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Determination of thermal shock resistance in refractory materials by ultrasonic pulse velocity measurement

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Abstract

Thermal shock resistance of refractory materials is one of the most important parameters in refractory material characterization since it determines their performance in many applications. Ultrasonic pulse velocity testing was used for non-destructive quantification of thermal shock damage in refractory plates used as support for the firing of porcelain articles. When refractory materials are subjected to the industrial thermal cycles crack nucleation and propagation occurs resulting in loss of strength and material degradation. The formation of cracks decreases the velocity of ultrasonic pulses travelling in the refractory because it depends on the density and elastic properties of the material. Therefore measuring either of these properties can directly monitor the development of thermal shock damage level. Young's modulus of representative samples was calculated using measured values of ultrasonic velocities obtained by ultrasonic pulse velocity technique. Results were compared with industrial statistical data of thermal shock behaviour of the investigated materials. The capability of the ultrasonic velocity technique for simple, sensitive, and reliable non-destructive characterisation of thermal shock damage was demonstrated in this investigation.

Keywords: Ultrasonic velocity; Refractories; Mullite; Thermal shock resistance

1. Introduction

The evaluation of thermal shock damage of commercial refractories in service is of prime concern to the worldwide industry. Many of the characterisation tests used by refractory manufacturers and users are based on agreed national and international standards.[1,2] Different authors have worked on the assessment of degradation of physical properties during thermal shock tests of refractory and ceramic materials and have characterized thermal shock resistance, considering one or more of the following criteria: modulus of rupture; modulus of elasticity by sonic resonance[3]; modulus of elasticity calculated from ultrasonic velocity[4]; modulus of elasticity by transient vibration[5]; internal friction and damping obtained from forced resonance methods.[6] These tests can distinguish between excellent and poor thermal shock resistant materials, particularly when resistance is quoted as number of quenching cycles, e.g. +20 or +30 cycles, but are limited in their ability to differentiate between different levels of "good" materials where no obvious physical damage has occurred to the material after thermal shock.[2]

The use of the ultrasonic pulse velocity testing (UPVT) is rapidly becoming a standard method for the quality assessment of refractories.[7] Ultrasonic velocity measurement permits accurate and repeatable calculation of modulus of elasticity, bulk density and the detection of cracks. On a comparison basis, density variations within a single piece or between similar parts can be detected. Ultrasonic velocity can be correlated to modulus of elasticity, modulus of rupture, and degradation of thermal shock resistance.[4–8]

The use of pulse ultrasonics on refractory materials has been reported from the 1960's.[9] Firstly sonic velocity was dedicated to specialized applications such as fireclay coke oven shapes[10] but from the 1980's it has been applied to bulk refractories.[11] An electro-acoustical transducer that is held in direct contact with the surface of the refractory under test generates pulses of longitudinal elastic stress waves. After traversing through the material, the pulses are received and converted into electrical energy by a second transducer. Most standards describe three possible arrangements for the transducers: (a) the transducers are attached to the same surface and separated by a known distance (indirect transmission); (b) the transducers are located diagonally to each other; that is, the transducers are across corners (diagonal transmission); (c) the transducers are located directly opposite each other (direct transmission). Direct transmission is

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the most sensitive, and indirect transmission the least sensitive. The velocity, v, is calculated from the distance between the two transducers and the electronically measured transit time of the pulse as:

$$v(m/s) = \frac{\text{path length}}{\text{transit time}} \quad (1)$$

Taken into account that the sensitivity to thermal shock damage of many refractory materials decreases as temperature increase,[12] the calculation of ultrasonic velocity at room temperature could be an efficient (cost-effective) procedure in determining the smallest difference between different behaviour of refractory materials under thermal shock.

It is possible to calculate the dynamic modulus of elasticity of a refractory, from the bulk density, Poisson's ratio and ultrasonic velocity values, using the equation below[13]:

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

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

The objective of this research is to analyse the thermal shock behaviour of two commercially available cordierite-mullite refractory plates which are widely used as supports in whiteware fast firing cycles. The materials have been tested on-duty in industrial kilns and they appear to exhibit different thermal shock failure mechanisms, one being characterized by early crack initiation and slow crack propagation, whilst the second material has shown delayed crack initiation and fast fracture propagation.[14,15] The UPVT was performed at an European company, using UPVT equipment on loan from CNSFarnell Limited, testing in situ the same lots of refractory plates after increasing number of cycles. The feasibility of the sonic testing method to characterize thermal shock damage and to pinpoint correlations between physical properties and modulus of elasticity with the microstructure is presented below.

