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CHARACTERIZATION OF THERMAL SHOCK DAMAGE IN CORDIERITE-MULLITE REFRACTORY MATERIALS BY NON-DESTRUCTIVE METHODS

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ABSTRACT

Ultrasonic pulse velocity testing and image analysis were used to predict thermal stability of refractories. Two cordierite-mullite compositions used as substrates in fast firing of porcelain whiteware characterized by different microstructure morphologies and crack propagation behaviour were investigated. The measurement of the ultrasonic velocity was used to asses the material degradation with increasing thermal shock cycles and specimen damage was monitored using image analysis and further results of material degradation were obtained. A brief discussion about the correlation between thermo-mechanical properties, microstructure, crack propagation behaviour and thermal shock resistance is presented. Moreover, empirical models are developed to predict thermo-mechanical properties from ultrasonic velocity and surface damage measurements. Then, service life prediction models of refractory plates from measured values of ultrasonic velocities in plates in the as-received state are presented.

Key words: refractory, cordierite-mullite, service life prediction, ultrasonic velocity

INTRODUCTION

The characterization of thermal-shock degradation of commercial refractories in service is of prime concern to the industry involving high temperature processes worldwide. When refractory materials are subjected to industrial thermal cycles crack nucleation and/or propagation occurs resulting in loss of stiffness, mechanical strength and overall material degradation. The testing of refractories has involved historically mostly destructive test methods for both room and high temperature characterization. In particular in the last years, measurement of fracture strength and Young's modulus after thermal shock have become popular characterization methods of thermal shock damage. Such testing, if conducted on a statistically representative sample population, results in a large number of specimens being destroyed. The development and use of higher quality raw materials has increased the cost of refractories and led to consider the use of non-

destructive testing methods for characterizing thermal shock damage. Of all the various available non-destructive test methods, the ultrasonic pulse velocity and image analysis technique have attracted a lot of interest[1,2].

The aim of this work was to study the thermal degradation of commercially available cordierite-mullite refractory materials subjected to industrial thermal cycles by comparing the degradation curves obtained from non-destructive testing methods, e.g. ultrasonic velocity testing (UPVT) and image analysis, with those obtained from flexural strength and fracture toughness measurement by three point bending test and chevron notched technique, respectively.

EXPERIMENTAL

Two series of commercially available refractory plates of cordierite-mullite composition indicated as RSE and BRT, which are widely used as supports in whiteware fast firing cycles, were investigated. These refractory plates tested on-duty in industrial kilns, exhibit different thermal shock failure mechanisms, RSE being characterized by early crack initiation and slow crack propagation, whilst BRT exhibiting delayed crack initiation and fast fracture propagation [3,4]. Scanning electron microscopy (SEM) (PHILIPS XL 40) was performed on polished sections of samples after gold coating to characterize the microstructure of the refractory materials investigated. Fig. 1 (a,b) corresponds to cordierite matrix of BTR and RSE samples, while Fig. 1(c, d) reports the aggregate microstructures of BRT and RSE samples, respectively. Fracture strength values were determined on prismatic bars (80 x 25 x 5mm^3) at room temperature by three-point bending test (MTS 810, USA). Fracture toughness data of selected samples were obtained on bars (4x3x16 mm) by the chevron notch (CN) technique at room temperature [3,4]. Ultrasonic pulse velocity testing (PUNDIT *plus* PC1006, CNS Farnell Ltd., Hertfordshire, England) and image analysis (IMAGE PRO PLUS program) were used to predict thermal stability of cordierite-mullite refractories. All the measurements from destructive and non-destructive testing methods were performed on selected samples/plates in the as-received condition and after 110, 360 and 510 industrial thermal cycles.

NON-DESTRUCTIVE TESTING

Ultrasonic pulse velocity testing

A commercial ultrasonic testing instrument of transmission type (PUNDIT *plus* PC1006, CNS Farnell Ltd., Hertfordshire, England) was used. The instrument consists of a pulse generator and timing circuit coupled to two transducers (220 kHz) that were positioned manually at opposite ends of each test. Each transducer had a 2 mm thick rubber tip to help overcome measurement problems due to the roughness of the refractory surface. The ultrasonic velocity, v, is calculated from the distance between the two transducers and the electronically measured transit time of the pulse as:

$$v(m/s) = \frac{d}{t} \qquad (3)$$

where d = distance between the two transducers (m) and t = transit time (s).

By determining the ultrasonic velocity and bulk density (ASTM C-134) of a refractory it is possible to calculate the dynamic modulus of elasticity using the equation below (ASTM C 1419-99a):

$$E_{dyn} = v^2 \rho \left(\frac{(1+\mu_{dyn})(1-2\mu_{dyn})}{1-\mu_{dyn}} \right) \qquad (4)$$

where v = pulse velocity (m/s), ρ = density (kg/m^3) and μ_{dyn} = dynamic Poisson's ratio.

Fifty refractory plates of each series with identical dimensions (520x340x12 mm^3) were investigated. For each refractory plate, measurements of ultrasonic pulse velocity through the length and thickness (hereafter indicated as v_L and v_T respectively) on direct transmission disposition were performed. Each test was run at least 5 times to correctly individuate the ultrasonic velocity. The measurements were performed on the same batch of refractory plates in the as-received condition and after 110, 360 and 510 industrial thermal cycles.

