MODELING OF STRENGTH DEGRADATION DURING WATER QUENCH TEST OF LOW CEMENT HIGH ALUMINA CASTABLE

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Low cement high alumina castable was synthesized, cured, and then sintered at 1100 °C for 3 hours. Water quench test was used as an experimental method for thermal stability testing. Image analysis program was applied in order to measure the damage to the samples at the surface and in the bulk before and during the water quench test. Ultrasonic measurements were carried out with the aim of measuring the changes of ultrasonic velocity. Strength degradation of the samples was calculated by using the model based on ultrasonic velocity changes during water quench test. Also, the strength of the samples before and during water quench test was measured by standard laboratory procedure. The model for prediction of strength degradation is presented.

INTRODUCTION

Technological developments in iron, steel, and metal industries led to improvement of today's castable structure, to provide a long-lasting fire resistance even after repeating occurrence of heating and cooling under mechanical load [1,2]. Lately, the unshaped monolithic refractories have been increasingly used instead of the shaped refractory bricks of the same class due to their easier replacement, lower cost, more efficient installation, higher safety, and lower material consumption. Since application of the refractory castables usually requires resistance to severe thermomechanical loading, it is very important to study behavior of the castable during thermal shock testing. In conditions of high temperature and sudden temperature changes, the refractory castables are frequently damaged by thermal stress induced by the temperature gradients. Actually, in such conditions, the crack nucleation and/or its propagation occur in the refractory castables which results in changes of ultrasonic velocity during traveling through the sample, loss of strength, and decrease of density and elastic properties of the material [3,4].

The behavior of low cement castable subjected to the water quench test was studied in this paper. Low cement castable (LCC) was designed by using the aggregates and commercial high alumina cement. Non-destructive test methods were applied in order to determine ultrasonic velocity, as well as degradation of surface area and structure inside the bulk. Damages to the surface and interior of the bulk were determined by image analysis; the changes in ultrasonic velocity due to thermal shock were determined by ultrasonic measurements. Strength degradation of the samples (residual strength) during thermal shock resistance testing was determined both by calculation using the model based on ultrasonic velocity changes and measurement by standard destructive testing. The calculated and measured values were then compared and correlated and the discrepancy between these values is shown below. Based on the results, critical number of water quench cycles was predicted. Using the both, calculated values of residual strength and real strength degradation, a new model for prediction of strength degradation has been proposed. The presented analysis of strength degradation could be very useful for material life time prediction.

EXPERIMENTAL

Material

For preparation of castable, the commercially available raw materials were used (Almatis, Germany): high alumina cement (CA-270, Almatis) as hydraulic binder, tabular alumina with maximum particle size of 5 mm as an aggregate, reactive alumina as ultra-fine filler, and dispersive alumina as an additive that allows castable flowing and placing with slight water addition. The castable was mixed with 4.67 wt.% of water (dry basis) dispersed with citric acid and water/cement ratio of almost 1 (w/c = 1). Optimum particle packing, and therefore maximum density and sufficient porosity are achieved by adjustment of the particle size distribution to the theoretical curve based on the modified Andreassen's packing model with the distribution coefficient q of 0.25. First, dry components were mixed for 2 minutes and then deflocculant containing water was added and mixing continued for another 4 minutes. The obtained mixture was cast in steel moulds by vibration. The cubes of 4 mm edge length were prepared for thermal shock testing as well as for compressive strength testing. After 24 hours, samples were demoulded, cured for 24 hours at room temperature, and dried at 110°C for another 24 hours. Finally, before thermal shock testing, samples were sintered at 1100°C for 3 hours and cooled down to the room temperature inside the furnace.

The chemical composition of the samples is given in the Table 1 and relevant mechanical properties are given in the Table 2.

Table 1. Chemical composition of the castable (dried at 105°C for 24 h).

