able to differentiate the different thermal shock behaviour of these refractory materials.

An hypothesis is being put forward regarding the use of fracture toughness data, measured by the chevron notched specimen technique, as indicators of thermal shock damage after different number of thermal shock cycles, as proposed in the literature for composite materials [13,14].

In the present study, the toughness of the CONC refractory plate was measured to be in the range 0.332 to 0.468 MPam^{1/2}, the mean value being $K_{IC} = 0.405$ MPam^{1/2}. The values of the REFO material are in the interval 0.304 to 0.336 MPam^{1/2}, with the mean value being $K_{IC} = 0.348$ MPam^{1/2}. How K_{IC} values change after different number of quenching cycles should give indication of the different thermal shock behaviour of the samples, this being the subject of current studies.

4. CONCLUSION

Two refractory materials of commercial origin denominated REFO and CONC, which have wide industrial application in kilns for fast firing cycles of porcelain articles, were investigated in terms of microstructure and microcracking behaviour. The different microcrack propagation mode observed in the two materials can be explained on the basis of their different microstructure. The presence of the glassy phase in the CONC samples should result in better high-temperature fracture toughness of the CONC material. The different microcrack propagation behaviour of REFO and CONC materials should explain also their different thermal shock resistance. However, determination of thermal shock resistance parameters from measured property values cannot be used to differentiate the two materials regarding their thermal shock behaviour. Therefore an hypothesis is being tested considering that the different microstructural damage caused by thermal shock in the materials and even the progressive damage originated in one material with increasing number of quench experiments, can be better evaluated by fracture toughness measurements. If successfully proven, this procedure should allow predicting which material will exhibit higher thermal shock resistance under on-duty industrial conditions.

REFERENCES

- [1] V. Cannillo, C. Leonelli, M. Montorsi, M. Romagnoli, P. Veronesi, Experimental Results and Numerical Modelling of the Fracture Behaviour of Ceramic Refractory Plates, *Tile & Brick Int.* Vol. 5 (2003) 324-327.
- [2] D. P. H. Hasselman, Unified theory of thermal shock fracture initiation and crack propagation in brittle ceramics, *J. Am. Ceram. Soc.* 46 (11) (1969) 600-604
- [3] D. P. H. Hasselman, Elastic energy at fracture and surface energy as design criteria for thermal shock, *J. Am. Ceram. Soc.* 46 (11) (1963) 535-540
- [4] J. Nakayama, Direct measurements of fracture energies of brittle heterogeneous materials, *J. Am. Ceram. Soc.* 48 (11) (1965) 583-587
- [5] J. Nakayama, M. Ishizuka, Experimental evidence for thermal shock damage resistance, *Am. Ceram. Soc. Bull.* 45 (7) (1965) 666-669

- [6] J. A. Rodrigues, V. C. Pandolfelli, M. Rigaud, Elevated Temperature Thermal Shock Parameters for Refractories, *Interceram* 51 (5) (2002) pp 322-326.
- [7] A. R. Boccaccini, R. D. Rawlings, I. Dlouhý, Reliability of the chevron-notch technique for fracture toughness determination in glass, *Mat. Sci. Eng.* A347 (2003) 102-108.
- [8] I. Dlouhy, M. Holzmann, J. Man, L. Valka, The Use of Chevron Notched Specimen for Fracture Toughness Determination, *Metal. Mater.* 32 (1994) 3-13.
- [9] D. N. Boccaccini, C. Leonelli, M. R. Rivasi, M. Romagnoli, A. R. Boccaccini, Microstructural investigations in cordierite-mullite refractories, *Ceramics Int.* (2004), in press.
- [10] C. Leonelli, F. Bondioli, P. Veronesi, V. Cannillo, M. Romagnoli, T. Manfredini, G.C. Pellacani, Enhancing porcelain stoneware tiles mechanical properties: a microstructural approach, *J. Europ. Ceram. Soc.*, **21** [6] (2001) 785-793.
- [11] C. Leonelli, P. Veronesi, V. Cannillo, G. C. Pellacani, A. R. Boccaccini, Porcelainized Stoneware as a Composite Material: Identification of Strengthening and Toughening Mechanisms, *Tile and Brick Int.* 17 (2001) 238-245.
- [12] Richerson D. W. *Modern Ceramic Engineering* 2nd Ed. Marcel Decker Inc., 1992, New York, pages 361-368.
- [13] A. R. Boccaccini, H. Kern, I. Dlouhy, Determining the Fracture Resistance of Fibre Reinforced Glass Matrix Composites by Means of the Chevron-Notched Flexural Technique, *Mat. Sci. Eng.* A308 (2001) 111-117.
- [14] A. R. Boccacini, J. Janczak-Rusch, I. Dlouhý, Thermal Aging Behavior of an SiC-fiber Reinforced Glass Matrix Composite in a Non-oxidizing Atmosphere, *Mat.Chem. Phys.* 53 (1998) 155-164.