FRACTURE BEHAVIOUR OF REFRACTORY CERAMICS AFTER CYCLIC THERMAL SHOCK

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Two commercially available refractory ceramic materials primary used as substrates for fast firing of porcelain stoneware were investigated. The first one, commercially known as CONC, contains cordierite and mullite in the ratio 50:50. The REFO refractory composite material with coarser microstructure compared to CONC has a cordierite-to-mullite ratio of 50:45 and the balance is filled by quartz. Both materials were exposed to water-quench tests from 1250°C, applying various numbers of thermal cycles (shocks). Subsequently the fracture toughness was evaluated on both as-received and shocked samples using the Chevron notched specimen technique. The results were analysed with respect to the microstructure damage caused by the thermal loading. Scanning electron microscopy was used to analyse both microstructure and fracture surfaces in samples with different thermal loading history.

INTRODUCTION

Reliability and long service life are the basic requirements when materials are introduced into their operational life. In order to achieve successful performance a suitable combination of physical, chemical and mechanical properties is needed. In the case of ceramic materials under mechanical and thermal loads the situation is complicated due to their low fracture resistance. However there are applications where exclusively such materials can be used. The typical example are refractory materials that are used broadly in many industrial branches [1]. In this case thermal stability and acceptable thermal shock resistance together with satisfactory mechanical properties are the key requirements on the material. To meet these demands composite materials are developed. The design of ceramic-based composite materials leads to the development of multi-component systems where each constituent has a specific function in the material. Examples of such composite systems are the cordierite-mullite refractory materials investigated in a number of investigations [2-5].

Cordierite and mullite are ceramic materials suitable for high temperature refractory components with good chemical resistance [3, 6]. Their target application is in furnaces for use at temperatures >1000 °C. Cordierite has a superior thermal stability, thermal shock resistance and low thermal expansion coefficient. On the contrary the mechanical properties are rather inferior and are the limiting factor for some of the envisaged applications [7]. Mullite has superior mechanical properties at both room and elevated temperatures but its thermal shock resistance is low and the thermal expansion coefficient is higher comparing to cordierite. An overview of typical basic properties of cordierite and mullite is given in table 1. The ceramic multi-component composite material could exhibit the advantages of its constituents when the components have optimised properties and they are mixed in the proper ratio.

Notwithstanding the promise of enhanced performance of cordierite-mullite refractories for fast firing applications [4], there is a current lack of understanding concerning the effect of microstructural features on the overall performance of the cordierite-mullite refractory composite, especially under severe in-service conditions, i.e. at elevated temperatures and under thermal shock loading [5].

Two commercially available systems of cordierite-mullite refractory materials have been evaluated in this paper. In particular, the materials were subjected to repetitive thermal shocks by the water-quench technique and subsequently the fracture toughness was evaluated using a Chevron notched specimen technique accompanied by an acoustic emission measurement monitoring crack propagation. The aim of the paper was to investigate fracture behaviour of both refractory materials tested, mainly from point of view of material constituent's effect on damage and crack development upon thermal shock loading.

EXPERIMENTAL

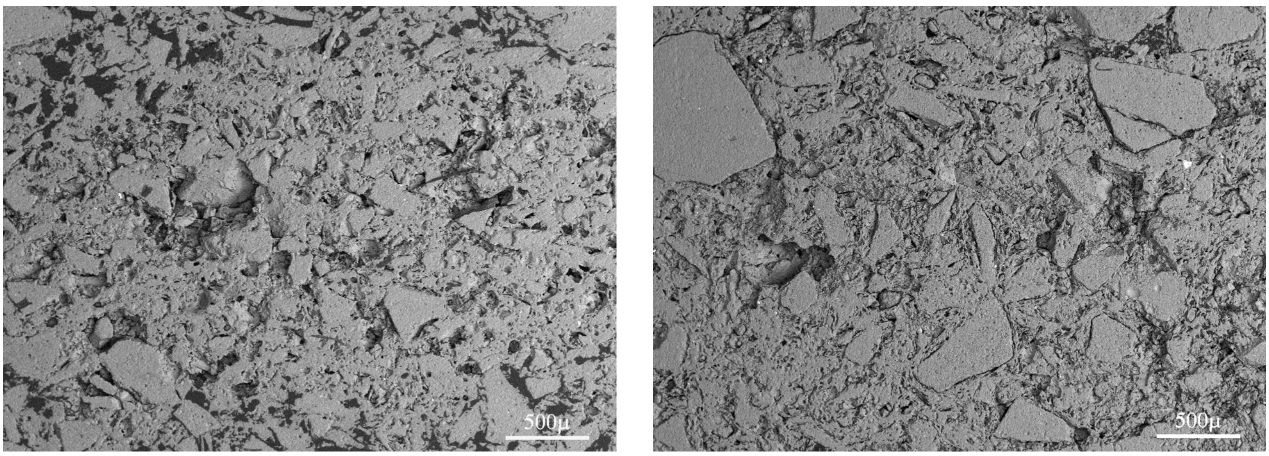
Two commercially available refractory ceramic composite materials known as CONC and REFO (in plate form) were selected for the investigation. The first one was the fine grained CONC composite having cordierite/mullite composition in ratio 50:50 and the second one was the coarse grained REFO composite formed by 45 wt.% of cordierite, 50 wt.% of mullite and 5 wt.% of SiO_2 in the quartz form. The density of the composite in the bulk form was determined for CONC on the level of 1.8947 g/cm^3 and for REFO on the level of 1.8781 g/cm^3, which leads to porosity of 28 % and 26 %, respectively. The porosity measurements were confirmed by the SEM micrographs analysis using an Image Pro Plus software. The microstructure of as-received materials is shown in figure 1. There is no visible difference between cordierite and mullite due to similar chemical composition, however it was detected by detailed analysis that bigger grains (white in daylight) are mullite grains and the smaller grains (brown in daylight) belong to cordierite, the detailed microstructural investigation of these materials was published elsewhere [5].

