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Thermal shock damage characterization of refractory composites

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Abstract

The possibility of using dolomite and bauxite for synthesis of high temperature castable was studied. Behavior of the material in conditions of rapid temperature changes was investigated. Water quench test was applied to determine thermal shock resistance. Level of surface deterioration before and during quenching was monitored by image analysis. Dynamic Young modulus of elasticity was determinated by ultrasonic measurements. The results show that dolomite and bauxite can be effective raw materials for low temperature synthesis of refractory composites.

Keywords: Thermal shock; Composite material; Water quench test; Image analysis

1. Introduction

It is well known that mortars or concretes made with aluminous cement and a heat-resistant aggregate did not crack or spall during repeated firings. Also they could be quenched in water without loss of stability. For this reason, these types composites are f widely used in furnace and kiln construction or reparation [1].

The manufacture of aluminous cement requires a source of alumina and of lime [2]. The customary raw materials are bauxite and limestone. Final products are obtained by melting appropriate proportions of raw materials at high temperature. A relatively high purity of starting materials is essential, particularly the contents of silica and magnesia have to be as low as possible. The concrete is made from aluminous cement and suitably refractory aggregate. A great variety of refractories may be used as aggregate. They have to exhibit stability at high temperatures and do not decompose, or show anomalous thermal expansion. The most commonly used aggregate is crushed aluminosilicate firebrick or chamotte and magnesitechrome. The refractoriness of the concretes rises with the higher temperature stability of the aggregate compounds.

Thermal shock resistance dictates refractory performance in many applications. In many instances, a twofold approach, i.e. (1) thermal shock damage resistance [3–6] or (2) thermal stress fracture initiation [7,8] are used to characterize thermal shock behavior of refractories. The thermal shock resistance of refractories can be obtained by quenching appropriate specimens from an oven at elevated temperature into a medium such as water, liquid metal, oil, or fused salts maintained at a lower temperature. A water quench test most commonly used determining the thermal shock resistance of refractories. Thermal quenching leads to the crack nucleation and/or propagation of cracks resulting in loss of strength. Since the formation of the cracks has a profound influence on the ultrasonic velocity and the Young's modulus of the material, measuring either of these properties may be used to monitor the development of the thermal shock damage level.

The goal of this work is to use nondestructive testing methods and their advantages for prediction of thermal shock behavior. Destruction of the samples was analyzed using the Image Pro Plus Program [11]. This is a very convenient method for determining the damage surface level in samples due to the thermal shock. In this paper the relationship between the change in mechanical characteristics (strength and Young

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modulus of elasticity) and behavior of the samples during thermal shock will be presented.

2. Experimental

2.1. Material

Usually, refractory castables are prepared by mixing an aggregate with cement in a water suspension. However, inhomogeneities introduced at any prior stage remain inside the material and degrade the mechanical properties and reliability of castables. Therefore, in order to produce materials with optimum properties it is important to find processing routes able to produce high homogeneity in powder premixes/mixtures. ''In situ'' synthesis of composite materials with twofold role (hydrolysis and refractory behaviors) is a preferred method. One of the more promising refractory castable mixes are calcium aluminates (Ca_3AlO_5, $CaAlO_4$, $CaAl_2O_7$) and spinel ($MgAl_2O_4$). Calcium aluminates are rapidly hardened materials with high melting point [9]. Spinel is a highly refractory compound with excellent chemical and thermophysical resistance properties [10]. In this paper the possibility of using dolomite and bauxite raw materials for synthesis composite materials was studied.

2.2. Specimen fabrication

The starting material used for green body fabrication were commercial dolomite powder (from the Gradac mine) and bauxite (Chine). The both are low cost powders. The chemical compositions are shown in Table 1. The starting materials were mixed by attrition milling in water. Two different mixtures, M1 and M2, were fabricated. Samples should have 65 and 80% of Al_2O_3, respectively, corresponding to mineral compositions of calcium aluminates and spinel, after firing. Green pellets were obtained by cold isostatic pressing at 240 MPa. Thermal treatment was accomplished in a electrical furnace under exothermic conditions in ambient atmosphere.

Holding time at sintering temperatures was 1 h. The range of sintering temperatures investigated was 1000–1500 °C. Samples were taken out of furnace very fast in order to preserve the frozen state of the reaction, which exists during sintering. For mixture M1, softening, melting temperatures and shrinkage were followed by a high temperature optical microscope. For this kind of investigation, sample in a powdered form was used for hand-press cylindrical specimens, which was then observed during heating. Phase compositions were followed by an X-ray method.