2. Experimental procedure

2.1. Ultrasonic velocity equipment

A commercial ultrasonic testing instrument of transmission type (PUNDIT *plus* PC1006, CNS Farnell Ltd., Hertfordshire, England) was used to evaluate each refractory sample. 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 plate. Each transducer had a 1.6 mm thick rubber tip to help overcome measurement problems due to the roughness of the refractory surface. Knowing the pulse time and the path length, the ultrasonic velocity was calculated using Eq. (1).

2.2. Samples and test method

Two series of commercially available refractory plates of cordierite–mullite composition, hereafter indicated as REFO and CONC, were investigated in this work. These materials are characterized by a different cordierite to mullite weight ratio, equal to 50:45 in REFO material, with excess of 5 wt% of SiO_2, while it is 50:50 in CONC material. Table 1 summarizes the basic properties of these materials, in the as-received condition, measured at room temperature in a previous work.[15,16]

One hundred refractory plates of each series with identical dimensions (520 mm × 340 mm × 12 mm) and different hole distribution, as depicted in Fig. 1(a) and (b), were tested. In particular for each refractory plate, measurements through the length and thickness on direct transmission disposition were performed. Fig. 1 shows the locations of the transducers during the test. Each test was run at least five times to correctly individuate the ultrasonic velocity. The measurements were performed on the same lot of refractory plates in the as-received condition and after 120, 260 and 410 thermal cycles. Furthermore, sonic velocity measurements through the length were related to the physical properties.

3. Results and discussion

Fig. 2 reports the values of ultrasonic velocity (v), measured through the thickness tested after 120, 260 and 410 cycles for the REFO and CONC plates, with their deviation bars.

Comparing similar materials, Eq. (2) indicates that sonic pulses travel faster through the less dense piece. This agrees with Fig. 2, where ultrasonic velocity of CONC is higher than REFO in the as-received condition, being CONC bulk density lower (Table 1). Moreover, CONC microstructure is characterized by the presence of a glassy silicate matrix,[15] which could act as better channel for ultrasonic waves than the coarse grained REFO microstructure, where dispersion and attenuation of the sonic waves at the grain surfaces could occur. In addition, measurements performed in amorphous and in crystalline compounds of the same chemical substance show that ultrasonic waves propagate faster in the amorphous structures, e.g. ultrasonic velocity of silica fused was 5960 m/s while for quartz 4260 m/s.

Table 1
Thermal and mechanical properties of the as-received refractories

Sample	Parameter						
	Bulk density, ρ (g/cm^3)	Thermal expansion coefficient, α (25–1250 °C) (°C^{-1} × 10^{-6})	Apparent porosity (%)	Dynamic Young's modulus, E_{dyn}, I.E.T., (GPa)	Poisson's ratio, μ	Three point bending strength, σ (MPa)	Fracture toughness, K_{IC} (MPa m$^{1/2}$)
REFO	2.198	2.77×10^{-6}	26	21.5	0.16	62	0.35
CONC	2.101	2.26×10^{-6}	28	15.7	0.16	60	0.40