Suitable samples for thermal shock tests by quenching of dimensions 20×5×40 mm were cut from the plates and subjected to various numbers of thermal shock cycles. Each thermal shock cycle consisted of several consequent steps. Slow heating up by a nominal heating speed of 10°C/min to the quench temperature set at 1250°C, holding at this temperature for 30 minutes to reach thermal equilibrium in the whole specimen volume and finally quenching into a water bath at temperature of 25°C. Samples of both CONC and REFO materials were thermally cycled up to 30 cycles.

Subsequently both as-received and thermally shocked samples were cut by a precise diamond saw to the shape of bars with rectangular cross-section of 3×4 mm recommended for fracture toughness test by ASTM standard [10]. The Chevron Notch Technique was used for fracture toughness determination. Three Chevron Notches with top angle of 90° were introduced into each bar using an ultra thin diamond blade by using a precision saw Isomet 5000. This technique was applied to achieve the best utilisation of the available material. The reliability of this approach was described elsewhere [11, 12]. A universal testing system Instron 8862 equipped with three point bend test fixtures with

Table 1. Typical values of selected properties of dense constituents used in refractory materials investigated [8, 9].

	Cordierite	Mullite	α-Quartz
Chemical Formula	$2MgO\text{-}2Al_2O_3\text{-}5SiO_2$	$3Al_2O_3\text{-}SiO_2$	SiO_2
Density (g/cm^3)	2.60	2.80	2.65
Modulus of Elasticity (GPa)	70	150	70
Poisson's Ratio	0.21	0.25	0.17
Compressive strength (MPa)	350	551	650
Tensile strength (MPa)	25.5	103.5	48
Bending strength (MPa)	117	170	80
Fracture Toughness ($MPam^{1/2}$)	-	2	-
Linear Thermal Expansion Coefficient (10^{-6} K^{-1})	1.7	5.3	0.45
Thermal Shock Resistence (°C)	500	300	1400



a) b)

Figure 1. Typical SEM microstructures of CONC (a) and REFO (b) materials (backscattered electron images).

span of 16 mm was used to apply the loading. A cross-head speed of 10 μm/min was used in all tests to achieve slow crack propagation during loading. An inductive extensometer was used for deflection measurement and force-deflection curves were recorded. Monitoring of fracture behaviour, mainly crack initiation and subsequently propagation during loading was performed by acoustic emission measurement. The fracture toughness values were calculated from the maximum force evaluated from the force-deflection curve and the specimen dimensions by the following equation:

$$K_{IC} = \frac{F_{\max}}{B\sqrt{W}} Y^{*}_{\min}$$

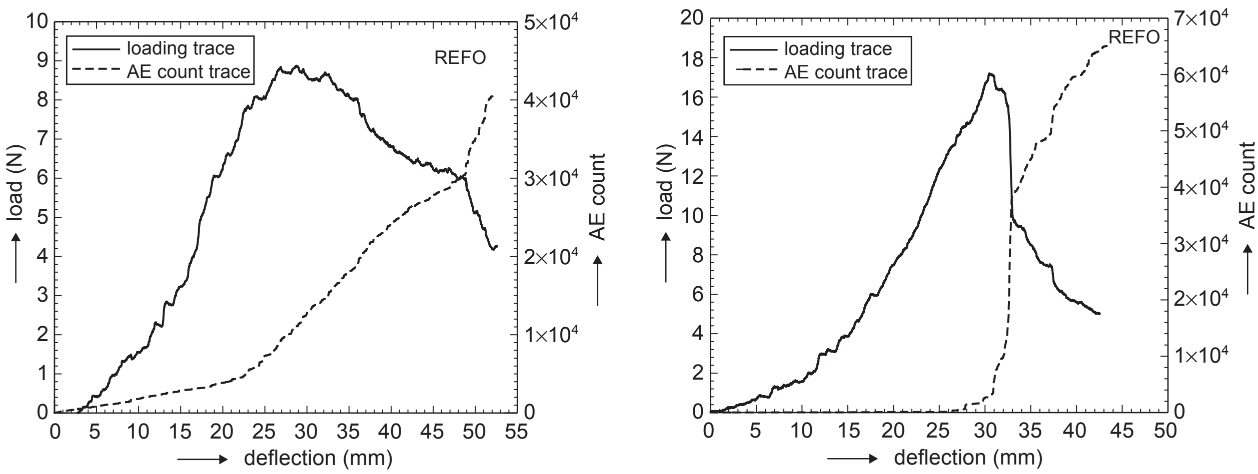
where $Y^{*}_{\min}$ is the minimum of geometrical compliance function Y^{*}. In this work a calculation of the geometrical compliance function based on the Bluhm's slice model was used [13], the details of the applied procedures have been described elsewhere [14].

Scanning electron microscopy was employed for both microstructural and fractographical analyses. These analyses facilitate the explanation of fracture behaviour of each material under investigation in the context of microstructural changes caused by cyclic thermal shock.

RESULTS AND DISCUSSION

The experimental materials used in this investigation were characterised from the point of view of their thermal shock resistance. As-received as well as thermally loaded samples after 7, 15 and 30 thermal shocks were compared. The fracture toughness as a possible criterion for quantifying microstructural damage caused by the cyclic thermal shock loading was investigated in this contribution. The Chevron Notch Technique together with an acoustic emission measurement was used to achieve this aim. A typical example of a loading trace suitable for fracture toughness determination is shown in figure 2a, where the full line represents the recorded force-deflection data and the dashed line indicates the cumulative number of acoustic emission counts (events) in the corresponding deflection (time) scale. Figure 2b is an example of an invalid loading trace due to the absence of slow crack propagation (possibly due to geometrical and/or microstructural reasons) for the REFO material.

A smooth maximum force necessary for fracture toughness determination did not occur in the loading trace and therefore the fracture toughness value would not be valid. It is evident from the fractographical analysis of fracture surfaces that in this case a large round mullite grain was placed in the vicinity of the Chevron tip. This grain most probably stopped the initiated crack and crack propagation continued trough the grain boundary after sufficient accumulation of elastic energy. The overestimated fracture toughness value of this sample would be 0.56 $MPam^{0.5}$ which is nearly 45 % above the average of the data set for 7 thermal shocks (see below). Even from the curve of cumulative AE counts it is evident that no crack propagation occurs before reaching the maximum force and then uncontrolled crack propagation starts. On the other hand the smooth onset of acoustic emission counts can be seen in case of the valid test (figure 2a), however the gain and noise level is dependent on the setting of acoustic emission measurement system and could vary from sample to sample. Other mechanical properties such as Young's modulus and brittleness index were also subjected to investigation and the corresponding results are analysed in detail elsewhere [15, 16].



a) b)

Figure 2. Typical loading traces for valid (a) and invalid (b) fracture toughness test of REFO composite. Also AE count traces are shown.

All valid fracture toughness data obtained during testing of both CONC and REFO refractory materials are plotted in figure 3. The relatively low level fracture toughness values were accompanied by a large scatter. All groups of test pieces exhibit high scatter independently of the number of thermal cycles. This behaviour is closely connected with the inhomogeneous and coarse-grained microstructure and/or the presence of pores in the materials under investigation [5]. The basic statistical characteristics of each test group are summarised in table 2.

