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THERMAL AND MECHANICAL PROPERTIES OF HIGH ALUMINA LOW CEMENT CASTABLE

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Abstract

Alumina based low cement castable (LCC) was synthesized and then treated from room temperature to 1600°C. Ultrasonic measurements were applied with the aim to obtain results of longitudinal and transversal ultrasonic velocities as well as Young's modulus of elasticity. Changes in microstructure of the samples treated at different temperatures were observed by SEM and image analyses. Correlation among mechanical, physical, and elastic properties and microstructure were also discussed. Results show that heating temperature, microstructure, and porosity have strong influence on cold crushing, flexural, and tensile strength as well as on Young's modulus of elasticity.

Key words: LCC, heating temperature, ultrasonic measurements, mechanical and physical properties, morphology

Introduction

Essential advances in technology of refractory castable over the last decades have led not only to important innovations in castable preparation and application, but also to significant improvements in product properties, as a response to the constantly

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increasing service requirements imposed mainly by steel and foundry industries [1-9]. Due to their superior technical and economical characteristics, the refractory castables are widely used in steel, cement, petrochemical industry, and nuclear engineering for high temperature installations and hot - face linings that are in direct contact with the molten or hot material [1-10]. During the past decades particular attention has been given to the development of low cement, ultra low cement and cement free castables. Nowadays dense low cement and therefore low water containing castables are complex mixtures composed by aggregate, ultra fine filler such is reactive alumina and/or micro silica, additive and high alumina cement. Castable composition should be designed in accordance with some model for obtaining the optimal particle packing. Namely, dispersing additives fluidize ultra fine particles allowing castable flowing and placing with low water addition. Also, reactive fillers and additives fulfil the space in the matrix between the particles of the aggregate thus providing optimal packing in the mixture. Application of castables is suitable especially at high temperatures in the case of complex constructions and they can be easily used for thin sections and regions that are difficult to reach. Exceptional performances that involve physical, mechanical, and thermal properties of refractory castables such are resistance to thermal shock, erosion, abrasion, attrition, corrosion by slags or melting metals are developed particularly after sintering [1-10]. Since refractory castables pass through the large changes from initial setting at room temperature to the final use at high temperatures, the goal of this work was to study development of properties and structure in this temperature range by using both destructive and non-destructive methods for material characterization. Non-destructive testing methods such are ultrasonic measurements and morphology analyses for tracking and study some castable properties were applied. Analysis of the material behaviour at different temperature treatment in order to monitor structure inside the samples was based on the results of ultrasonic measurements. Young's modulus of elasticity was calculated by using measured values of ultrasonic velocities obtained by ultrasonic pulse velocity technique [4-17]. The influence of different thermal treatment on propagation velocity of ultrasonic impulse, dynamic Young's modulus of elasticity, strength development, density, water absorption, apparent porosity, and microstructure are also described.

The purpose of this study was to describe how heating temperature, and therefore microstructure and porosity influence on cold crushing, flexural, and tensile strength as well as Young's modulus of elasticity.

Experimental

Material

A wide range of Al_2O_3 ceramics is commercially available with strength and temperature capability depending on Al_2O_3 content, which is usually in the range of 85 to 99 %. It is the most widely used engineering ceramic material due to such favourite properties as high hardness (25 GPa or 9 on the Mohs scale), high melting point (2054 ºC), good electrical and thermal insulation [1-8].

Particle size distribution was adjusted to the theoretical curve based on modified Andreasen's packing model with a distribution coefficient (q) of 0.25. Determined castable composition was as follows: 95 wt. % of alumina aggregate and ultra fine fractions of reactive alumina such as filler, 5 wt. % of calcium aluminate cement as

hydraulic binder, and 4.67 wt. % of water (dry basis) dispersed with citric acid. This composition provides optimally packed materials and dense particles packing. Therefore, the high value of density and low value of porosity as well as very good mechanical properties can be expected [18-21].