Table 1
Chemical composition of starting materials (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	L.I.
Bauxite	4.29	86.98	3.49	3.05	0.44	1.56	1.56
Dolomite	0.67	0.19	0.52	–	30.37	21.53	46.72

2.3. Quench testing

For the thermal shock stability validation samples dimensions 5.00 cm × 5.00 cm × 5.00 cm were used. This shape and dimensions were chosen for their suitability for analysis of the influence of anisotropy on thermal shock resistance.

Thermal stability was measured by water quench test [10,12–18]. The samples were dried at 110 °C and then transferred into an electric furnace at 950 °C and held for 15 min. The samples were then quenched into water and left for 3 min, dried, and returned to the furnace at 950 °C. This was repeated until total destruction of sample, or destruction of 50 and more percent of surface area before quenching. The number of quenches to failure was taken as a measure of a thermal shock resistance. The experimental method is similar to the procedure described in PRE Refractory Materials Recommendations 1978 (PRE/R5 Part 2).

2.4. Ultrasonic measurements

It is presented in Fig. 1, that thermal cycling negatively affect values of compressive strength during quenching. For the purpose of monitoring change in values of compressive strength and Young modulus during quenching additional experiments were performed.

The ultrasonic velocity was measured with the OYO model 5210 according to the standard testing (JUS. D. B8. 121). The transducers were rigidly placed on the two parallel faces of the cylindrical sample having 5 cm width and 5 cm height using petroleum jelly as the coupling medium. The ultrasonic velocity was then calculated from the spacing of the transducers and the wave form time delay on the oscilloscope. Dynamic Young's modulus was calculated using the expression:

$$E_{dyn} = \rho V_p^2 \frac{(1+\mu_{dyn})(1-2\mu_{dyn})}{(1-\mu_{dyn})} \quad (1)$$

where V_p is the velocity of longitudinal waves (m/s), μ_{dyn} the dynamic Poasson ratio and ρ is density (kg/m^3).

The expression for the compressive strength degradation, based on decrease in ultrasonic velocity was used [15]:

$$\sigma = \sigma_0 \left(\frac{V_L}{V_{L0}} \right)^n \quad (2)$$

where σ_0 is compressive strength before exposure of the material to the thermal shock testing, V_L the longitudinal velocity after testing, V_{L0} the longitudinal velocity before testing and n is the material constant ($n = 0.488$, ref. [15]).

2.5. Image analysis

In this study image analysis was used for the determination of damage surface level before and during testing [11–18]. For the analysis of influence of the anisotropy the samples surfaces were marked by different colors. Results for the damage surface level for the samples before quench experiments are given in Fig. 1A. All results were calculated and related to the ideal

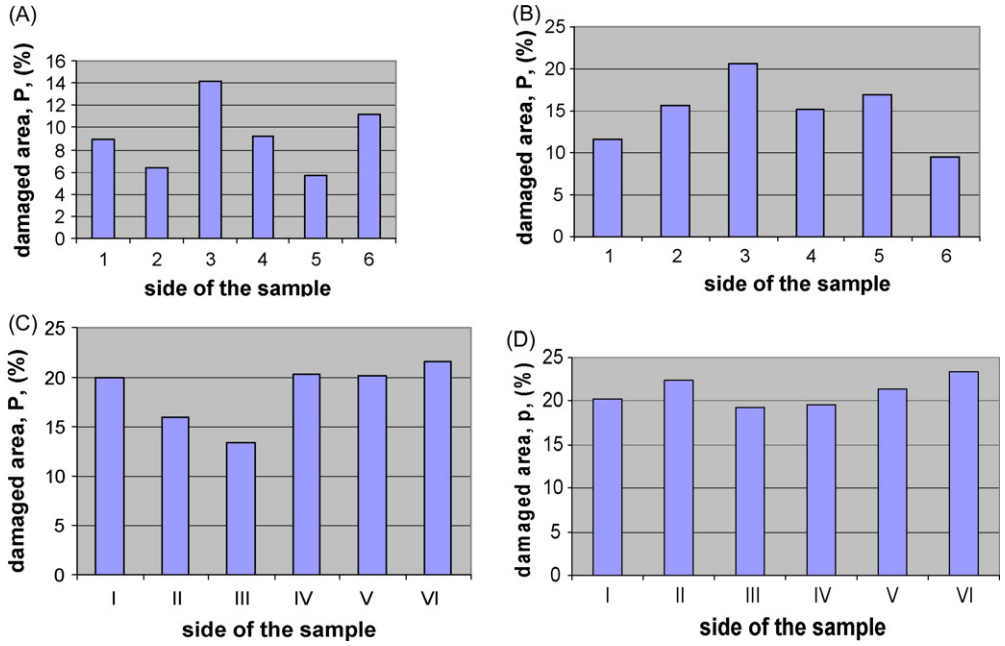

Fig. 1. Histogram of damaged area, P of the sample for the each side of the sample (surface area) (A) before quenching, (B) after 2 cycles, (C) after 5 cycles and (D) after 7 cycles.

surface and results were given in percent (P is measured damaged surface and P_0 = ideal surface before quenching = $a \times b = 5$ cm $\times$ 5 cm = 25 cm^2, P/P_0, %). As can be seen samples before quenching exhibit some deterioration. Level of deterioration is different for the different side of the sample. Average level of deterioration is 9.27%, which is a very high level comparing to the ideal surface ($P_0 = 25$ cm^2).

