



Preparation and properties of low cement castable sintered at different temperatures[#]

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Abstract

The low cement high alumina castable (LCC) studied in this paper was synthesised, cured and then treated at different sintering temperatures. Since any inhomogeneity introduced during the castable preparation can remain inside the material degrading its properties and therefore the quality during service life, particular attention was given to the processing procedure in order to produce the material with the optimum characteristics. Composition of the castable regarding particle size distribution was adjusted according to the Andreassen's packing model. The samples were sintered at 1100, 1300 and 1600°C for three hours. Influence of the different sintering temperatures on the castable properties is discussed. Compressive and flexural strengths were determined by destructive testing method, while the water immersion method was used for determination of the bulk density and the water absorption. Changes of elastic properties and microstructure (porosity) were observed by the non-destructive testing methods, ultrasonic measurements and image analysis. Based on the results, it can be concluded that sintering temperature has strong influence on the properties of the LCC. Exceptionally good properties were obtained for the sample sintered at 1600°C, but it should be highlighted that the samples treated at 1100 and 1300°C were provided with good properties, too. This should not be neglected because of the energy saving importance, in cases where the material sintered at lower temperature satisfies the application requirements.

Keywords: refractory castable, sintering, mechanical properties, physical properties

1. Introduction

Over the last decades, use of unshaped monolithic refractories has been increasing greatly because of their significant advantages over other shaped refractories of the same class. Among the unshaped refractories, the refractory castables are one of the most important groups of these materials due to their superior technical and economical characteristics. The refractory castables are widely used in a lot of high temperature installations for hot-face linings that are in direct contact with the molten or hot material, for example in

the steel, cement, petrochemical industry, and nuclear engineering [1]. During the past decades, particular attention has been given to the development of low and ultra low cement as well as cement free castables. Initially, the castables were composed only of cement and aggregates, but nowadays modern LCC are characterized by an addition of deflocculants, fine and ultrafine fillers with the aim to optimize castable properties. In addition, the castable grain-size composition should be designed in accordance with a packing model that provides maximum dense particle packing [1–5]. Dispersed additives fluidize ultra fine particles, thus allowing castable flowing and placing with low water addition [1,2]. Selection and amount of added high alumina cement depend on the castable application temperature and required physical properties.

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Thus, if the content of cement and hence amount of CaO in the cement is lower, less quantity of water will be required for preparing and moulding of castables leading to the increase of density, decrease of porosity, better mechanical properties, and therefore high resistance on abrasion attrition [6]. Also, the LCC show very high performance in terms of thermo-mechanical properties, particularly after sintering, such as: thermal shock resistance, superiority during erosion, abrasion, corrosion by slags or melting metals, mechanical and thermal spalling [3–5]. Due to formation of hydraulic bond in the cement (and therefore in the structure as well) that strengthened the “green” body, it should be expected that castable samples, cured and dried at 105°C, show quite impressive “green” cold crushing strength. Samples treated at higher temperatures show considerable increase of strength because of “recrystallization” or “ceramization”, formation of anhydrous stable oxides and sintering [7,8]. The key component that strongly influence the castables degree of sintering and strength development at high temperatures is reactive alumina. During the sintering, the reaction between calcium aluminates and fine alumina (reactive and fraction under 20 µm aluminas) is happened, whereas the coarse alumina remains virtually inactive. Also, the reactive alumina, besides the binding agent, is the main component for achieving good rheology of the castable mixture [1]. Therefore, refractory castable should be considered as composition comprised of a matrix and coarse aggregate grains. Fractions under 45 µm form a matrix, where the main component is the cement containing the certain amount of CaO. By adding of water, fine and ultra fine particles of alumina and CaO form calcium aluminate hydratable phases inside the matrix; during the heating (drying and sintering), they pass throughout the transformation. Phase changes in the matrix with temperature increasing from room temperature to 800°C can be assumed by system A-C-H, while phase changes above 1000°C can be determined by binary system A-C considered in this study (in this paper Bogue’s notation is used, where C is CaO, A is Al₂O₃, and H is H₂O [9–12]). Also, all phase transformations observed by XRD of the matrix (not presented here) and SEM analyses of the castable confirmed presence of the phases proposed by the literature.