Image analysis

Photographs of thermally degraded specimens were taken before and after 110, 360 and 510 industrial thermal shock cycles. The IMAGE PRO PLUS program was used for image analysis. The specimens were covered with thin chalk-powder film before surface damage was investigated. The film provided better contrast and differentiation of damaged and non-damaged surfaces. The ratio between sample surface area (P_0) and damaged surface area (P) was calculated for each refractory material. The results of (P_0/P%) ratio against number of thermal shock cycles for both compositions were plotted [2].

RESULTS AND DISCUSSION

Fracture strength-ultrasonic velocity correlation

Refractory materials inevitably contain some flaws in the form of porosity, micro-cracks and impurities. When containing inherent flaws ceramics are subjected to severe thermal shock, damage concentrated at tips of those preexisting flaws will be generated leading to higher number of microcracks and hence the fracture strength is degraded. Figure 2A shows the effects of the industrial thermal shock cycles on tensile strength and ultrasonic velocity measured through the length (v_L) of the refractory plates. The values are given relative to the values of flexural strength and ultrasonic velocity of BRT samples measured on as-received state (σ_{E0} and v_{LE0}). It is evident observing Figure 2A that the fracture strength of RSE material is higher than that of BRT in the as-received condition. The strength of both materials decreases initially rapidly, in particular for RSE material, and after about 100 thermal shock cycles the values tend to saturation with increasing cycles. Figure 2A also shows a remarkable similarity between the trends of σf and v_L probably due to the presence of cracks longer than the critical length value, as established by Griffith theory [5]. In a previous investigation it was demonstrated that the on-duty fracture of these refractory plates can be assimilated to a single dominant phenomena with the crack aligned with the transversal direction of the sample[6]. The suitable set-up of the UPV transducers during the measurement of v_L permitted to detect

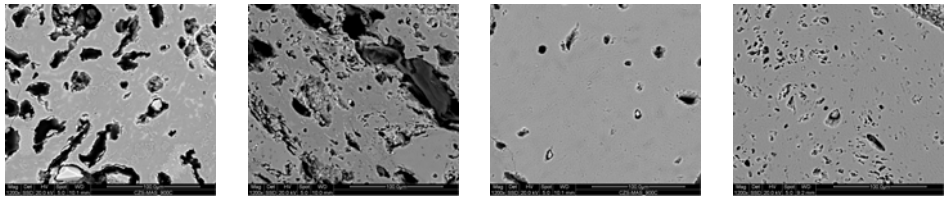
the onset of crack initiation and the further microcracking development into macroscopic damage. In many of the investigated samples, cracks are already visible after approximately 100 cycles, with crack lengths higher than 1mm[6]. The fitting of the experimental trends, by using an 1st order exponential equation[7] of the thermo-mechanical properties against industrial thermal shock cycles indicates that the service life obtained from the average value of P_0/P ratio has the higher correlation coefficients for both materials (0.99 and 0.97 for RSE and BRT samples respectively). The higher retained strength of BRT material indicates that it should behave better under service life relevant thermal shock conditions. In fact from the 50 refractory plates studied of each composition, 13 plates of BRT material survived 510 cycles without visible fractures, while for RSE material the number of plates was only 5. Such damage of RSE material could be induced by stresses arising from thermal expansion mismatch between the coarse grain aggregates (molochite, tabular alumina, etc.) and the cordieritic matrix. Thermal expansion anisotropy of the aggregate grains and stresses from the non-linear temperature distribution present during the thermal cycles [5] should also contribute to the observed different behavior of the materials.

Fracture toughness-surface damage parameter correlation

Figure 2B shows the variation of K_{IC} and surface damage parameter ($P_0/P\%$) with industrial thermal shock cycles. The values are given relative to the fracture toughness and damage surface of as-received BRT samples. It is evident that BRT presents higher values of K_{IC} and P_0/P than RSE material during all their service life. Likewise there is a clear significant correspondence between the trends of K_{IC} and P_0/P for both materials. This could be due to the capability of image analysis to monitor the development of surface degradation, which is strongly related to the quality of the mullitic-aggregate-grains/cordieritic-matrix interface. Thermal shock cycles induce change in microstructure and thermal ageing effects, leading to weakening of this interface and as consequence grains can be removed easier. The more detailed analysis of fracture morphology has been presented elsewhere [4].When the specimens were covered with thin chalk-powder film, the grain pull-out effect was evident from the optical microscopy images used for P/P_0 ratio assessment, reported in Figure 3) (a,b). The film was employed since it has been demonstrated that it provides better contrast and differentiation of damaged and non-damaged surfaces [4]. The higher fracture toughness values of BRT material can be mainly attributed to the presence of silicate glassy phases in the mullitic-aggregates/cordieritic-matrix interface and to the higher amount of cordieritic matrix. The effect of microstructure on fracture toughness has been investigated elsewhere[4]. Briefly, the presence of this glassy cordieritic matrix is responsible for crack blunting, shielding and crack bridging, while the silicate glassy phases in the grain-matrix interface can lead to a crack branching toughening mechanisms. In addition, the smaller size of mullitic aggregates of BRT material leads to better thermo-mechanical properties including lower thermal expansion coefficient [6].