The average fracture toughness value for CONC material in as-received state is 0.34 $MPam^{0.5}$ and for REFO material 0.39 $MPam^{0.5}$. After 7 thermal cycles the REFO material stays on the same level of fracture toughness, on the contrary the CONC material exhibits a slight decrease by about 0.1 $MPam^{0.5}$. This difference in fracture behaviour can be explained by the positive role of the low silicate content in the REFO material. This component is partially melted during heating up to the quenching temperature which could lead to crack tip blunting or possibly to some kind of crack healing. However this mechanism is not inexhaustible and therefore when more than 7 thermal shock cycles are applied the average fracture toughness values drop to nearly the same level as the value obtained for CONC refractory material. It is measurable that the REFO material has higher scatter than CONC material. The higher scatter in fracture toughness data is due to a coarser microstructure. Generally defects as microcracks, pores and decohesion of grains are present even in the microstructure of as-received samples and there are imposed by the fabrication technology.

Both CONC and REFO materials exhibit a very heterogeneous microstructure which causes a rather difficult interpretation of the obtained fracture toughness results. However from the statistical point of view these data are very consistent and therefore the testing and evaluation procedures can be used for comparison of this type of refractory composites when they are evaluated for thermal loading effects. The summary of obtained data is presented in figure 4, where all data independently of thermal shock conditions are displayed in the normal distribution chart. On the X-axis fracture toughness values are plotted and on the Y-axis the sequential probability is plotted. The black triangles represent all data for CONC composite material and grey diamonds represents REFO material. From the direct comparison the same trend for each material independently on thermal loading history is observed. Statistical analysis could help to find measuring artefacts and/or invalid fracture toughness values when acoustic emission or other supporting methods are used.

The fractographical observation of all fracture surfaces was conducted using both optical and scanning electron microscopy. The images obtained from optical microscopy at low magnification were processed by image analyses and the resulting shape characteristics

Table 2. Statistical characteristics of fracture toughness data for each thermal shock condition.

	CONC				REFO			
Number of thermal shock cycles	0	7	15	30	0	7	15	30
K_{IC} - average ($MPam^{0.5}$)	0.34	0.24	0.28	0.22	0.39	0.39	0.28	0.28
K_{IC} - standard deviation ($MPam^{0.5}$)	0.04	0.04	0.05	0.01	0.05	0.06	0.03	0.12

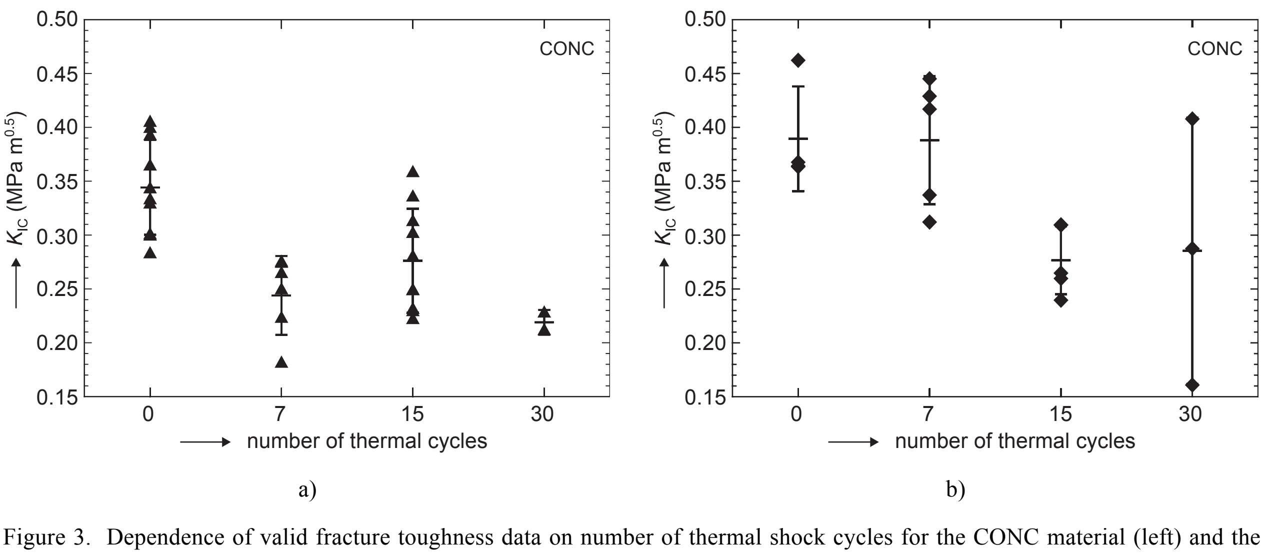


Figure 3. Dependence of valid fracture toughness data on number of thermal shock cycles for the CONC material (left) and the REFO material (right).

(especially the measured Chevron notch geometry) were used as input data for fracture toughness calculation. An example of fracture surface is shown in figure 5. for a REFO material. The Chevron notch keeps the fracture plane parallel to the loading direction and the fracture mode is mode I.