All formed phases possess particular characteristics such as density, crystal structure, and number of water molecules which affect the physical properties and castable behaviour during the heating [10]. The initial phases in castable were developed by hydraulic bonding of cement. Metastable hexagonal hydrate phases are occurred in the castable matrix at room temperature: CAH₁₀ with low density ($\rho=1.72$ g/cm³) and C₂AH₈ ($\rho=1.95$ g/cm³) [2]. After drying,

they transform to the more densely packed structure and reducing porosity, stable phases: cubic phase of C₃AH₆ ($\rho=2.52$ g/cm³) and hexagonal structure of AH₃ ($\rho=2.42$ g/cm³). At elevated temperature, the hydraulic bonds break due to the liberation of bonded water from hydrate structures, and at 800°C matrix structure is consisted of A and CA phases. At still higher temperature, ceramic bond formation takes place by interdiffusion of atoms and ions among the components to develop an energetically stable structure. After heating to 1100°C, besides A phase presented in the structure, the reactive alumina and CaO react and produce CA and CA₂ phases. All these phases enhance high temperature thermomechanical behaviour. Treatment at 1600°C leads to the formation of CA₆ phase, the high temperature bonding phase, which is formed through solid phase sintering of fine alumina and calcium aluminate cement during the castable heating [1–12].

Purpose of this study was correlation between sintering temperature, morphology, physical, and mechanical properties. Both non-destructive and destructive testing methods were used in study of the LCC properties.

The formation of different microstructure and porosity at different temperatures results in differences in the ultrasonic velocity during travelling through the sample and leads to different values of material properties, such are strength, bulk density, and elastic properties. Young’s modulus of the samples is calculated by using measured values of ultrasonic velocities obtained by ultrasonic pulse velocity technique [12–26]. Mechanical and physical properties of the prepared samples were measured by using the standard laboratory procedures that is the method of destructive testing and the water immersion method, respectively. Porosity of the samples was determined by using the SEM images and appropriate program for the image analysis. The influence of different thermal treatment on ultrasonic velocity values, dynamic Young modulus, strength development, density, water absorption, porosity, and microstructure changes are also described.

II. Experimental

2.1. Material

Low cement castable tested in this paper was prepared by tabular alumina (*T-60, Almatiss*) used as an aggregate with the maximum particle size of 5 mm, and the matrix composed of fine fractions of the tabular alumina, reactive alumina as an ultrafine filler (*CL-370, Almatiss*), 5 wt. % of the calcium-aluminate cement (*CA-270, Almatiss*), and the dispersing alumina (*ADS-3 and ADW-1, Almatiss*). The castable was mixed with 4.67 wt.% of water (dry basis) dispersed with citric acid. Particle size distribution was adjusted to the theoretical curves based on modified Andreassen’s packing model, with a distribution coefficient (*q*) of 0.25.

2.2. Specimen preparation

In order to produce the material with optimum characteristics, finding the appropriate processing procedure that enables high homogeneity in powder mixture is very important [27]. First, the dry components of the castable were mixed, and then deflocculant containing water was added and mixed for 4 min. The castable was moulded by vibration forming specimens of the cubes shape with 40 mm edge length for physical properties and compressive strength tests as well as the prisms of 40×40×160 mm for flexural strength testing. After demoulding, all samples were cured for 24 hours at room temperature, dried at 110°C for 24 hours, sintered at various temperatures of 1100, 1300 and 1600°C for 3 hours, and cooled down to the room temperature inside the furnace. Prepared alumina based refractory material had 98.11 % of Al₂O₃ and 1.22 % CaO. Since chemical composition indicates that amount of the components that can form low melting phases (CaO) is quite small, good mechanical characteristics and corrosion resistance were expected [1–12].

2.3. Physical Properties

Density, apparent porosity and water absorption of LCC samples were determined by water immersion method according (ICS 81.080 SRPS B.D8.302) on the three specimens of cube shape with 40 mm edge length for each sintering temperature.

2.4. Mechanical Characteristics

Compressive and flexural strengths of the samples treated at different sintering temperatures were determined by classic method of destructive testing following standard laboratory procedures ICS 81.080 SRPS B. D8. 304 and ICS 81.080 SRPS B. D8 307, respectively.