Component	Values (%)
Al_2O_3	98.11
CaO	1.22
Na_2O	0.348
Fe_2O_3	0.018
MgO	0.016
Tabular alumina	85
Reactive alumina	10
Cement	5
Dispersive alumina	1

Destructive testing

Destructive test methods were applied for both the room and high-temperature characterization. The 40 mm edge cubes were prepared for compressive strength test (ICS 81.080 SRPS B. D8. 304) and water quench test (ICS 81.080 SRPS B. D8 319) used for thermal stability testing.

Thermal stability of the refractories was determined experimentally by water quench test (ICS 81.080 SRPS B.D8.308.). First, the samples were dried at 110°C for 24 hours, then moved into an electric furnace at 950°C and kept there for 15 minutes. Then, the samples were quenched into the water for 3 minutes and then dried before being returned to the furnace at 950°C. This procedure was repeated until the failure occurred; the number of quenches prior to failure was taken as a measure of thermal shock resistance. According to the standard test, failure is defined as a total destruction of sample, or destruction of 50 and more percent of the surface area before quenching. Experimental method is similar to the procedure described in PRE Refractory Materials Recommendations 1978 (PRE/R5 Part 2).

Non-destructive testing

Ultrasonic pulse velocity testing and image analysis were used to determine the level of changes in material structure with the increase of number of water quench cycles, and to measure the elastic properties of the material. Based on the measured values of ultrasonic velocity and image analysis, the service life of refractory castable can be predicted [5-7].

Ultrasonic measurements

Ultrasonic pulse velocity testing (UPVT) [4-10] was first reported being used on refractory materials in late 1950's. Various publications have dealt with the practical application of UPVT to characterize and monitor the properties of industrial refractory materials non-destructively. The UPVT method has been considered in detail in ref. [4-17]. Briefly, pulses of longitudinal elastic

Table 2. Relevant properties of the castable sintered at 1100°C.

Property	Symbol	Unit	Value
Compressive strength (20ºC/24 h)	σc	MPa	59.43 MPa
Compressive strength (1100°C/3 h)	σc	MPa	110.003 MPa
Flexural strength (105°C/24 h)	σf	MPa	20.01 MPa
Density	ρ	g/cm^3	3.09
Water Absorption	ω	%	4.5
Maximum grain size	–	mm	5
Hardness		Mohs scale	Over 9
Refractoriness	SK	–	>35 (1780°C)

stress waves are generated by an electro-acoustical transducer that is held in direct contact with the surface of the refractory under test. After travelling through the material, the pulses are received and converted into electrical energy by another transducer.

The measurement of ultrasonic velocity was performed using the equipment OYO model 5210 according to the standard testing procedure (ICS 81.080 SRPS D. B8. 121.). The transducers were fixed by the Vaseline as the coupling medium onto two parallel sides of the cylindrical sample having 1 cm diameter and 1 cm height. The ultrasonic velocity was then calculated from the spacing of the transducers and the waveform time delay on the oscilloscope.

The expression for the strength degradation, based on decrease in ultrasonic velocity was used [5-7,10-12, 15, 17-19]:

$$\sigma = \sigma_0 \left(\frac{V_L}{V_{L0}} \right)^n \quad (1)$$

where σ_o is compressive strength before exposure of the material to the thermal shock testing, V_L is longitudinal ultrasonic velocity after testing, V_{L0} is longitudinal ultrasonic velocity before testing and n is material constant. This equation was used for calcu-lation involving longitudinal ultrasonic velocity. Mode-ling of strength degradation was obtained by assigning two different values to n in Equation (1), n = 0.488 (ref. [7], model 1) and 0.588 (model 2).

Image analysis

Image analysis program was used to measure the level of both surface deterioration and degradation inside the bulk before and during the water quench test. Monitoring of damage level of the samples surface and inside the bulk was realized by taking the photographs and microphotographs, respectively, before and during the water quench test, in order to observe the difference between undamaged and damaged areas of the material, Figure 1. Five surfaces of each sample were photographed and analyzed, while the sixth surface was used for marking. Internal structure degradation of the samples cross sections was monitored by using SEM type JEOL JSM-5800. Changes of surface appearance and microstructure were detected by using the image analysis program Image Pro Plus Program; the level of porosity was adopted as a measure of internal degradation of the bulk. Surface and bulk structure deterioration and damage are presented as the erosion ratio (P/P_0), Figure 2.

