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Influence of Raw Materials Ratio and Sintering Temperature on the Properties of the Refractory Mullite-Corundum Ceramics

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***Abstract*—**The alumosilicate ceramics with mullite crystalline phase are used in various branches of science and technique. The mullite refractory ceramics with high porosity serve as a heat insulator and as well as a constructional materials. The purpose of the work was to sinter high porosity ceramic and to increase the quantity of mullite phase in this mullite, mullite-corundum ceramics. Two types of compositions were prepared during the experiment. The first type was the compositions with commercial alumina and silica oxides. The second type was from mixing these oxides with 10, 20 and 30 wt% of kaolin. In all samples the Al_2O_3 and SiO_2 were in 2.57:1 ratio, because that was conformed to mullite stechiometric compositions ($3Al_2O_3 \cdot 2SiO_2$). The types of alumina oxides were α-Al_2O_3 (d_{50}=4μm) and γ-Al_2O_3 (d_{50}=80μm). Ratios of α-: γ-Al_2O_3 were (1:1) or (1:3). The porous materials were prepared by slip casting of suspension of raw materials. The aluminium paste (0.18 wt%) was used as a pore former. Water content in the suspensions was 30-47 wt%. Pore formation occurred as a result of hydrogen formation in chemical reaction between aluminium paste and water. The samples were sintered at the temperature of 1650°C and 1750°C for one hour. The increasing amount of kaolin, α-: γ-Al_2O_3 at the ratio (1:3) and sintering at the highest temperature raised the quantity of mullite phase. The mullite phase began to dominate over the corundum phase.

***Keywords*—**Alumina, Kaolin, Mullite-corundum, Porous refractory ceramics

I. Introduction

THE mullite is the only stable crystalline phase in the alumosilicate system under normal atmospheric pressure. The high levels of the functional properties of alumosilicate ceramics depend on the general content of mullite, on its structural and morphological state [1], [2]. The industrial methods for producing alumosilicate ceramics are based on the highest formations of mullite quantity. This is achieved by using the refractory clays with high amount of SiO_2 and Al_2O_3. The kaolin is an example of such clay [3], [4]. The mullite ceramic can be achieved from alumina and silica oxides mixing with refractory clay in certain ratios [4], [5].

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The flow complex of physic-chemical processes is important at the time of sintering at the high temperatures. These are dehydration, decomposition of the components of the mass, combustion of organic impurities, the reaction between the components of the mass with the formation of other crystalline phases and polymorphic transformations [6]. The kaolinite and other minerals of clay are converted into mullite and cristobalite, quartz into various modifications of silica. When kaolin is heated, its important minerals – kaolinite is transformed to mullite by several steps according to the following reaction scheme (Fig. 1). The mullite is formed at the sintering time of alumina and silica mixing at the temperature of 1300-1750°C (Fig. 2) [5], [6].

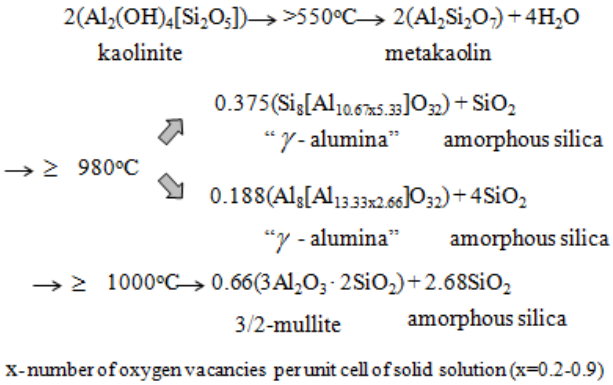

Fig. 1 Kaolinite phases transformation in the time of kaolin heating [6]