2.5. Microstructure analyses

Microstructure of the sintered samples was monitored by using SEM type JEOL JSM-5800. Before SEM testing, the samples size of 5–8 mm were prepared by the spattering with nitrogen for 30 minutes.

2.6. Ultrasonic determination of Dynamic Young modulus of elasticity

The ultrasonic pulse velocity testing (UPVT) [13–18] was first reported being used on refractory materials in the late 1950's. The 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. 13–26. Briefly, pulses of longitudinal elastic stress waves are generated by an electro-acoustic 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 [m/s], is calculated from the distance between the two transducers and the electronically measured transit time of the pulse as:

$$v = \frac{L}{T} \quad (1)$$

where L [m] is the path length and T [s] is the transit time.

By measuring the bulk density, the Poisson's ratio, and the ultrasonic velocity of a refractory material, it is possible to calculate the dynamic modulus of elasticity by using the equation below [17–22, 28]:

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

where v is the pulse velocity [m/s], ρ is the bulk density [kg/m³] and μ_{dyn} is the dynamic Poisson ratio.

The measurement of ultrasonic velocity was performed by using the equipment OYO model 5210 according to the standard testing procedure (ICS 81.080 SRPS 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 the Vaseline grease as a coupling medium. The ultrasonic velocity was then calculated from the spacing of the transducers and the wave from time delay on the oscilloscope.

III. Results and discussion

During the heating above 900°C, the castable is subjected to the sintering and at higher temperature to densification where the structure undergoes through the significant transformations that furthermore influence on physical and mechanical characteristics particularly on the bulk density, strength, and porosity. As already mentioned, all changes of the castable properties can be correlated to the phase transformation in the castable structure according to the systems C-A-H and C-A, while XRD and SEM analyses for the specific chemical composition at certain temperature treatment can confirm the presence of particular phases.

The results of compressive and flexural strength changes depending on sintering temperature obtained by the destructive testing method are presented in Fig. 1. After 24 hours of curing at room temperature and drying at 105°C for 24 h, samples show remarkable high values of initial mechanical characteristics due to formation of hydraulic bond in the cement and the structure composed of the metastable and stable (AH₃, C₃AH₆) phases, respectively. Samples treated at 1100, 1300 and 1600°C for 3 hours show significantly improved strength due to formation of the ceramic bond which occurs by the inter-diffusion of atoms and ions among the components with the aim to develop

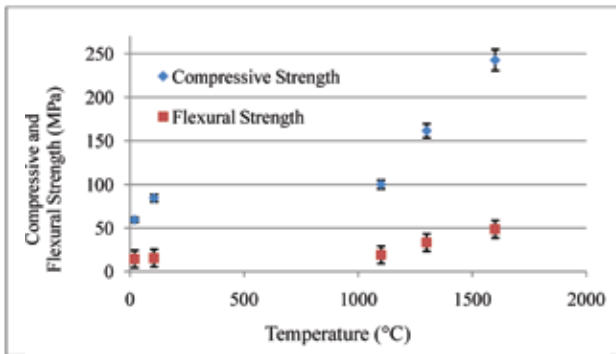


Figure 1. Compressive and flexural strength changes depending on sintering temperature

