THERMAL SHOCK DAMAGE CHARACTERIZATION OF HIGH TEMPERATURE CERAMICS BY NON DESTRUCTIVE TEST METHODS

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In the present work a mixture of commercially available spinel, quartz (SiO_2) and alumina (Al_2O_3) corresponding to a cordierite stoichiometry was used as starting material for obtaining cordierite/SiC composite ceramics with weight ratio 30:70 and 50:50. Cordierite and silicon carbide are ceramic materials suitable for high temperature application with superior thermal stability, thermal shock resistance, low thermal expansion coefficient and good chemical resistance.The composite material could exhibit advantages of its constituents when the components have optimized properties and they are mixed in the proper ratio. Behavior of composite ceramics after thermal shock treatments was investigated. Thermal shock of the samples was measured using standard laboratory water quench test. Level of surface deterioration before and during quenching was monitored by image analysis. Ultrasonic measurements were used as non-destructive quantification of thermal shock damage in refractory specimens. Dynamic Young modulus of elasticity and strength degradation were calculated using measured values of ultrasonic velocities obtained by ultrasonic measurements.

INTRODUCTION

The knowledge of the thermal shock resistance of refractory materials is of outmost importance since it determines their performance in many applications, from ceramic manufacturing to oil refinery, thermal insulation, nuclear power, chemical and petrochemical industries. Thermal shock resistance is measured in terms of the number of cycles that a refractory material can withstand when subjected to sudden temperature changes [1]. When refractory materials are subjected to the rapid temperature changes crack nucleation and/or propagation occurs resulting in loss of strength and material degradation. The formation of cracks decreases the velocity of ultrasonic pulses traveling in the refractory because it depends on the density and elastic properties of the material [1-4]. Therefore measuring either of these properties can directly monitor the development of thermal shock damage level.

Ultrasonic pulse velocity testing (UPVT) was first reported being used on refractory materials in the late 1950's [2]. Various publications have dealt with the practical application of UPVT to characterize and monitor the properties of industrial refractory materials nondestructively [3-8]. The UPVT method has been considered in detail in ref. [2]. Briefly, pulses of longitudinal elastic stress waves are generated by an electro-acoustical transducer that is held in direct contact with the surface of the refractory under test. After traveling through the material, the pulses are received and converted into electrical energy by a second transducer.

It is important to develop an appropriate test methodology to determine accurately the damage propagation in refractory materials required for component life prediction. The main objective of this work was the demonstration of good thermal shock resistance of the used cordirete/SiC composite material and to demonstrate the capability of the ultrasonic velocity technique and image analysis for simple and reliable non-destructive characterization of thermal shock damage.

EXPERIMENTAL

Materials

A mixture of commercially available spinel, quartz (SiO_2) and alumina (Al_2O_3) corresponding to a cordierite stoichiometry was attrition milled using Al_2O_3 balls and ethyl alcohol as media for four hours. Commercially available SiC (99 %, Alfa Aesar) was used.

Cordierite/SiC composite ceramics with weight ratio 30:70 (KS 30) and 50:50 (KS 50), respectively, were prepared by milling with Al_2O_3 balls in DI water in polyethylene bottle for 24 hours, shaping by by cold uniaxial pressing under 60 MPa and than isostatic pressed under 110 MPa and firing at 1300°C and 1250°C, respectively.

Some of the selected properties of the materials KS 50 and KS 30 used in present work are given in Table 1.

Table 1. Values of selected properties of refractory materials investigated.

Property	KS 50	KS 30
Density (g/cm^3)	1.83	2.10
Modulus of Elasticity (GPa)	1.02	1.05

Thermal shock

Thermal stability of the refractories was determined experimentally by water quench test (JUS. B. D8. 319.). Samples were cylinders with 1 cm diameter and 1 cm height. The samples were dried at 110°C and then transferred into an electric furnace at 950°C and held for 40 minutes. The samples were then quenched into water and left for 3 minutes and dried before returning to the furnace at 950°C. This procedure should be repeated until failure, the number of quenches to failure is taken as a measure of a thermal shock resistance. Failure is defined according to the standard test as total destruction of sample, or destruction of 50 and more percent of surface area before quenching. Experimental method is similar to the procedure described in PRE Refractory Materials Recommendations 1978 (PRE/R5 Part 2).

Both of the materials exhibited excellent resistance to the rapid temperature changes. Samples did not exhibit total destruction during test procedure till 36 cycles. According to the standard applied to the samples, procedure could be stopped if material is not damaged over 50% of original surface till 30 cycles. For the further investigations test procedure was performed till 36 cycles for both materials.