Fig. 1B–D indicate a significant damage with increasing number of cycles. Results suggested level of anisotropy which has to be included in further investigation, as based of the results of the anisotropy low level of thermal stability could be explained. Summary of the results are presented in Fig. 2. Excellent correlation between damaged surface and number of cycles was obtained ($R^2 = 0.955$).

Results for the damaged areas suggested that behavior of the samples could be explained in two ways:

1. Damaged area of the samples before quenching is very high, average value is 9285% of area, which represent very high level of damage. Or this reason high thermal stability and resistance to thermal cycles is not expected.
2. Damage level increases with increasing number of cycles. After only two cycles average value for damaged area was 14,955% which was high level for only two cycles. After seven cycles surface damage rise to 20,998%, and that explained such low thermal shock resistance.

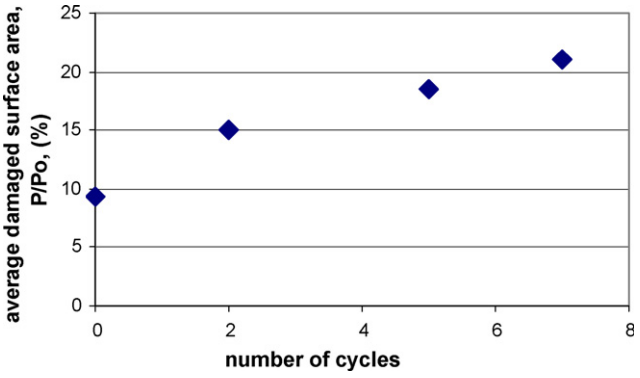

Fig. 2. Average values of damaged area, P/P_0 (%) before and during quenching.

Results of the measurement for decreasing velocity versus number of cycles (A) and damaged surface area (P/P_0, %) are presented in Fig. 3.

The results obtained indicated that ultrasonic velocity could provide us information about behavior of the sample during quenching. These results could be connected to the number of cycles, as well as with the results for damage during quenching.

Applying Eqs. (2) and (1), results for the strength and Young modulus of elasticity degradation during quenching versus surface damage area (P/P_0, %) and number of cycles (N) are presented in Figs. 4 and 5.

The experimental evidence indicate a strong correlation between strength degradation during quenching with the damaged surface area as well as number of cycles. Regression analysis point out high values of coefficients of correlation. For Fig. 4A multiple $R = 0.98591$ and for number of cycles multiple $R = 0.931368$. For the degradation of Young modulus of elasticity similar results were obtained. High levels of coefficient of correlation for E_{dyn} versus P/P_0 (0.942711) and number of cycles (0.853667).

These results allowed prediction of material behavior during water quench test, in parameters such as degradation of: strength, Young modulus of elasticity, damaged surface area or number of cycles. Based on presented results estimated values of either of these parameter could be achieved.

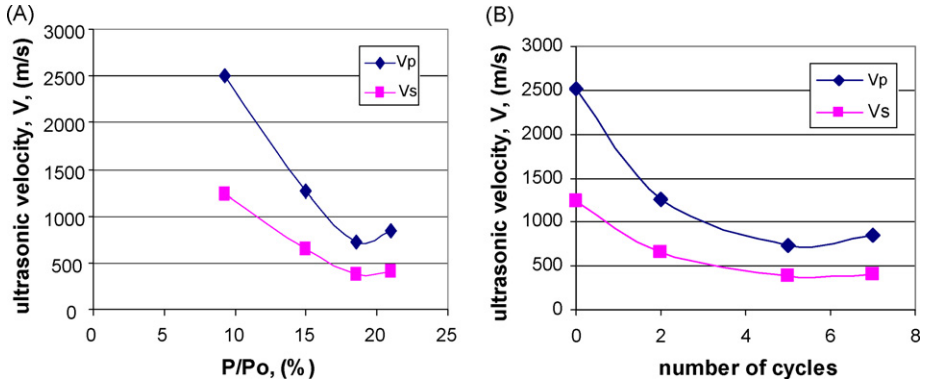

Fig. 3. (A) Decreasing ultrasonic velocity vs. damaged surface area (P/P_0, %) and (B) decreasing ultrasonic velocity vs. number of cycles (N).