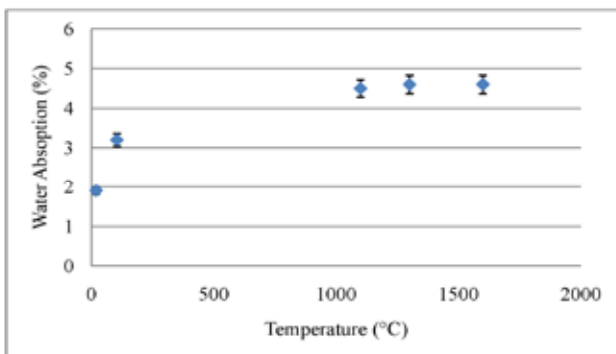


Figure 2. Water absorption depending on sintering temperature

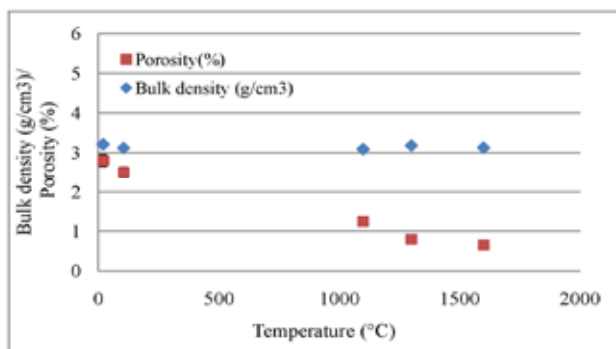


Figure 3. Bulk density and porosity versus sintering temperature

an energetically stable structure, and therefore better mechanical properties. It is obvious that the samples sintered at 1100°C and 1300°C for 3 hours achieves 41 % and 66 % of the compressive strength, respectively, than the sample treated at 1600°C for 3 hours. Similar results and trends can be noticed for the flexural strength values depending on the sintering temperature. Ultimate strength of the sample sintered at 1600°C are very high reaching almost five-fold greater value than the reference sample (dried at room temperature) due to more sintering and the formation of CA_6 phase.

Obtained results of the water absorption, porosity, and bulk density depending on sintering temperature are presented in Figs. 2 and 3.

It is obvious that the water absorption increases from the room temperature to 1100°C, while during the further heating to the temperature of 1600°C changes in values of the water absorption is almost negligible. It is important that the values of water absorption do not exceed 5% for all samples.

Due to the good packing of particles, high density of the castable is obtained even for the reference samples (cured at 20°C and dried at 105°C for 24 hours) and that they amount around 3.1–3.2 g/cm³. Slight increase in bulk density and decrease in porosity above 1100°C shows the beginning of densification and liquid phase formation, which occupied the pore spaces, Figs. 2 and 3. Similar trends of porosity and bulk density were observed in LCC elsewhere. By using the image analysis of the SEM images, it can be concluded that the porosity remarkably decreases, while the densification slightly increases with rising of the sintering temperature.

Porosity of the samples was determined by implementation of SEM and image analysis program. Initial porosity of the castable is quite low (< 3 %), probably because of the both small amounts of microcracks between the large aggregates and the matrix and low value of coarse aggregate tabular alumina open porosity which is ≤ 5 %. Possible explanation of low initial porosity and high bulk density is formation of AH_3 -stable gelatinous phase that can close pores between interfacial defects and form denser structure filled with gel [2]. Implementation image analysis by using the Image Pro Plus Program showed that the porosity at 1100°C was 1.25 %, and for higher temperatures measured values were below 1 %.

Typical microstructure of the castable samples heated at the temperatures 1100 and 1600°C for 3 hours was obtained by using the SEM, Fig. 4. The smaller grains with high contact surface area is noticeable in the microstructure of the sample treated at 1100°C. Besides, the coarser plated shaped CA_6 crystals is observed in the microstructure of the sample sintered at 1600°C.

Results for monitoring changes of the Young modulus of elasticity during different sintering temperatures are shown in Fig. 5. Since the sonic pulse travel faster through the less dense sample and the structure with higher porosity and its velocity is directly proportional on E_{dyn} , there is possibility to correlate elastic properties with the porosity, bulk density, and strength of the castable.

Obtained results for the dynamic Young modulus of elasticity indicate that the values of the reference samples (cured and dried) did not change significantly, but remarkable increase of the elasticity modulus occurs for the sintered samples. The trend curves of dynamic Young's modulus reported in Fig. 5 show that this material is anisotropic, heterogeneous, elastic material. The changes in the slope of the $E=f(T)$ at 1100°C and 1300°C must be related to the expansive formation of CA_2 phase and volume expansion that associate to the