An unexpected increasing trend of K_{IC} values for both refractory compositions was found in the first 7 cycles, in particular for RSE material, as Figure 2B depicts. After 15 industrial thermal cycles, the fracture toughness trend of BRT material is less pronounced than for RSE, suggesting again that BRT is less sensitive to repeated thermal shocks than RSE material. From an industrial point of view, where a reliable parameter is desired that after few cycles can describe the future thermal shock behavior, it seems that the σ_r/σ_0 is more suitable than K_{IC}/K_{IC0} ratio since it does not present the unexpected

increasing trend and with fewer initial cycles the thermal shock behavior can be predicted likewise.



a) b) c) d)

Fig. 1. SEM micrographs of as received samples where a) and b) correspond to cordierite matrix of BTR and RSE samples, respectively, and c) and d) correspond to aggregate microstructures of BRT and RSE samples, respectively

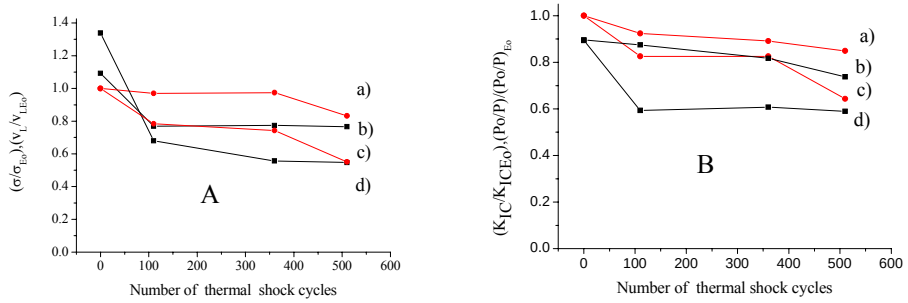
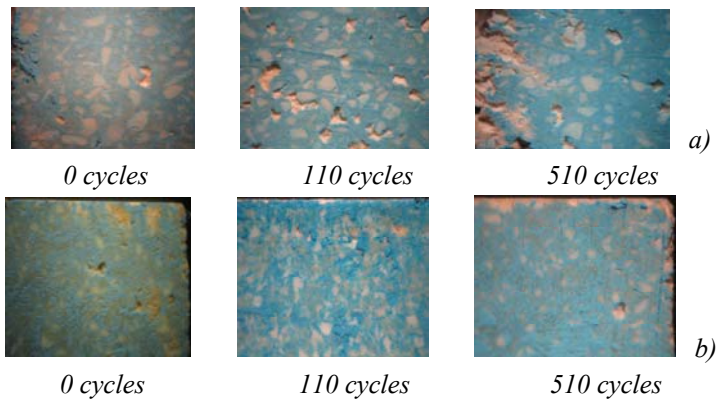


Fig. 2. A) Measurement of flexural strength and ultrasonic velocity through the thickness as function of number of thermal shock cycles, where the curves labelled a) corresponds to σ_f of BRT, b) v_L of RSE samples, c) v_L of BRT and d) σ_f of RSE material respectively. B) K_{IC} and damage surface values against number of thermal shock cycles. The curves labelled a) corresponds to K_{IC} of BRT, b) K_{IC} of RSE samples , c) P_0/P of BRT and d) P_0/P of RSE material, respectively



a)

0 cycles 110 cycles 510 cycles

b)

0 cycles 110 cycles 510 cycles

Fig. 3. Images of surface degradation for samples before and after 110, 510 thermal shock cycles for a) RSE and b) BRT refractory materials

CONCLUSIONS

The thermal shock resistance of two refractory materials was investigated by destructive tests (flexural strength and fracture toughness) and non-destructive examination (ultrasonic pulse velocity testing and image analysis). A remarkable similarity was found between the variations of ultrasonic velocity (when measured through the length of the refractory plates) and flexural strength with number of thermal shock cycles. It is thought that this is related to the suitable setting of the UPVT transducers able to detect the development and propagation of critical cracks from the micro to the macro-structure level in the transversal direction; cracks that lead this refractory plates to fracture. On the other hand, the development of surface microcracking as monitored by image analysis, is in good agreement with the variation of K_{IC} with the number of thermal shock cycles. A possible explanation for this good fitting could be the high dependence of fracture toughness values with the quality of the aggregate-matrix bond interface and grain pull-out effect; and the high capability of the software used for image analysis to detect the increasing extent of grain-pull-out due to thermal ageing of the refractory microstructure. Finally, from the analysis of the retained property ratios an assessment about which parameter could be used to predict thermal shock behaviour during service life can be made. The retained values of all investigated thermo-mechanical properties as well as image analysis and ultrasonic velocity measurements coincide in the assessment that the BRT material exhibits better resistance to thermal shock. This suggests that non-destructive testing, like image analysis and UPVT measurement, can be used to find reliable empirical models for prediction of service life of materials under thermal shock conditions.

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