Image Analysis of the Samples during Water Quench Test

Level of degradation of the samples was monitored before and during testing using Image Pro Plus program for image analysis. Samples surfaces were marked by different colors, in order to obtain a better resolution and difference in damaged and non/damaged surfaces in the material. Results for material destruction were given as function of number of quench experiments, N. Damaged surface level was described as ratio P/P_0, in percent, where P is level of destruction and P_0 is original ideal surface of the sample (1 cm diameter).

Ultrasonic determination of Dynamic Young modulus of elasticity

The velocity, V, is calculated from the distance between the two transducers and the electronically measured transit time of the pulse as:

$$V(m/s) = \frac{L}{T} \tag{1}$$

where L = path length (m) and T = transit time (s).

By determining the bulk density, the Poisson's ratio and ultrasonic velocity of a refractory material it is possible to calculate the dynamic modulus of elasticity using the following equation [3,8]:

$$E_{dyn} = V^2 \rho \left(\frac{\left(1+\mu_{dyn}\right)\left(1-2\mu_{dyn}\right)}{1-\mu_{dyn}} \right) \tag{2}$$

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

The measurement of ultrasonic velocity was performed using the equipment OYO model 5210 according to the standard testing procedure (JUS. D. B8. 121.). The transducers were rigidly placed on two parallel faces of the cylindrical sample having 1 cm diameter and 1 cm height using Vaseline grease as the coupling medium. The ultrasonic velocity was then calculated from the spacing of the transducers and the waveform time delay on the oscilloscope.

Ultrasonic determination of strength degradation

The following expression for the strength degradation, based on decrease in ultrasonic velocity was used 3,6,9 :

$$\sigma = \sigma_0 \left(\frac{V_L}{V_{L0}} \right)^n \tag{3}$$

where σ_0 is compressive strength before exposure of the material to the thermal shock testing, V is longitudinal (V_L) or transversal (V_T) ultrasonic velocity after testing, V_{L0} is longitudinal (or transversal V_T) ultrasonic velocity before testing and n - material constant (n = 0.488, [3]).

RESULTS

Damaged surface level during quench experiments

Monitoring the surface area of the sample before and during water quench test was performed taking photographs of the surface and implementing program for image analysis (Image Pro Plus Pogram). Obtained results are given at the Figure 1. representing damaged surface level (P/P_0) versus number of quench experiment (N).

Low level of damage was observed at the surface area for both samples before testing. Samples made of material KS 30 exhibited lower values , about 1.3 % and samples based on KS 50 showed 2.9 % of damaged surface. Level of degradation for KS 30 was 12.41 % and for the KS 50 it was 20.69 % after 36 cycles.

Ultrasonic velocities

Obtained results for the ultrasonic velocity during testing were given at the Figure 2 .

Obtained results and values of the measured ultrasonic velocity (V_L) about 1000 m/s indicate porosity of the sample [3-5]. The velocity changes in both materials suggest that materials were very stable during testing, as decrease of the velocity was very low during water quench test. These results indicates that number of nucleated cracks and crack propagation did not resolute in rapid degradation of strength and Young modulus of elasticity, and samples exhibited an excellent thermal shock behavior. For material KS 50 small degradation of ultrasonic velocity was observed after 20 cycles, and for KS 30 after 25 cycles.

Young modulus of elasticity

Results of the monitoring changes of the Young modulus of elasticity during quenching are shown in the Figure 3. Some of the selected properties of the materials KS 50 and KS 30 used in present work are given in Table 1.

The dynamic Young modulus of elasticity values before testing indicate that material is porous, but degradation during testing was very low, which explained 36 cycles of water quench test. Small degradation in Young modulus was observed after 25 cycles for both materials.

Strength degradation

Results for the strength degradation presented at the figures 4a. and b showed that degradation at the end of the test was between 1.0 and 0.93 % (calculated with V_L) and 0.94 % (with V_T) for material KS 50 and 1.0 and 0.97 % (calculated with V_L) and 0.94 % (with V_T) for the material KS 30. These results indicate minimal strength degradation and explain excellent results of water quench test, as result of 36 rapid temperature change.