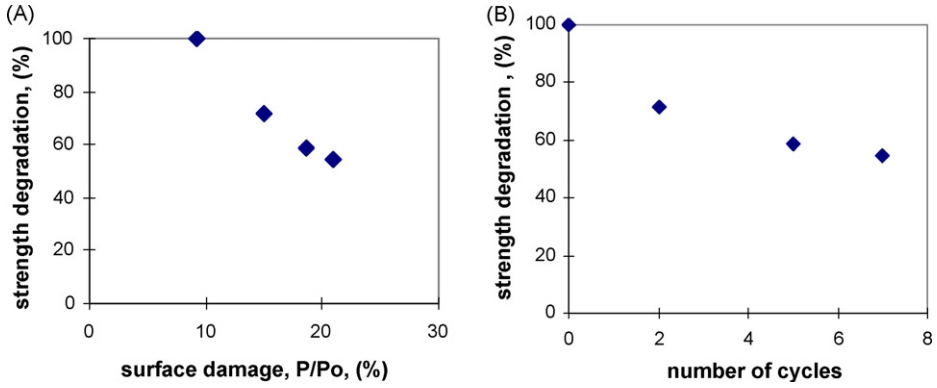

Fig. 4. (A) Strength degradation (%) during quenching vs. surface damage (P/P_0) and (B) strength degradation (%) during quenching vs. number of cycles (N).

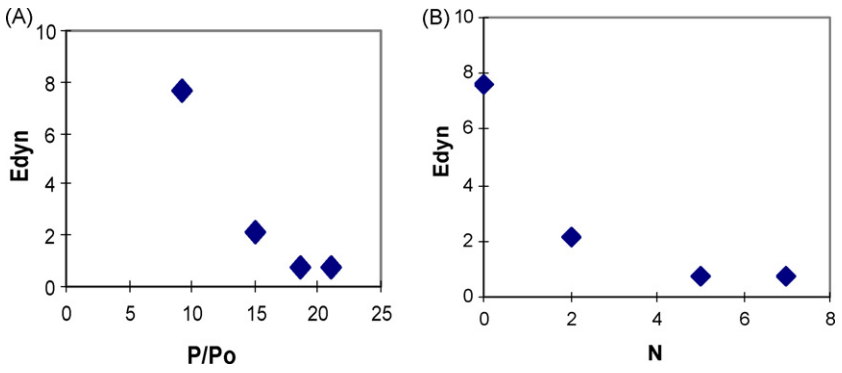

Fig. 5. (A) Dynamic Young modulus of elasticity degradation during quenching vs. surface damage (P/P_0) and (B) dynamic Young modulus of elasticity degradation during quenching vs. number of cycles (N).

3. Discussion

Different tests were performed to investigate thermal stability behavior of the samples. Experimental method, water quench test was used, as most common method for this purpose. Other tests such as image analysis of the surface area during testing and ultrasonic measurement were applied to the samples also.

Obtained results pointed out low thermal stability according to the standard method, only 7 cycles to failure. Other test methods (image analysis and ultrasonic measurements) were very useful in explained results of water quench test.

3.1. Results of image analysis

Image analysis showed very high level of deterioration of the samples before quenching. Also, samples exhibit anisotropic behavior, which was illustrated in Fig. 1, where damage of the each side of the sample was presented. According to the results damage of the samples before quenching is very high, and each

side exhibit different values for damage, in range between 5713 and 14,187%, average value was 9285%. For the seventh cycle these values were in range of 19,217% and 23,413%, average value 20,997%. Results for deterioration and its anisotropy explains low values for thermal resistance measured by water quench test.

Ultrasonic velocity, strength degradation, as well as Young modulus of elasticity degradation were also detected during experiments. These results were expected as they are closely connected to the damaged surface area of the samples. Degradation of these parameters were presented in Figs. 3–5. In all cases high values of coefficient of correlation were obtained between these parameters with the number of cycles of water quench test and damaged surface area.

4. Conclusion

The goal of this paper was to determine if the new material is suitable as refractory insulation. For these purpose set of tests were applied to the samples. Groups of parameters were measured to determine thermal stability resistance of the material based on image analysis and ultrasonic measurements.

Results presented in this paper pointed out the necessity of including other test for thermal stability behavior analysis, beside water quench test, as most popular experimental procedure. Benefits from using image analysis could be as followed:

1. It is fast, nondestructive method, so samples could be used for further tests, and financial aspect in minimising of number of samples for testing is also very important.
2. Analysis of the surface before quench test is possible, and very important information about state 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 for degradation of parameters such are 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.

According to the obtained results, material presented in this paper is material with satisfactory behavior for the insulation. Some changes should be made in process of forming, so better results for thermal stability and less anisotropy of the samples could be expected.

As the experimental procedure added to 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 properties and synthesis conditions for achieving the best results in thermal stability resistance characteristics of material.

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