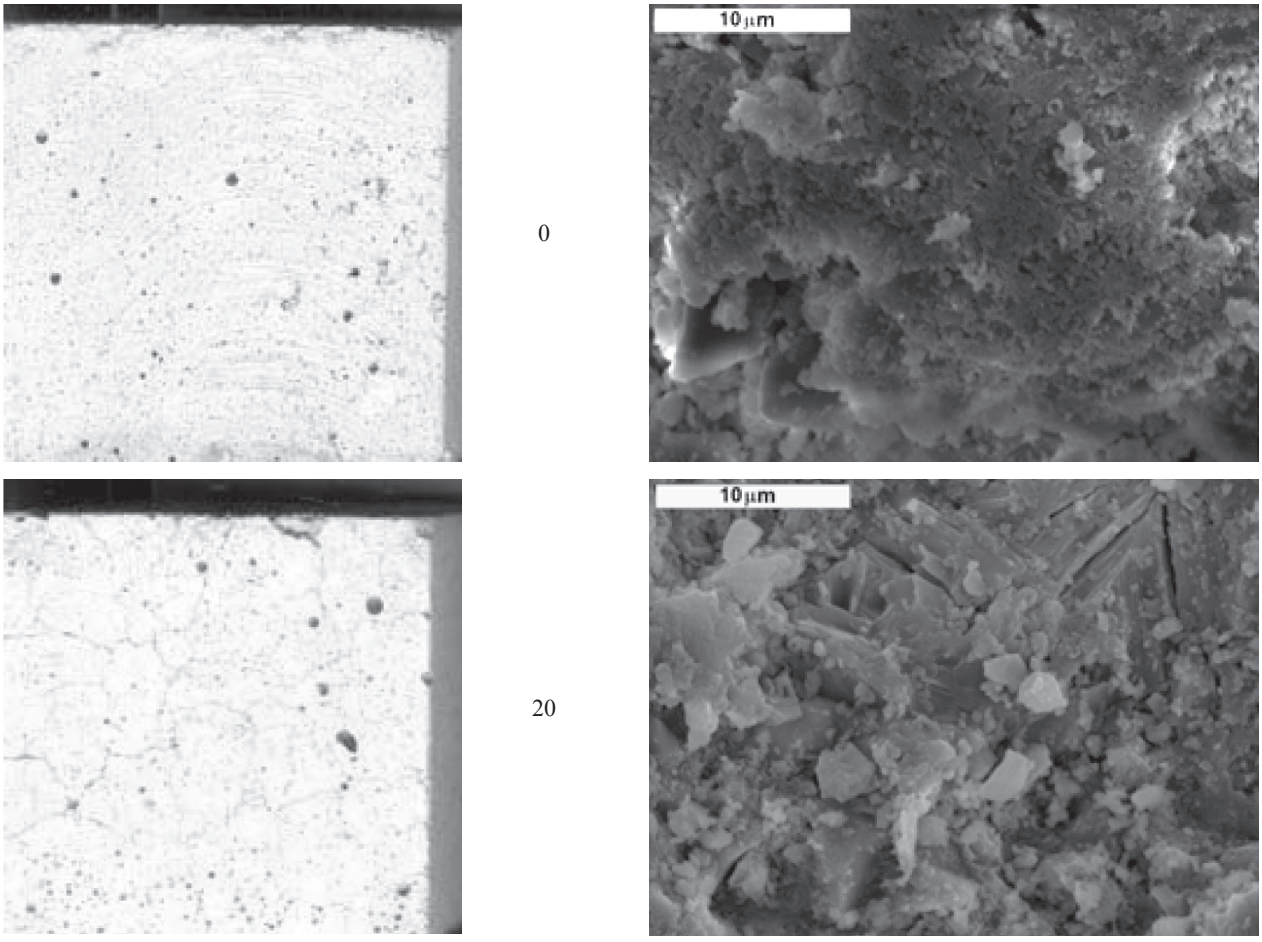

Figure 1. Samples before and during testing.