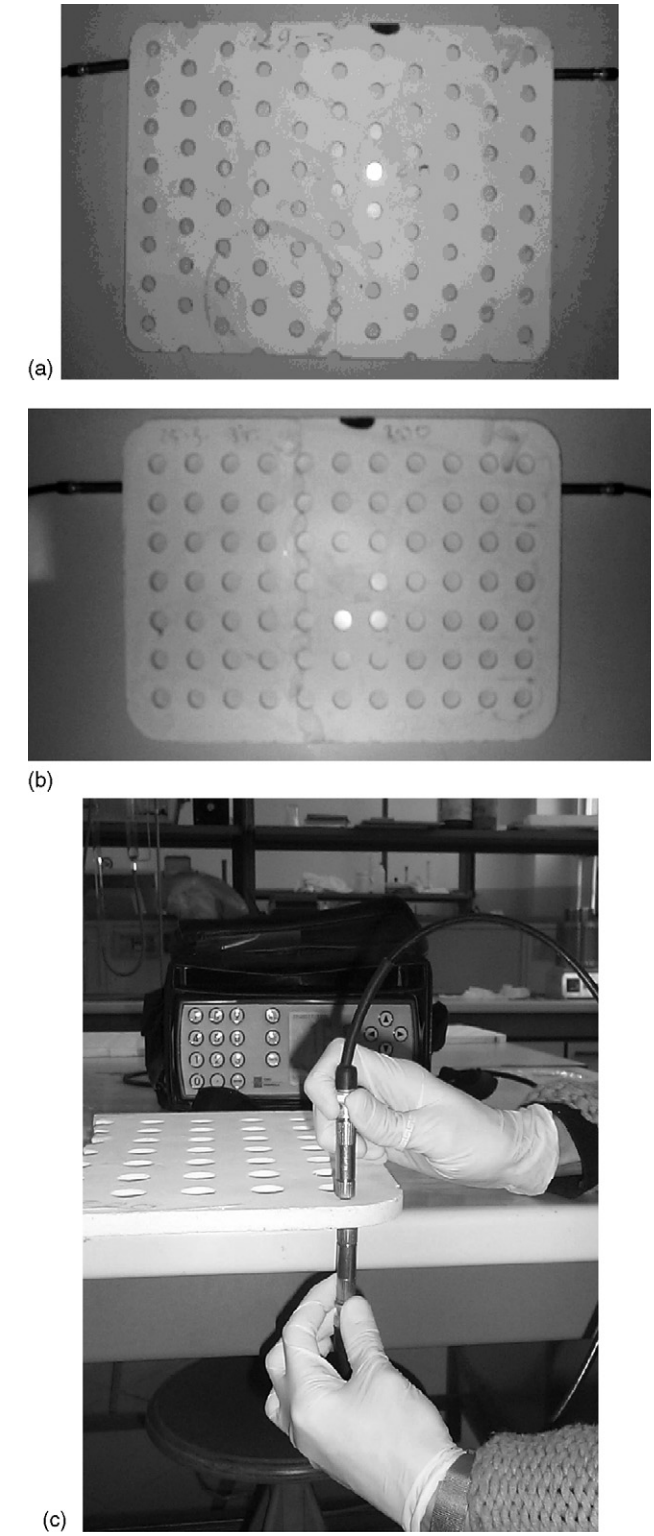

Fig. 1. Pictures showing the location of the transducers during the tests (a) CONC and (b) REFO refractory plates respectively.

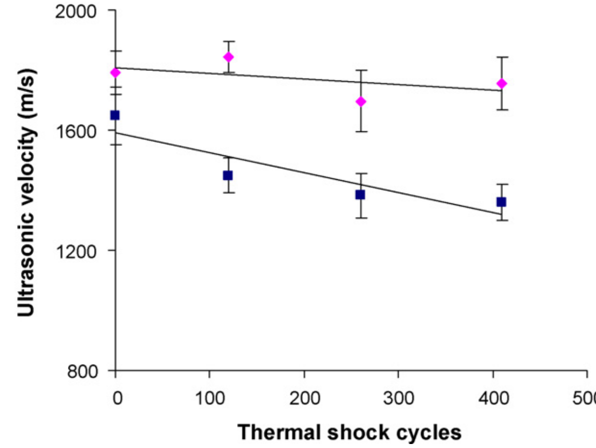

Fig. 2. Values of ultrasonic velocity (v) measured through the thickness path tested after 120, 260 and 410 cycles: (■) REFO (◆) CONC.

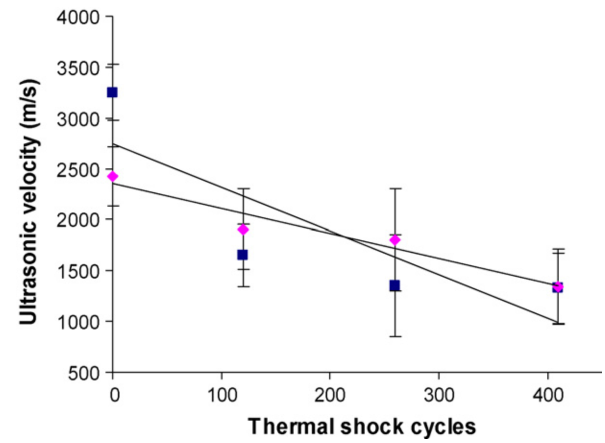

Fig. 3. Ultrasonic velocity against number of thermal shock cycles through the length path: (■) REFO (◆) CONC.

It is evident in Fig. 2 that ultrasonic velocity decreases while standard deviation increases with number of cycles (N) being REFO material more affected. Since the hole distribution of the refractory plates can not affect the measurements in the thickness path, these values are deeply related with microcracking of the microstructure. The better thermal shock behaviour of CONC plates can be attributed once more to its glassy silicate matrix. In fact, at high temperature, this glassy phase in the CONC refractory microstructure should become viscous, and it could fill or blunt the propagating microcracks. This mechanism should explain that CONC, despite of a faster crack initiation,

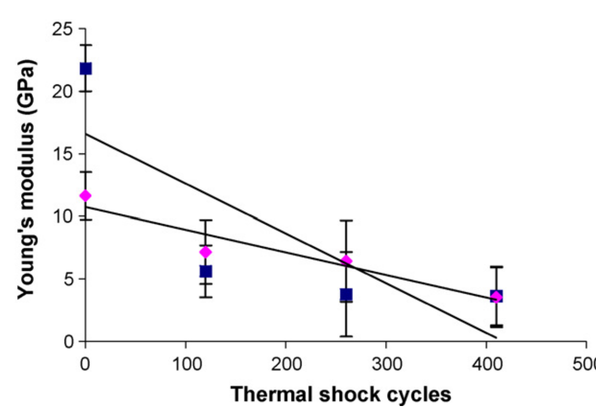

Fig. 4. Dynamic Young's modulus versus number of thermal shock cycles through the length path: (■) REFO (◆) CONC.