Sample preparation

Since inhomogenity introduced during the preparation of refractory castables remains inside the material and degrade mechanical and physical properties and therefore quality of the castable, particular attention should be directed to this part of investigation. In order to produce the material with high homogeneity in powder mixture, it is important to find processing procedure [1-8]. The procedure applied during this experiment is presented hereafter. As a first step, dry components of the castable were mixed for 1 minute. Then, deflocculant containing water was added and mixed for another 4 minutes. The castable was moulded by vibration and different shapes of specimens were prepared. Cubes (40 x 40 x 40 mm) were prepared for ultrasonic testing, physical properties, and cold crushing strength, while rectangles (40 x 40 x 160 mm) were prepared for flexural strength testing. After demoulding, all samples were cured for 24 hours at room temperature, dried at 110 °C for the next 24 hours, and treated at various temperatures for 4 hours in the range of 20-1600 °C. Finally, they were cooled down to the room temperature inside the furnace.

Chemical composition of the castable dried at 105 ºC is given in Table 1 and relevant physical, thermal, and mechanical properties are given in Table 2.

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

Component	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
(%)	98.11	0.018	1.22	0.02	0.35	<0.001	2.43

Since chemical composition of the castable indicates that amount of the component forming low melting phases (CaO) is quite small, good mechanical properties and corrosion resistance might be expected [3-8].

Table 2. Relevant mechanical, physical, and thermal properties of dried samples.

Property	Value
Compressive strength after drying at 105ºC/24 h	84.37 MPa
Flexural strength after drying at 105ºC/24 h	16.09 MPa
Density	3.12 g/cm^3
Water Absorption	3.2 %
Apparent Porosity	9.1 %
Modulus of Elasticity	23.5 GPa
Refractoriness	SK > 35 (1780 °C)
Refractoriness under load	Ta, Te > 1780 °C

Further results show the effect of heating temperature on microstructure, physical, and mechanical properties of samples.

Samples characterization

Microstructural analyses

Evaluation of microstructure with heating temperature increase was monitored by using SEM type JEOL JSM-5800 with an energy dispersive X-ray spectroscope (EDX). Level of porosity and specimens morphology were observed by image analyses and Image Pro Plus Program.

Physical Properties

Density, apparent porosity and water absorption of low cement castable samples were determined by water immersion method according (ICS 81.080 SRPS B.D8.302). Average values of measurement on three specimens (cube shaped with 40 mm edge length) for each observed temperature were presented in this paper.

Apparent porosity or portion of open pores refers to the pores or voids connected to the surface. The open pores directly affect the properties such as slag resistance and permeability. On the other hand, porosity is the ratio of pore volume percentage contained in a sample and volume of investigated sample together with pores and voids. During this research, the porosity was established by optical methods which include determination of the material area versus the area of the pores visible under the microscope.

Mechanical Properties

Cold crushing and flexural strength as well as ultrasonic measurement of the samples treated at different temperatures were determined by classic method of destructive testing following procedures prescribed by standards, i.e. ICS 81.080SRPS B.D8.304, ICS 81.080SRPSB.D8, and ICS 81.080 SRPS D.B8.121, respectively.

Ultrasonic measurement

First application of ultrasonic pulse velocity testing (UPVT) on refractory materials was reported in the late 1950s[4-14] . The various publications have dealt with the practical application of UPVT as a nondestructive method to characterize and monitor the properties of industrial refractory materials. Briefly, pulses of longitudinal elastic stress waves are generated by an electroacoustical 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 a second transducer.

The velocity (V) is calculated from the distance between two transducers and electronically measured transit time of the pulse may be expressed as:

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

where L is the path length (m) and T is the 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 equation below [10-17, 22-24]:

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

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

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.). Using vaseline grease as the coupling medium the transducers were tightly placed on two parallel faces 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 wave from time delay on the oscilloscope.