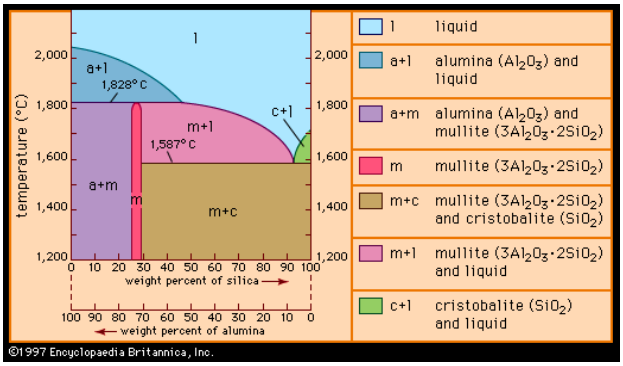

Fig. 2 Phase diagram of the alumina-silica system. Dependence on the temperature, on the content of silica and alumina quantity [7]

The mullite ceramics have high mechanical strength, chemical stability and high refractoriness. The mullites are produced by heat treatment of the starting materials, essentially via solid-state reactions. These mullites tend to have "stechiometric", i.e., 3/2-composition ($3Al_2O_3 \cdot 2SiO_2$, i.e., ≈72 wt% Al_2O_3) [6]. Therefore, the Al_2O_3 and SiO_2 were in 2.57:1 ratio in all experimental samples. The sintering temperature and process influence on the bulk density, mechanical strength, thermal stability, porosity and shrinkage of the samples. Our mullite, mullite-corundum porous materials are prepared by slip casting of suspension of raw materials. Raw materials are alumina oxides with different grain size, pure silica and kaolin, which are used in corresponding ratio. The aluminium paste (0.18 wt%) is used as a pore former. Therefore, the purpose of our work is to find the optimal conditions for the production of ceramic with the best structural properties, high quantity of mullite phase and porosity. These conditions are the temperature of sintering and ratio between raw materials.

II. Materials and Methods

Three series (S, L, and M) of porous mullite-corundum ceramic samples were prepared from suspension of raw materials (Table I). Two types of Al_2O_3 (*Nabalox, Germany*): α-Al_2O_3 (d_{50}=4 μm) and γ-Al_2O_3 (d_{50}=80 μm), pure SiO_2 (d_{50}=6.94 μm), kaolin (*MEKA, Germany*) (with SiO_2-56.5 wt%, Al_2O_3-31.0 wt%, Fe_2O_3-0.33 wt%, kaolinite 72 wt%, quartz 21 wt%, illite 7 wt%), 1 % polyelectrolyte of carboxymethylcellulose sodium salt *"Optapix 1000"* and distilled water were used as raw materials, aluminium paste (*Aquapor 9008*) was used as pore former.

The Al_2O_3 and SiO_2 were in 2.57:1 ratio in all samples, because that was conformed to mullite stechiometric compositions ($3Al_2O_3 \cdot 2SiO_2$). The types and ratios of Al_2O_3 were different in first and second series of samples.

The first three compositions of samples were prepared only from α- or γ-Al_2O_3, and from these alumina oxides mixing (α-:γ-Al_2O_3) in 1:1 ratio, also 20 wt% of 1 % polyelectrolyte of carboxymethylcellulose sodium salt *"Optapix 1000"*.

In the others compositions of samples α-Al_2O_3 and γ-Al_2O_3 were used in 1:3 ratio between themselves. The quantity of kaolin was 10, 20 and 30 wt% of dry raw materials mass.

TABLE I
The Raw Materials Compositions Of Samples

wt%	Kaolin	α-Al_2O_3	γ-Al_2O_3	SiO_2	Al paste
S1	-	72	-	28	0.18
S2	-	-	72	28	0.18
S3	-	36	36	28	0.18
L1, M1	10	16.2	48.6	25.2	0.18
L2, M2	20	14.4	43.2	22.4	0.18
L3, M3	30	12.6	37.8	19.6	0.18

Water content in the suspensions was 30-47 wt%, aluminium paste was 0.18 wt% in all samples.

Three important technological processes were necessary for preparation of samples (Fig. 3). These include the making of suspension from raw materials, drying and sintering of samples.