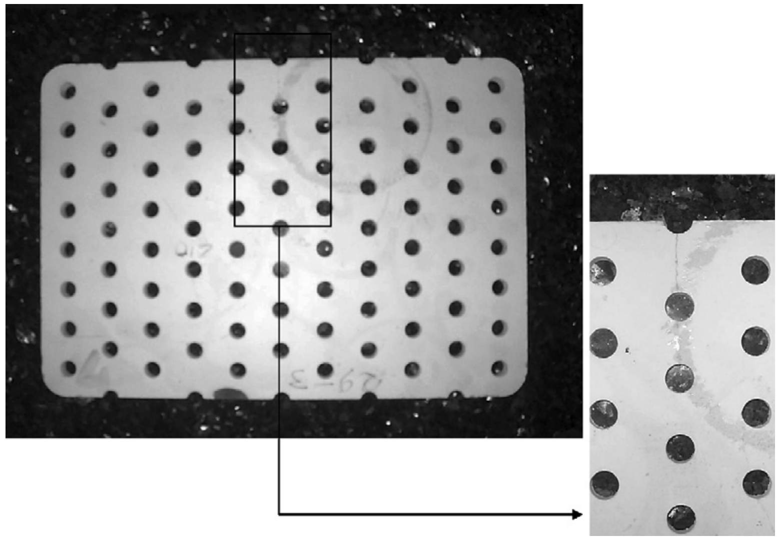

Fig. 5. Picture of a refractory plate. Enlargement of the central region evidentiate the presence of a crack propagating in the transversal direction.

shows a delayed crack propagation, as Fig. 2 depicted in. In addition, a relaxing mechanism of stresses due to this viscous phase could be expected.

Fig. 3 plots the measurements of ultrasonic velocity through the length path while Fig. 4 reports the dynamic Young's modulus calculated from Eq. (2). It was assumed that Poisson's ratio and density would not substantially change with thermal shock cycles. Since the hole distribution of the refractory plates in the length path is different, no comparison of the values can be done, but it is possible to study the development of thermal shock damage through the slope of the trend lines. The propagation of the cracks, visible after a certain number of cycles (∼100), causes the material fracture in the transversal direction (Fig. 5). Even if refractory plates showing extensive macrocracks close to breakdown were permanently eliminated from the beginnings of the measurements, it is still evident the increase of standard deviation for the measurements obtained after 100 cycles.

Therefore in this case the degradation of the physical properties is related to structure macrocraking of the refractory plates. Considering Fig. 3 it is evident that the material degradation trend is higher in the case of REFO material and once more the standard deviation increases with the number of cycles.

The values of dynamic Young's modulus for the refractory plates calculated by UPVT in the as-received condition are similar to those determined by the impulse excitation technique (IET) (GrindoSonic® MK5, J.W. Lemmens, Leuven, Belgium) available from a previous work[15,16] and shown in Table 1.

The trend curves of dynamic Young's modulus shown in Fig. 4 indicate that the most critical degradation for both materials occurs during the first 100–120 cycles, in particular for REFO material.

Monitoring modulus of elasticity for refractories through results of pulse velocity is not normally recommended due to refractory heterogeneous microstructure, since the validity of Eq. (2) requires homogenous, isotropic and elastic materials.[13] This information has to be taken into account because the examined refractory plates are subjected to a flexural moment maximum in the centre since they are used as supports for porcelain articles in fast-firing cycles. Therefore Young's modulus becomes a critical parameter of design and the use of correlations between ultrasonic velocity and modulus of rupture (MOR) are not recommended without facing the UPVT data with other Young's modulus determination techniques, such as IET. The scope or range of applicability of the mathematical relationship(s) between E_{dyn} and σ_{f} can be broadened by using the widest range of values applicable to any product type(s) of interest.[5,17]

However it can be attained an idea about quality, uniformity, condition and strength of the refractories and the progress of thermal shock damage.

4. Conclusion

Ultrasonic pulse velocity testing was employed to determine ultrasonic velocity, Young's modulus and the presence of major defects in cordierite–mullite refractory materials. The UPV apparatus employed is well adapted to the non-destructive, in situ study of elastic changes in refractories submitted to heat treatment. The method exhibits high reproducibility and sensibility as current improvements in UPVT equipment made it more reliable. The comparison between UPVT values and those obtained by IET technique for as-received materials confirm this presumption. In this investigation was demonstrated the capability of the ultrasonic velocity technique for simple, sensitive, and reliable non-destructive characterisation of thermal shock damage. Furthermore, data of statistical importance for future investigations was obtained.

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