Results and discussion

From room temperature to 800 ˚C, the castable is subjected to the dehydration process when the matrix undergoes through the significant transformations that can influence the microstructural development as well as change of physical and mechanical characteristics of the castable [1-8,16,17,22]. Heating the castable above 900 °C particularly affects bulk density, strength and porosity due to removal of chemically bound water. All changes of castable properties can be correlated with the phase transformation in castable structure. Phase composition of the castable can be predicted by ternary phase diagram CaO - Al_2O_3 - H_2O. Also, the composition can be detected and proved by XRD and SEM analyses after treatment at particular temperature. Stable phases AH_3 (crystalline) and C_3AH_6 (cubic), and methastable phases CAH_{10} and C_2AH_8[†] are present in the structure of the sample cured at room temperature. Dried sample show presence of only stable phases AH_3 and C_3AH_6. Sample heated at 400 °C has an AH phase and residual C_3AH_6 phase, while sample treated at 800 °C contains A, CA, CA_2 phases. During the heating of samples above 800 °C, transformation of A, CA, CA_2 occurrs. The only phase present in the sample treated above 1400 °C is CA_6 which is the bonded phase of high refractoriness.

Obtained results of apparent porosity, water absorption, bulk density, and cold crushing strength versus treatment temperature are presented in Figure 1 and Figure 2. Flexural and tensile strength changes depending on treatment temperature are shown in Figure 3.

Apparent porosity increases with temperature treatment as well as water absorption except in case of sample treated at 400 °C. Apparent porosity of investigated castable is quite low, probably beacuse of both small amount of microcracks between large aggregates and matrix and small open porosity of coarse aggregate tabular alumina (≤ 5 %). Apparent porosity and water absorption of cured samples show quite low values. This can be explained by hydration of cement and concret, in other words, by formation of hydrated cement phases such as CAH_{10}, C_2AH_8, C_3AH_8, and AH_3. Actually, AH_3 is the stable phase in the form of gel that can fill and close the pores making the dense structure. During drying, apparent porosity increases probably due to free water evaporation. Apparent porosity slightly increases with the rise of treatment

[†] Bouge's notation is used in this research (C=CaO, A=Al_2O_3).

temperature up to 800 °C due to evaporation of crystalline water, organic, and inorganic compounds. The evaporation creates free space in the material and therefore cause an increase of apparent porosity.

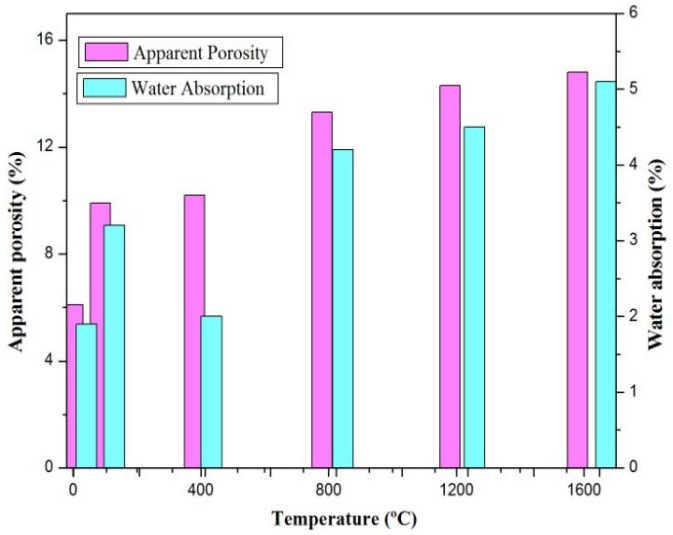


Fig. 1. Changes of apparent porosity and water absorption with temperature of treatment.

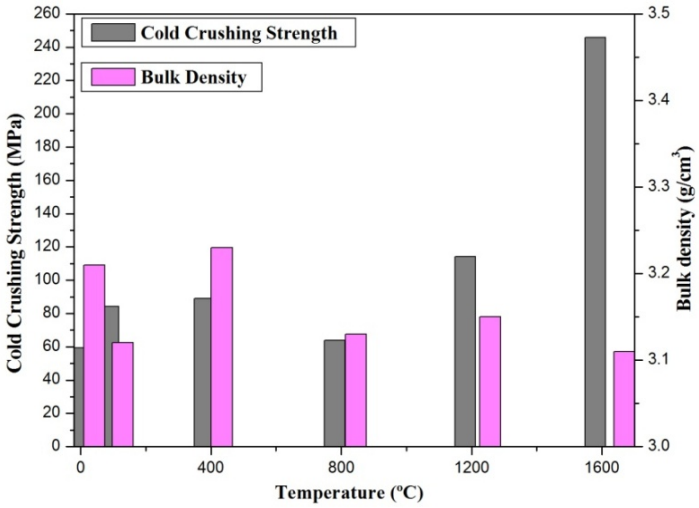


Fig. 2. Cold crushing strength and bulk density changes as dependence on heating temperature.