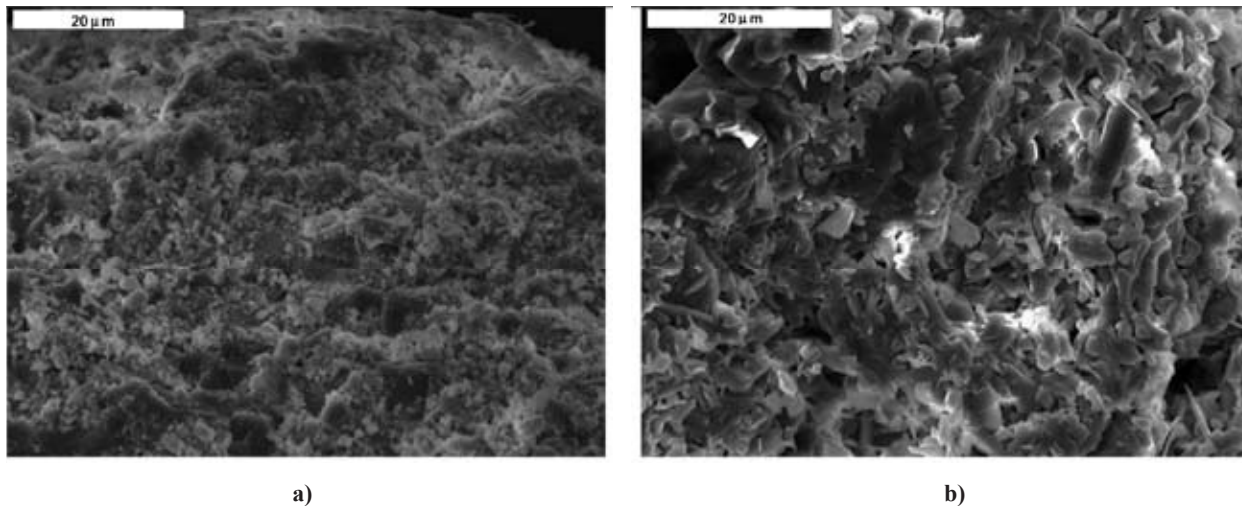


Figure 4. SEM images of the samples structure after heating at different temperatures:
a) 1100°C for 3 hours and b) 1600°C for 3 hours

reaction between CA and A. On the other side, shrinkage due to sintering and densification occurs at the same temperature. The trend of shrinkage by densification of the materials is opposed to the formation of CA_2 associated with an increase of porosity, and the consequence is increase of the elastic modulus at 1300°C; namely, more pronounced densification developed at 1300°C. The sharp increase of the elastic properties is noticeable in sample treated at 1600°C because of the formation of CA_6 crystals inside tabular alumina grains, improved grain-grain contacts between the matrix and aggregates, and intensive sintering. There is a strong correlation between elastic modulus and mechanical strength, thus an increase in E yields an increase in mechanical strength. The increase of the elasticity modulus can be explained by microstructure that became denser with lesser porosity and improvement of the physical and mechanical properties that is indeed related to sintering of the material. The values of Young modulus of elasticity start to increase first slowly and after 1100°C faster. There is a strong correlation between elastic modulus (E) and mechanical strength, thus an increase in elasticity modulus yields an increase in mechanical strength. Also, results of the Young modulus of elasticity and strength changes

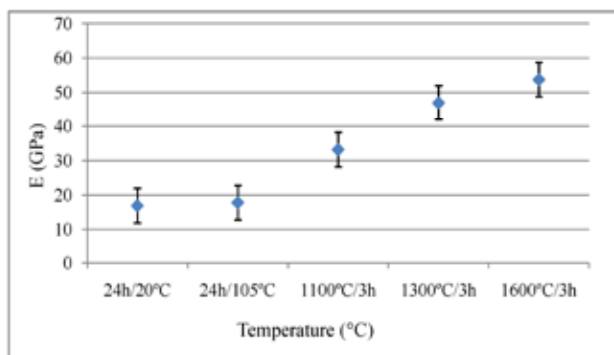


Figure 5. Dynamic Young modulus of elasticity versus sintering temperature

can be correlated to the structure of the samples sintered at the different temperatures.

Based on the above study, it is obvious that the sintering temperature has strong influence on mechanical and elastic properties, and on the microstructure as well.

IV. Conclusions

Low cement high alumina castable was synthesized and sintered by using different temperatures in order to investigate influence of sintering temperature on structure, physical, and mechanical properties of the samples. Microstructure analysis of the samples sintered on various temperatures was observed. It is obvious that increasing the sintering temperature leads to densification and decrease of the porosity, which exhibit strong influence on mechanical and physical properties. The highest values of mechanical properties was obtained in the sample sintered at temperature of 1600°C. However, very good mechanical properties were obtained in the sample sintered at 1300°C for 3 hours. It is very important in means of energy saving.

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