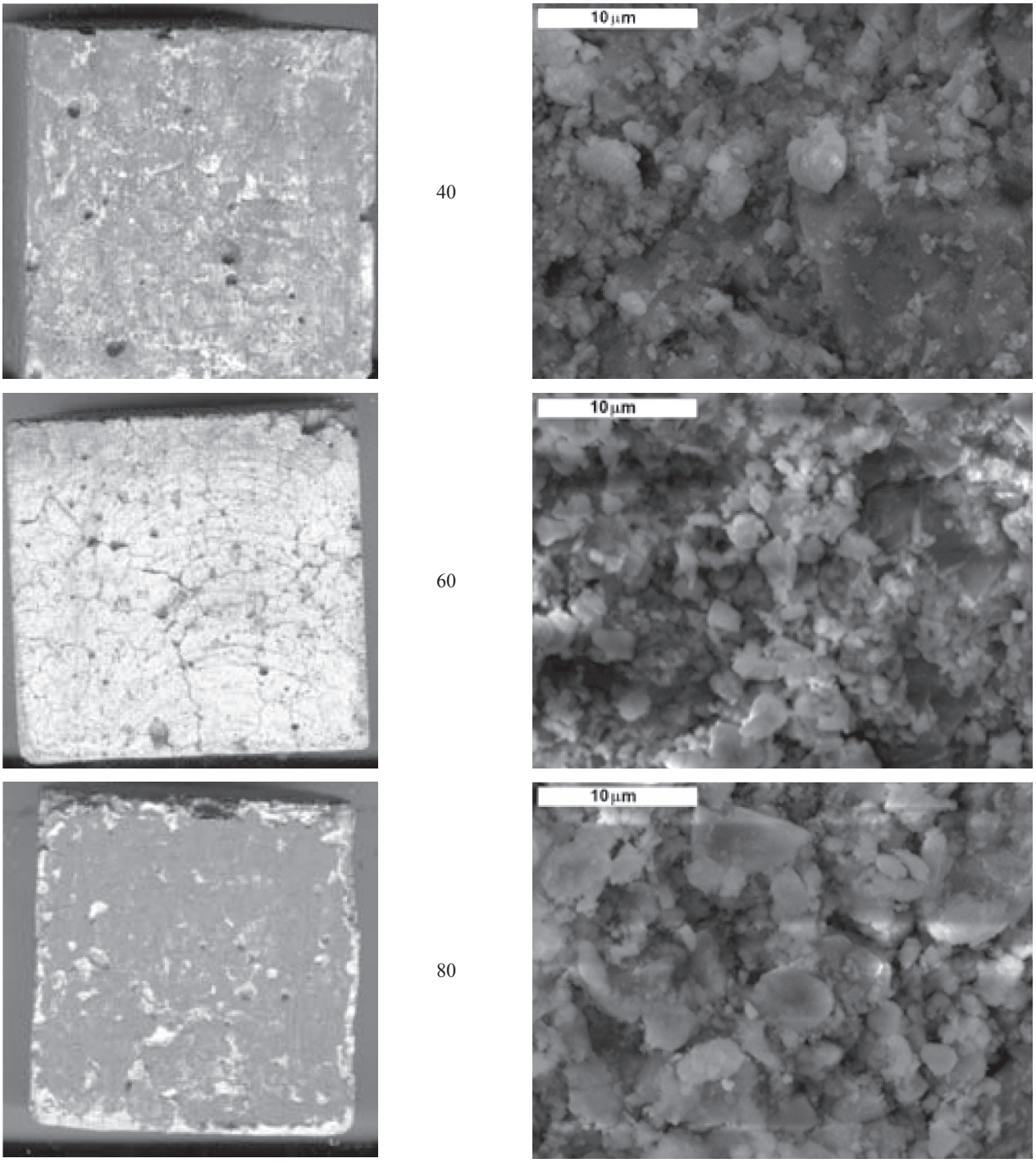

Figure 1. Samples before and during testing *(continue)*.