Formation of hydraulic bond in cement and matrix leads to the appearance of the structure composed of stable phases AH_3 and C_3AH_6 with remarkably high initial strength after curing at room temperature and drying at 105 °C, Figure 2. Firstly, physically bound water is removed from the sample during drying. Secondly, in the range from 200 to 800 °C chemically bound water (crystalline water) is released by breaking hydraulic bonds which is followed by slight decrease of the strength, Figures 2 and 3. It is obvious that for the sample treated at 800 °C the slight drop of cold crushing strength reaches the value of 75.88 % compared with the initial value obtained for the sample after drying. It can be explained by the fact that the hydraulic bond was broken at this temperature, whereas processes of sintering and formation of ceramic bond are still inactive. Heating the samples above 900 °C leads to the sintering and strong densification of material caused by the formation of ceramic bond and inter - diffusion of atoms and ions among the components in order to achieve an energy stable structure and therefore better mechanical properties, Figures 2 and 3 [1-8]. Strong ceramic bond is formed above the temperature treatment of 1400 °C and apart from the presence of A phase, CA_6 phase also appear in the structure. Therefore, the ultimate cold crushing strength, after treatment at 1600 °C is very high reaching almost triple value than the cold crushing strength of dried sample.

Similar trend is observed in the case of bulk density change with increase of temperature treatment. Typical density gap is noticeable for the sample treated at 800 °C. It should be noticed that values of bulk density for all observed temperatures are around 3.2 g/cm^3.

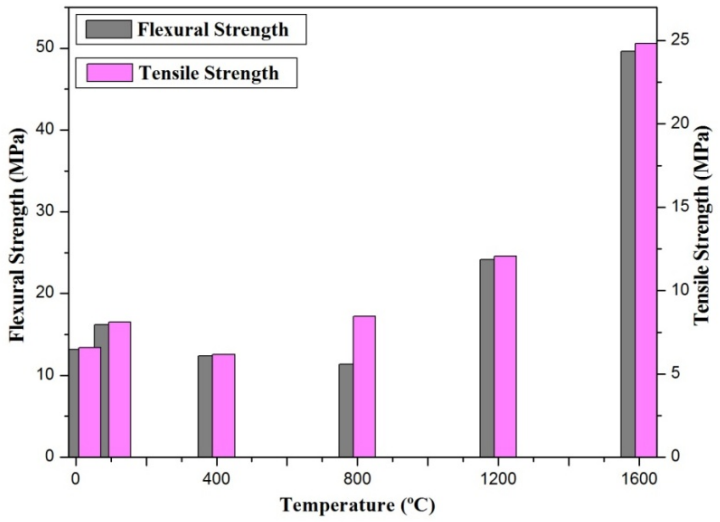
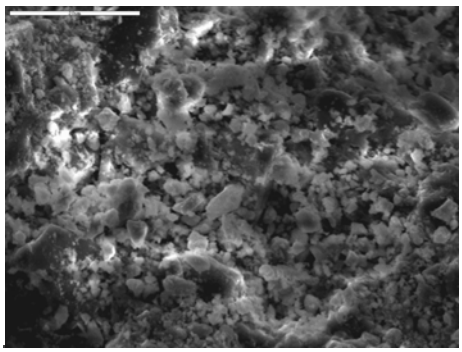


Fig. 3. Change of flexural and tensile strength versus treatment temperature.