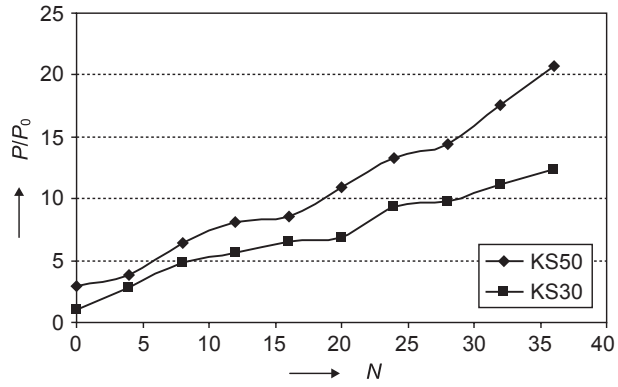


Figure 1. Damaged surface level (P/P_0) versus number of quench experiments (N).

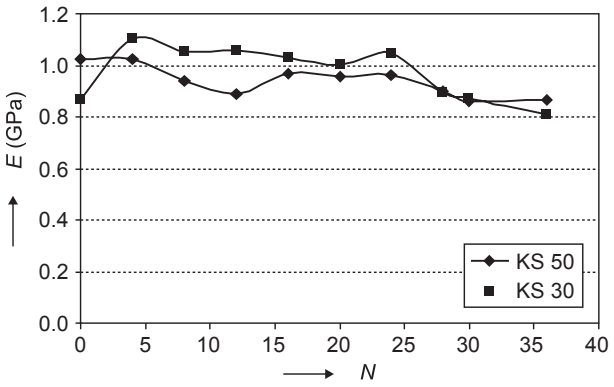
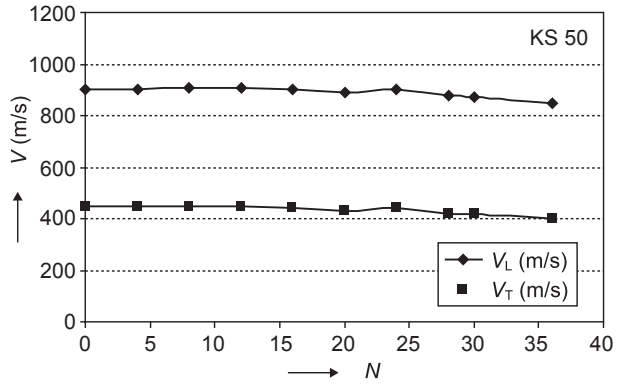
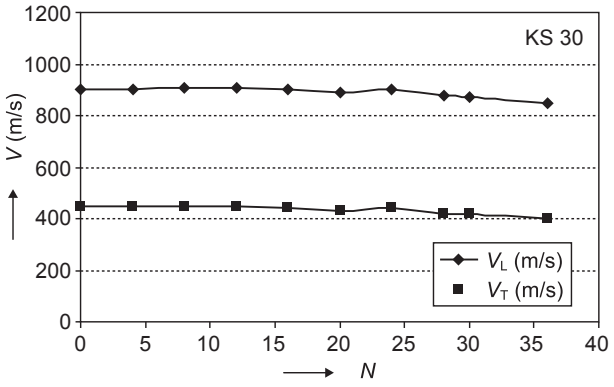


Figure 3. Dynamic Young modulus of elasticity versus number of quench experiments (N).



a)



b)

Figure 2. Values of ultrasonic velocity (V) during testing (longitudinal V_L and transversal V_T) versus number of quench experiments of materials KS 50 (a) and KS 30 (b).

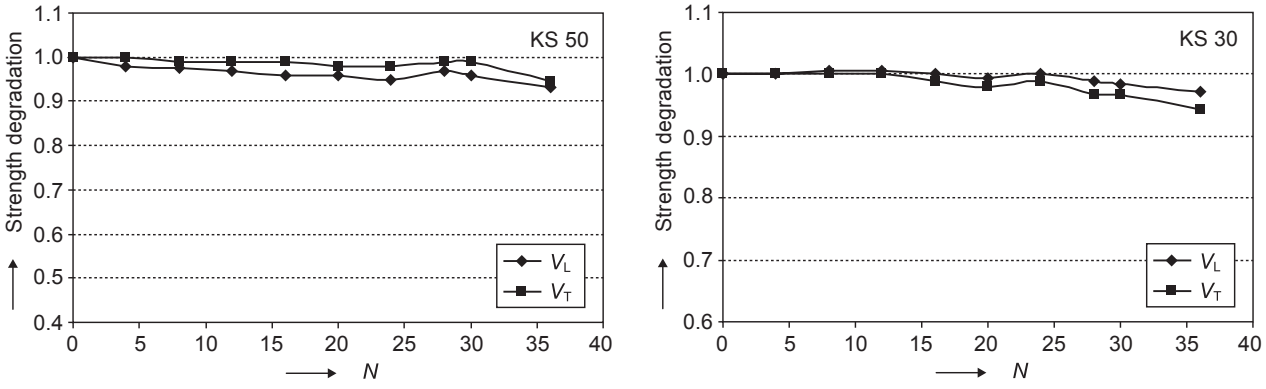


Figure 4. Strength degradation versus number of quench experiment of material KS 50 (a) and KS 30 (b).