RESULTS

Destructive testing

The results of water quench test were observed in connection with the mechanical characteristics as well as with the results of image analysis and ultrasonic measurements. Also, the results of compressive strength obtained by standard laboratory procedure (destructive test method) were used for comparison and correlation with the calculated values of strength degradation.

Non-destructive testing

Image analysis

Image analysis by Image Pro Plus Program was used for determination of the sample destruction level. The results of the image analysis are given in Figure 2. as function of number of water quench cycles. All results were calculated and compared to the ideal surface and they were presented in percentages ((P/P_0)·100 %). Since it was evident that some level of surface destruction

occurred after preparation of the samples and before the testing, value of P_0 presented the original surface area (cm^2) before quenching was determined according to the ideal facets of the 16 cm^2, as the samples were cubes (a = 4 cm); P was the measured damaged surface area (cm^2). Similarly, in case of microstructure analysis, levels of degradation were presented in percentages ($(P/P_0)\cdot 100$ %), where P was the destructed area and P_0 was the damaged area of the micrograph before the testing according to the ideal analyzed area of the microphotograph (areas of 74 μm × 74 μm and 31.5 μm × 31.5 μm).

As it could be seen, damage levels of the surface and inside of the sample are very similar until completion of 40 cycles. After that, the surface damage is increasing faster than inside of the samples. This different level of damage could induct additional stress, and have additional influence on samples behavior.

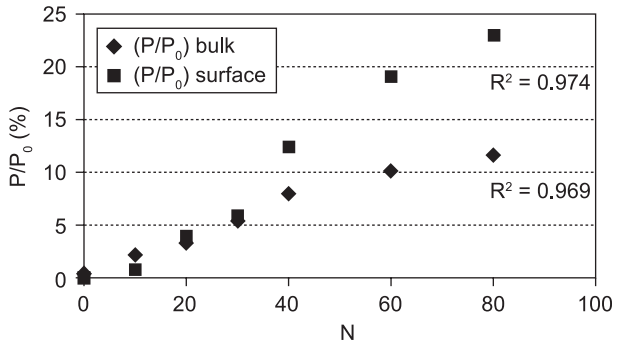

Figure 2. Damage of the samples (P/P_0) during water quench test.

Ultrasonic measurements

The results of ultrasonic velocity changes are given in Figure 3. as a function of the number of cycles (Figure 3a), level of degradation of the sample surface (Figure 3b) and bulk (Figure 3c).

Strength degradation

Equation (1) was applied for calculation of strength degradation. Model 1 represents the results of Equation (1), with coefficient n = 0.488, and model 2 includes different values of n, n = 0.588. The results for models 1 and 2 were compared to the experimental values of strength during testing, and the results are given in Figure 4. The obtained results are given versus number of cycles (Fig. 4a), level of degradation of the sample surface (Figure 4b) and bulk (Figure 4c).

DISCUSSION

Thermal shock behavior measured by water quench test did not answer the questions related to the damage level, as well as strength degradation, which mainly dictate application and life time of refractories. In order to improve the standard testing, image analysis was applied for damage monitoring (surface and inside of the samples) and ultrasonic measurements were used for calculation of strength changes during testing.

The image analysis of the samples before and during testing indicated:

- Certain surface damage of the samples could be present before testing. For our samples, damage was 0.007 % which could be negligible. Also, the same level of damage was present inside the sample. Similar behavior of the damage at sample surface and inside the sample was observed until completion of 40 cycles. After 40 cycles of water quench test, surface deterioration was more rapid then inside of the sample.