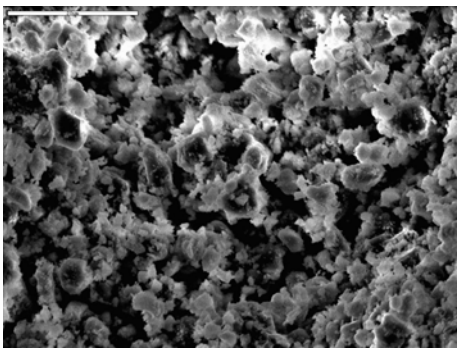
Results of flexural and tensile strength show similar trend as results obtained for cold crushing strength. Namely, after 24 hours of curing and drying, samples show good flexural and tensile strength. Unlike a slight drop of cold crushing strength observed for the sample treated at 800 °C, a negligible decrease of the flexural and tensile strength

appears for the sample treated at 400 °C. Possible explaination for the slight decrease of both strengths in case of the samples treated at 400 °C can be found in release of the bound water (crystalline) from the hydrated castable structure. Sintering starts above 900 °C which is followed by improvement of mechanical, physical, and elastic properties caused by phase changes and development of strong atomic bonds typical for ceramic compound. In the intermediate period of hydraulic and ceramic bond formations, mechanical strengths deteriorate as a natural consequence. Values of flexural strength are moderate due to anisotropic grain growth and small content of impurities forming low melting compounds such are SiO_2, Fe_2O_3, Na_2O. Results indicate that for the sample treated at 1600ºC the exceptionally high value of strength is achieved due to densification, sintering, and formation of CA_6 phase. Reactive alumina is the key component strongly influencing the degree of sintering and strength of castables at high temperatures. During sintering, the reaction between calcium aluminate cement and fine fractions of alumina (reactive and aluminas smaller than 20 μm) occurs, whereas the coarse grains of alumina remain virtually inactive. Also, the reactive alumina is not only the binding agent, but is also the main component to achieving good rheological and flowing properties of the castables [16-17].

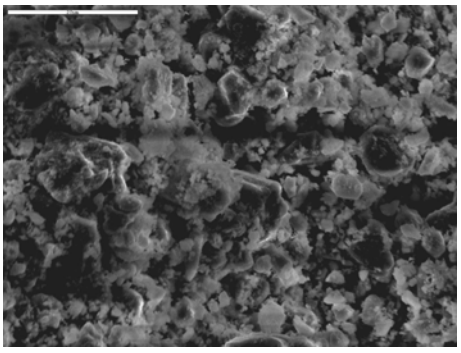
Typical microstructure of the castable treated at different temperatures for 4 hours was obtained by using SEM, Figure 4.



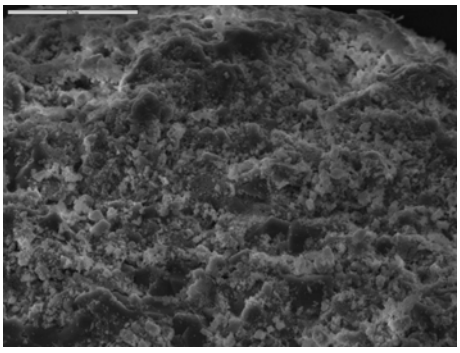
T = 105 °C



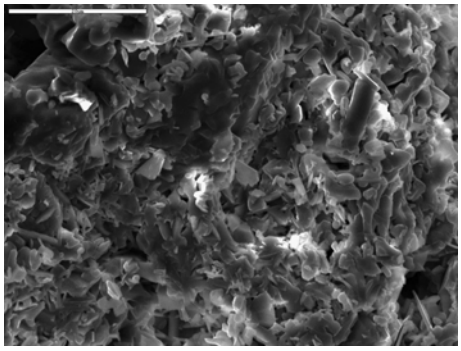
T = 400 °C



T = 800 °C



T = 1200 °C



T = 1600 °C

Fig. 4. SEM images of structure after heating at different temperatures.

SEM images proved that the microstructure of dried sample consists of stable cubic phase C_3AH_6 of trapezohedral crystal and stable gibsite phase AH_3 in the form of monoclinic prisms. Beside the newly formed A phase, plated crystals of CA_6 are observed in the microstructure of the sample sintered at 1600 °C. These phases induce remarkable increase of the castable strength [1-8] Microstructure of the samples is changed during the heating especially at higher temperatures, over 1000 °C. The microstructure is characterized by the occurrence of smaller grains, increase of the contact surface, decrease of porosity, and significant densification. In addition, sintering is clearly noticeable above 1200 °C [16-17]. These changes in the structure at different temperature are expected and correlated with phase transformations during the heating.