CONCLUSION

Both refractory materials under investigation were exposed to certain numbers (7, 15 and 30) of thermal shock. The influence of microstructural changes caused by thermal shock cycling on the fracture behaviour was studied using three-point bending tests employing the Chevron Notch Technique for fracture toughness determination. Data obtained from thermally loaded specimens were compared with those measured on as-received samples. The fractographical analysis of all fracture surfaces was conducted using scanning electron microscopy to confirm the validity of each test. The average fracture toughness value for the CONC material in the as-received state is 0.34 $MPam^{0.5}$ and for the REFO material 0.39 $MPam^{0.5}$. The high scatter of fracture toughness data is linked to the high inhomogeneity of the microstructure. Considering a low level and high scatter of fracture toughness values it is possible to identify trends of fracture toughness values with increasing number of thermal shocks. The decrease of fracture toughness values occurred after a low number of thermal shock cycles for CONC material. However, after 30 cycles the level of fracture toughness appears to be the same for both materials.

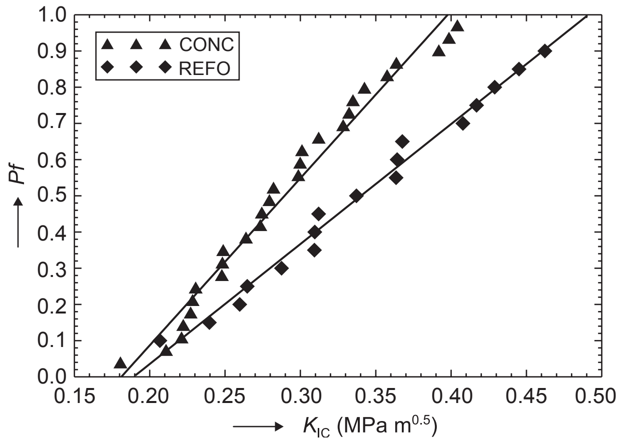


Figure 4. Comparison of fracture toughness data for both materials in the normal probability plot.

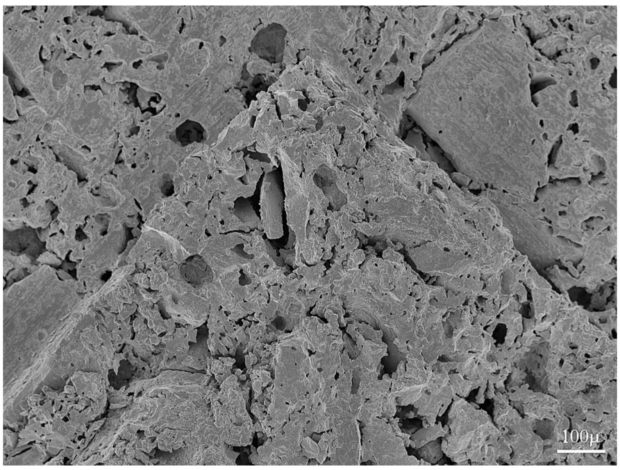


Figure 5. SEM image of the fracture surface near the Chevron Notch Tip in a REFO material.

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LOMOVÉ CHOVÁNÍ ŽÁRUVZDORNÝCH KERAMIK VYSTAVENÝCH TEPELNÝM ŠOKŮM

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Žáruvzdorné keramiky jsou široce využívány ve sklářském a keramickém průmyslu a v mnoha případech jsou vystaveny teplotnímu cyklování nebo dokonce teplotním šokům. V této práci byly zkoumány dva komerčně dostupné žáruvzdorné keramické materiály primárně používané jako podložky při rychlém vypalování porcelánu. První z nich, známý pod obchodní značkou jako CONC, má podíl cordieritu a mulitu 50:50. Druhý žáruvzdorný kompozitní materiál, známý jako REFO, vyznačující se hrubší mikrostrukturou v porovnání s CONC, má podíl cordieritu a mulitu 50:45 a zbytek do sta procent je tvořeno křemenem. Oba tyto materiály byly vystaveny různému počtu tepelných šoků tj. opakovanému prudkému ochlazení do vody z teploty 1250°C. Následně byly provedeny zkoušky lomové houževnatosti využívající techniku chevronového vrubu u všech získaných stavů včetně stavu po dodání. Výsledky byly podrobeny analýze s ohledem na mikrostrukturu a její poškození způsobené tepelným zatěžováním. Rastrovací elektronová mikroskopie byla použita jak pro analýzu mikrostruktury, tak i lomových ploch u vzorků s různou historií tepelného zatěžování.