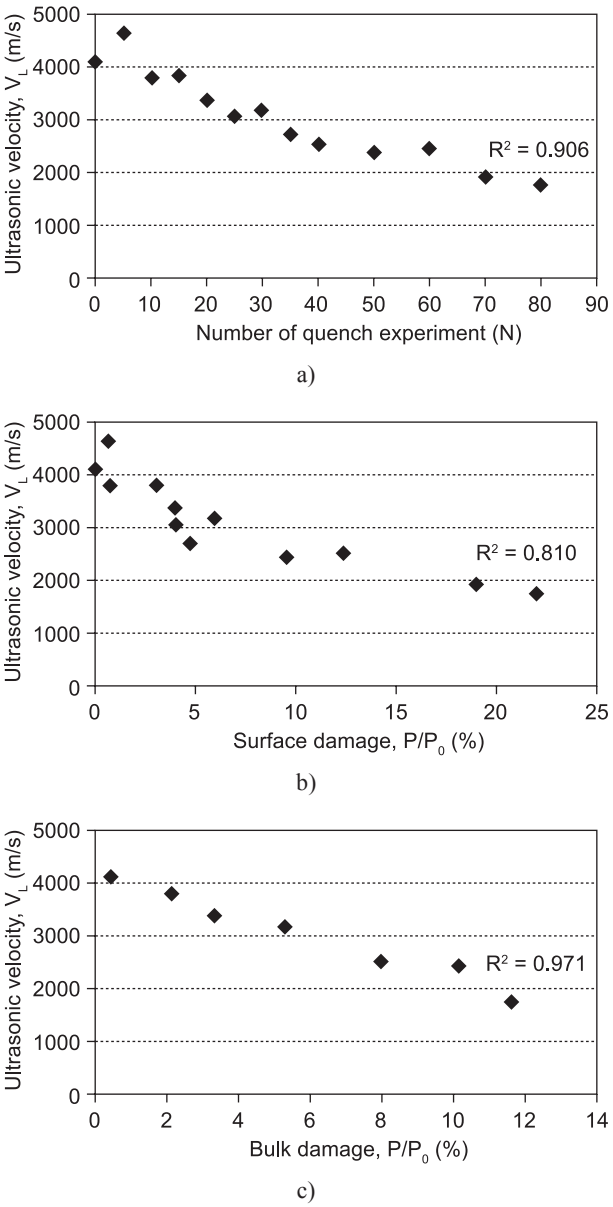

Figure 3. Changes of ultrasonic velocity during testing versus a) number of quench experiments (N); b) level of surface degradation; c) level of degradation inside the sample.

- According to the standard procedure, testing is performed until 50 % of the original surface remains undamaged. For our samples, 23 % was enough to achieve critical moment for damage level during thermal stability testing.

Ultrasonic measurements led to the following conclusions:

- Changes in ultrasonic velocities could be correlated to the number of cycles and level of damage. During testing, ultrasonic velocity is decreasing. The best results of correlation were observed for ultrasonic velocity degradation and level of damage inside of the sample, as expected.