By image analysis of the SEM microphotographs, level of porosity was obtained using Image Pro Plus Program. Results are given in Figure 5. It can be observed that the porosity decreases with the increase of treatment temperature

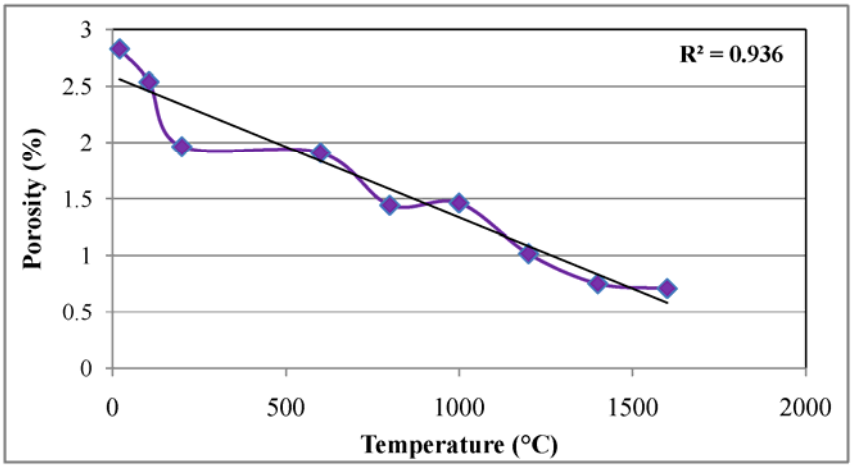
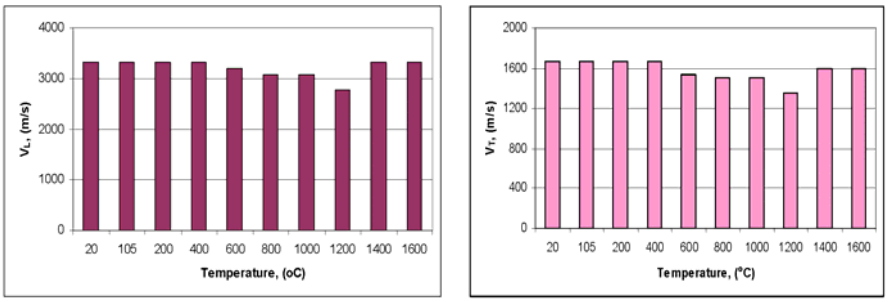


Fig. 5. Change of porosity during heating.

Results indicate low values of the porosity for all observed samples. Porosity decreases with the rise of treating temperature, from 2.83 % for the sample cured at the room temperature to 0.71 % for the sample treated at 1600 °C. It is important to emphasize that the porosity is below 1.00 % for all samples treated above 1200 °C.

Obtained results of ultrasonic velocity during passing through samples treated at different temperatures are presented in Figure 6. Measuring is based on the fact that the sonic pulses travel faster through the less dense sample and structure with higher porosity.



a) b)

Fig. 6. Dependence of longitudinal and transversal ultrasonic velocity (V_L) and (V_T) on treatment temperature.

Besides the changes in mechanical and physical properties, heat treatment yields changes in ultrasonic velocity, Young's modulus of elasticity and porosity, as well. It is evident that changes of the ultrasonic velocities are almost negligible for the samples dried at 105 °C and heated at 400 °C in comparison with the cured samples. Ultrasonic velocity starts to attenuate till 800 °C and is partly reduced at 1200 ºC. Then, it increases for the sample sintered at 1600 °C. This can be explained by the microstructure which became denser with lesser porosity enabling the sonic pulses to travel faster. The described tendency can be related with improvement of physical and mechanical properties. Degradation trend of the ultrasonic velocity for the samples treated at 800 °C and 1200 °C is related to the typical density and cold crushing strength gaps induced by breaking of hydraulic bond, and before the forming ceramic bond [1-8,16-17].