DISCUSSION

Thermal shock behavior of the two materials was investigated. Three different techniques were applied:

- water quench test, as most popular experimental method,
- detection of damaged surface area in refractory specimen during thermal shock and
- nondestructive determination of dynamic Young modulus of elasticity and strength degradation.

Obtained results showed that both materials are excellent candidates for the application where thermal shock resistance is required. Water quench results showed that samples were stable till 36 cycles. Behavior of the samples was monitored during water quench test in order to determine damage of the original surface of the samples. Results given at the Figure 2 showed that during quenching damage of the original surface did not exceed 50 %. Original surface showed damage about 1.3% for the KS 30 and 2.9 % for the KS 50. For the KS 30 degradation was 12.41 % and for the KS 50 it was 20.69 % after 36 cycles. That was very low level of deterioration after respectable 36 cycles of quenching.

Behavior of the bulk of the sample was monitored using ultrasonic measurements of the Young modulus of elasticity. Results presented at the Figure 3 showed very small changes and degradation of the Young modulus. These results are pointing out that the level of destruction in the bulk of the material and fracture nucleation and growth did not exceed level of surface destruction. Results of velocity and strength degradation pointed out these conclusions.

CONCLUSION

Ultrasonic pulse velocity testing was used to determine ultrasonic velocity and Young's modulus of elasticity in cordierite/SiC composite material. Presence of defects on sample's surface before testing, as well as during thermal shock testing was monitored using Image Pro Plus Program.

Results presented in this paper pointed out the convenience of including other test for thermal stability behavior analysis, beside water quench test. Benefits from using image analysis could be as follow:

1. It is fast, nondestructive method, so samples could be used for further tests, and financial aspect in minimizing of number of samples for testing is of a grate importance.
2. Analysis of the surface before quench test is possible, and very important information about damage of surface could be obtained.
3. Damage level during quenching could be measured. These results could be useful for prediction of sample behavior during testing.

Ultrasonic measurements could provide benefits such as :

1. It is also non destructive method, very fast and reliable.
2. Results of degradation of parameters such as ultrasonic velocity, strength and Young's modulus could be connected with the results for number of quench experiments (N) as well with damaged surface area (P/P_0).
3. These parameters showed very strong correlation with number of quench experiments (N) as well with damaged surface area (P/P_0) and that could be used for prediction of sample behavior.

As the experimental procedure accompanying the water quench test for thermal stability behavior determination was described and discussed in detail, it appears that implementation of these methods and their advantages will improve materials characterization and help in preventing and improvement of material proper-

ties and synthesis conditions for achieving the best results in thermal stability resistance characteristics of material.

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CHARAKTERIZACE POŠKOZENÍ VYSOKOTEPLOTNÍ KERAMIKY PŘI TEPLOTNÍM ŠOKU NEDESTRUKTIVNÍMI METODAMI

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V práci byly jako výchozí materiály použity komerčně dostupný spinel, křemen a oxid hlinitý smíchané v poměru odpovídající stechiometrii cordieritu. Dále byly připraveny kompozity cordierit/SiC v hmotnostních poměrech 30:70 a 50:50. Cordierit i karbid křemíku jsou vhodnými vysokoteplotními keramickými materiály s vynikající teplotní stabilitou, odolností k teplotním šokům, nízkým koeficientem teplotní roztažnosti a dobrou chemickou odolností. Kompozitní materiál může vykazovat výhodné vlastnosti jednotlivých složek, pokud mají optimalizované vlastnosti a jsou smíchány ve vhodném poměru. Bylo studováno chování kompozitní keramiky při teplotním šoku, který byl prováděn standardním laboratorním testem při ochlazení ve vodě. Rozsah povrchového poškození před a po testu byl sledován obrazovou analýzou. Nedestruktivní kvantifikace poškození materiálu při teplotním šoku byla provedena na základě ultrazvukového měření, stejně jako výpočet dynamického Youngova modulu pružnosti a degradace napětí v materiálu.