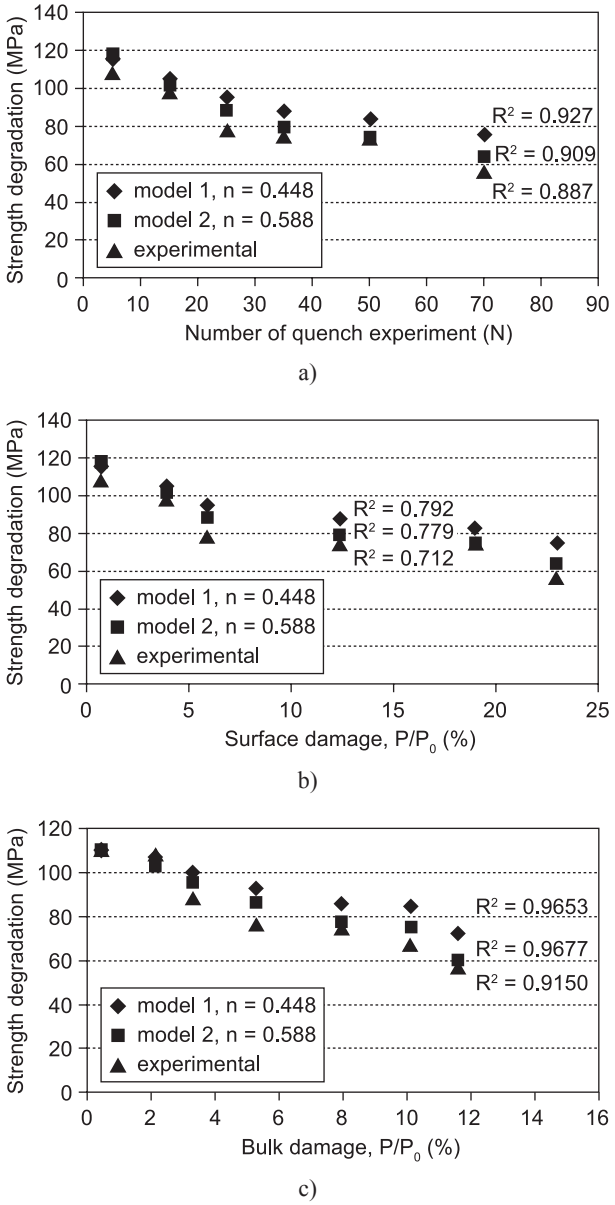

Figure 4. Strength degradation during testing versus a) number of quench experiments (N); b) surface level of degradation; c) level of degradation inside of the sample.

- Strength degradation was measured, and experimental results were correlated to the calculated values obtained by using the models 1 and 2. The best correlation with experimental results was observed for model 2, with $n = 0.588$.
- Strength degradation versus P/P_0 inside of the sample showed the highest values of coefficient of correlation. However, strength degradation could be correlated to the number of cycles with enough accuracy, to make a model for prediction of critical (maximum) number of cycles.
- According to the obtained results, strength degradation was from 110 MPa to average 60 MPa (72.25 MPa from model 1 and 57.06 from experimental results) which is a decrease to 45% of the strength before testing. This strength decrease that occurs after large number of water quench cycles (80 cycles) could be one of the indicators of good thermal shock behavior of the samples.
- The results pointed out that the best result of modeling the strength degradation could be achieved when model 2 is used ($n = 0.588$) and correlated to the bulk damage (inside the sample).
- If value of 60 MPa is defined as a critical strength, than critical number of cycles could be predicted, as it is given in Figure 5; number of 80 cycles will be the predicted critical value.

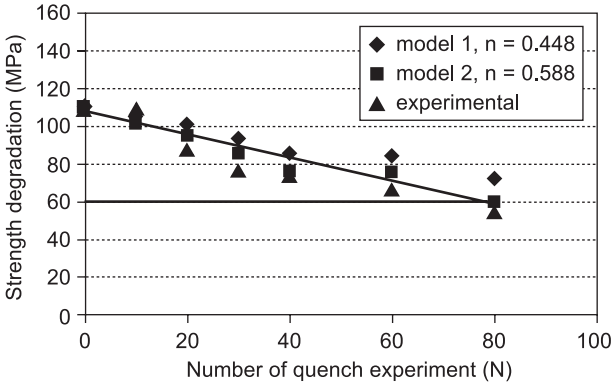

Figure 5. Prediction of the critical number of cycles (N).

CONCLUSION

LCC were synthesized at the sintering temperature of 1100°C in order to investigate thermal stability, surface damage and damage inside the samples, as well as modeling strength degradation in order to predict the thermal shock behavior of the samples. The obtained results during investigation led to the following conclusions:

- Water quench test as an experimental method is insufficient to give a reliable thermal shock behavior prediction and analysis.