Results of the Young's modulus of elasticity as a function of the thermal treatment are shown in Figure 7. Obtained results indicate that at higher temperature values for elasticity modulus are lower than at the beginning of the treatment, but at all applied temperatures values of Young's modulus of elasticity are around 20 GPa.

In Figure 7 the trend of curve which describes changes of dynamic elasticity modulus with increase of treatment temperature shows that this material is anisotropic, heterogeneous and elastic. Slight drop of elasticity modulus for the samples treated at 800 °C and 1200 °C for 4 hours is observed. Sample sintered at 1600 °C shows increase of elasticity modulus. Probably, modulus of elasticity attenuates due to dehydration of the hydrated cement phases. At the same time hydration of still anhydrous CA phase by water released during the transformation of hydrated phases takes place [16-17]. This is

confirmed by morphology which shows that decrease in the CA content is accompanied by increase in modulus. This means that the castable can compensate the effects of the phase transformation and recover certain mechanical properties by further hydration of anhydrous phases. There is a strong correlation between Young's modulus and mechanical strength, thus an increase in E yields to the increase in mechanical strength. This assumption can be confirmed by the drop of slope of cold crushing, flexural, and tensile strength only for the sample treated at 800 °C, Figures 2. and 3. According to the literature data [19,25], tabular alumina does not have smooth surface like fused grains but rough surface with shallow semispherical pores. This surface structure of the aggregate enhances reaction and mechanical interlocking with bonding matrix providing better mechanical strength of the material.

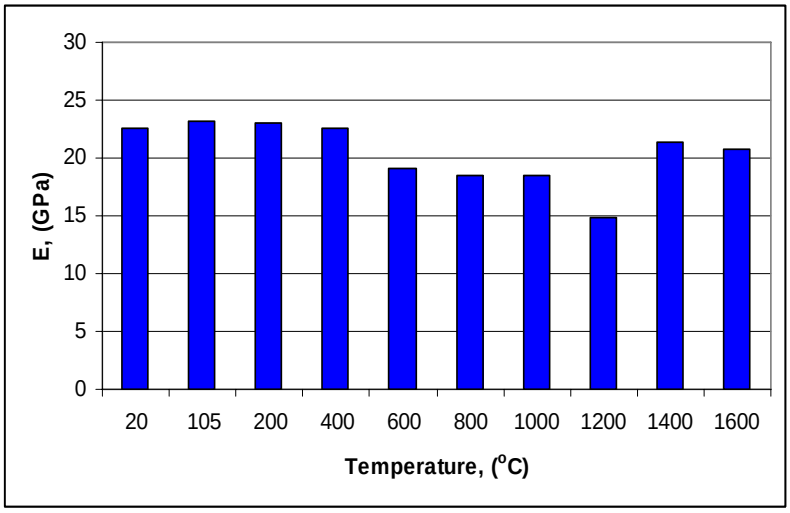


Fig. 7. Dependence of dynamic Young's modulus of elasticity on treatment temperature.

SEM images give evidence of the different microstructure after treatment at various temperatures. Results of the ultrasonic velocities, Young's modulus of elasticity, and strength can be correlated to the structure of the material considering decrease of porosity with increase of temperature treatment. Beacuse of the sintering effect, porosity decreases for the sample sintered at 1600 °C due to structure with small porosity and high portion of small pores.

Conclusion

Low cement high alumina castable was synthesized and treated by heating at different temperatures in order to investigate the influence of heating temperature on structure and mechanical properties of the samples. Purpose of this extensive analysis is very important particularly beacuse of its significant influence on application and life time of refractory castables. Morphology of the samples treated at various temperatures were different. Based on image analysis, changes of porosity are monitored. Increasing the temperature of treatment leads to decreasing of porosity which exhibited strong

influence to the mechanical properties. Also, it was concluded that treating temperature has a strong influence on cold crushing, flexural, and tensile strength as well as modulus of elasticity. Based on obtained results, samples treated at temperatures over 1000 °C show significant improvement of mechanical properties. The best mechanical properties were obtained for the sample sintered at 1600 °C. However, lower heating temperature (1000 - 1600 °C) will also provide very good mechanical properties, and in this case the influence on energy saving cannot be desregarded.

Acknowledgements

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