First, at the time of suspension preparation, raw materials were mixed in dry state and then part of distilled water was added to this composition and mixed for 20 minutes at the (20-25°C) room temperature. The suspension of aluminium paste was created from the second part of distilled water, then it was inserted into suspension of the raw materials, supplementary mixed about 3-5 minutes. The forms were filled with final suspension of compositions of raw materials. Hydrogen elimination was observed at this period in result of the chemical reaction of Al with water. The Pore formation process occurred approximately after 15 minutes at the temperature of 20-25°C. Overall, H_2 elimination process took 40-60 minutes. As the result the volume increased by 1-1.5 times. After that the samples were drying for 24 hours at the temperature of 50°C.

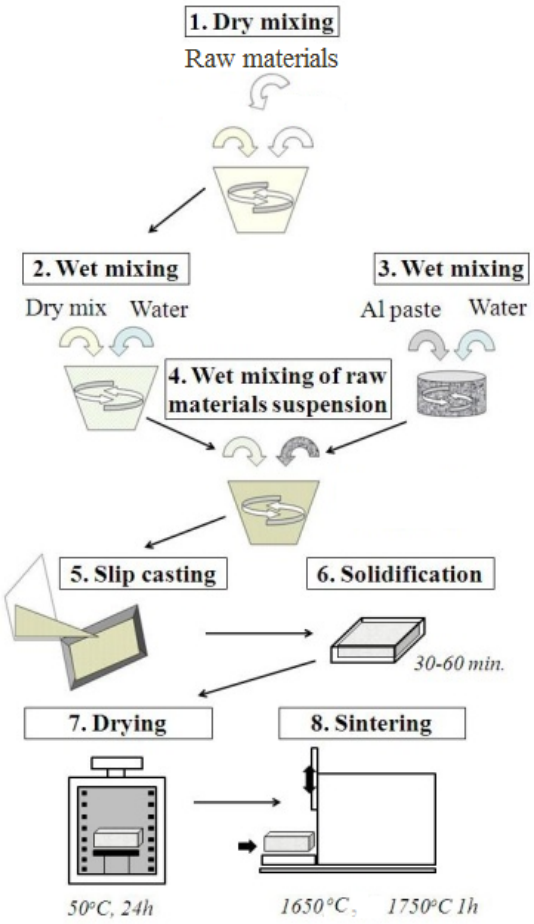

Fig. 3 Scheme of technological process of ceramics preparation

TABLE II
SINTERING TEMPERATURE OF THE SAMPLES

Samples			Sintering temperature
S1	S2	S3	1650°C
L1	L2	L3	1650°C
M1	M2	M3	1750°C

The porous samples were fired at the temperature of 1650°C and 1750°C with a temperature raising speed of 250°C/h of conditioning at these temperatures for 1 hour and with following gradual cooling in this furnace (Table II). Obtained materials were sawed up into bars (15x15x140 mm).

Various testing methods such as XRD analysis (Rigaku Ultima+), shrinkage, bulk density, hydrostatic weighting, pores sizes distribution by Hg porosimetry (Pore Master), optical microscopy (Optical Stereomicroscope Leica 420) and three point bending strength (ZwickBDO-FB020TN) were used to study the properties of the samples.

III. RESULT AND DISCUSSION

The properties of produced materials depend on the composition and firing temperature. The mullite phase is the determinative factor of refractoriness of our porous ceramic. From XRD results of S and L series samples, that were sintered at the temperature of 1650°C (Fig. 4, Fig. 5), all materials contain phases of the mullite and corundum.

The samples of L series also contain these both phases. However, the quantity of mullite phase is bigger than it contained at the samples of S series. The corundum phase decreases with increasing of kaolin quantity. Comparatively, the intensity of mullite phase goes up with increasing of kaolin quantity.