- As in thermal shock testing, the procedure recommends visual inspection as a method for test ending (50 % destruction of surface area), implementation of the quantitavive procedure by image analysis of the samples for measuring of surface destruction and degradation inside the bulk could be a way to improve the procedure.
- Image analysis of the samples before and during testing and ultrasonic measurements could be applied and accounted for the samples thermal shock behavior.
- Strength degradation could be predicted by using the proposed models 1 and 2, with different values of n. For model 1, n was 0.488 and for model 2, $n = 0.588$. The best results were obtained with model 2. The analysis of strength degradation could be very useful for life time prediction of the material.
- Based on critical strength (40-50 % of original), the critical number of cycles could be predicted.
- Results of image analysis of the surface and inside of the sample could be correlated to the number of cycles and degradation of ultrasonic velocity and strength. Better correlation was achieved with P/P_0 inside the samples, but surface monitoring is much easier and nondestructive, and could be used for further analysis of the sample behavior subjected to the thermal shock.
- According to the ref. [7] it was suggested that n represents the constant of the material. As privious investigations [15,17-19] were using samples based on SiC and cordierite, this paper was focused on alumina based samples prepared as refractory monolithic material (LCC); the goal of the investigation was to check the possibility to use the same n for a different material. Our results showed that for LCC better correlation with the parameters N, (P/P_0) were obtained with $n = 0.588$. This result pointed out the need to use different values of n for different types of materials.

References

1. Mukhopadhyay S., Sen T. N., Hassan S. M., Pal P.: Ceramics-Silikaty *49*, 97 (2005).
2. Schmitt N., Hernandez J.F., Lamour V., Berhaud Y., Meunier P., Poirier J.: Cem. Concr. Res. *30*, 1597 (2000).
3. Kakroudi M. G., M. Huger, Gault C., Chotard T.: J. Eur. Ceram. Soc. *29*, 2211 (2009).
4. Marenovic S., Dimitrijevic M., Volkov Husovic T, Matovic B.: Ceram. Int. *35*, 1077 (2009).
5. Semler C. E.: Interceram *5*, 485 (1981).
6. Aly F., Semler C. E.: Am. Ceram. Soc. Bull. *64*, 1555 (1985).
7. Nyiog S. K., Das A. C.: Interceram *43*, 453 (1994).
8. Meetxam G.W. & Van de Voorde M.H.: *Marterials for High Temperature Engineering Applications*, Springer, Berlin 2000.
9. M. Bengisu: *Engineering Ceramics*, Springer, Berlin 2001.
10. http:// www.matweb.com
11. Russell R. O., Morrow G. D.: Am. Ceram. Soc. Bull. *63*, 911 (1984).
12. Lockyer G. E., Proudfoot E. A.: Am. Ceram. Soc. Bull. *46*, 521 (1967).
13. Boccaccini D. N., Romagnoli M., Veronesi P., Cannio M., Leonelli C., Pellecani G., Volkov Husovic T., Boccaccini A. R.: Int. J. Appl. Ceram. Technol. *4*, 260 (2007).
14. Boccaccini D. N., Cannio M., D. Volkov-Husović T., Dlouhy I., Romagnoli M., Veronesi P., Leonelli C.: J. Eur. Ceram. Soc. *28*, 1941 (2008).
15. Posarac M., Dimitrijevic M., Volkov-Husovic T., Egelja A., Devecerski A., Matovic B.: J. Optoelectron. Adv. Mater. *10*, 883 (2008).
16. Boccaccini D. N., Kamseu E., Volkov-Husovic T., Cannio M., Romagnoli M., Veronesi P., Leonelli C., Dlouhy I., Boccaccini A.R.: J. Mater. Sci. *43*, 4079 (2008).
17. Posarac M., Dimitrijevic M., Volkov-Husovic T., Devecerski A., Matovic B.: Ceramics-Silikaty *52*, 115 (2008).
18. Posarac M., Dimitrijevic M., Volkov-Husovic T., Devecerski A., Matovic B.: J. Eur. Ceram. Soc. *28*, 1275 (2008).
19. Posarac M., Dimitrijevic M., Volkov-Husovic T., Devecerski A., Matovic B.: Ceram. Int. *35*, 1077 (2009).