Also the quantity of mullite phase increases with increasing of firing temperature. Therefore, the diffraction maximums of mullite phase are more intensive at firing temperature of 1750°C than at 1650°C. Both mullite and corundum phases are when firing temperature is 1750°C and 10 wt% of kaolin is used (Fig. 6). The mullite phase dominates in M2 samples with 20 wt% of kaolin. Only mullite phase is in M3 samples with 30 wt% of kaolin, that were sintered at the 1750°C (M3 - Fig. 6). This can be explained as the result of mullite ceramic producing by heat treatment of the starting materials of kaolin, alumina and silica oxides, essentially via solid-state reactions. The increasing amount of kaolin and sintering at the highest temperature raised the quantity of mullite phase. It begins to dominate over the corundum phase. This is observed with decomposition of kaolin to mixed oxides and the formation to 3/2-mullite in the reaction with additional alumina and silica oxides at the sintering process.

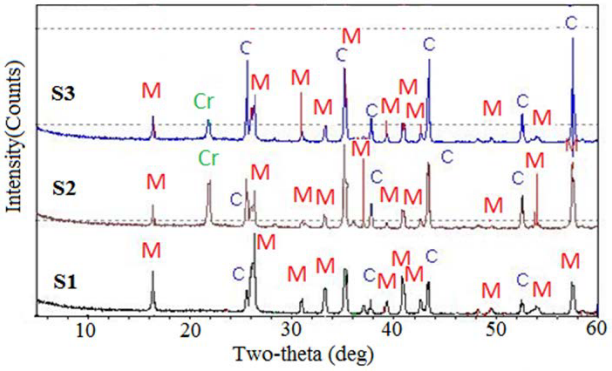

Fig. 4 XRD patterns: Comparison of phases of S series samples. (M- Mullite, C-Corundum, Cr- Cristobalite)

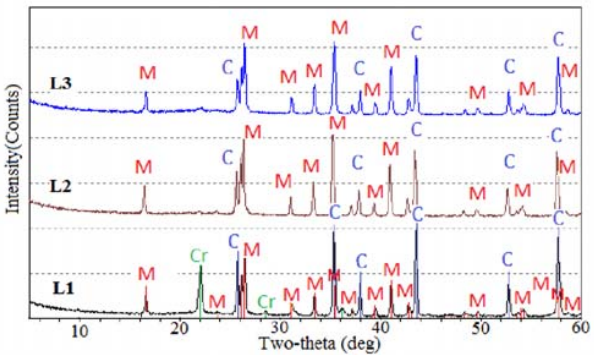

Fig. 5 XRD patterns: Comparison of phases of L series samples. (M- Mullite, C-Corundum, Cr- Cristobalite)

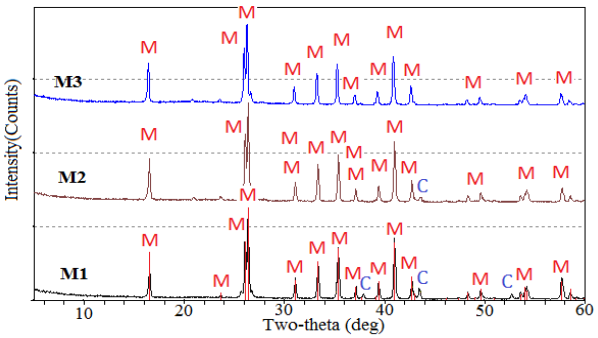

Fig. 6 XRD patterns: Comparison of phases of M series samples. (M- Mullite, C-Corundum)

Application of α- and γ- Al_2O_3 in ratio 1:3 and sintering at the 1750°C provide its reaction with amorphous silica that is formed from decomposition of kaolin.

The shrinkage of samples increases with kaolin quantity increasing from 10 to 30 wt% in raw materials compositions that were sintered at the temperature of 1650°C and 1750°C (Fig. 7). The samples with 10 wt% of kaolin and 1650°C sintering temperature have the smallest shrinkage (about 4%). The samples with 30 wt% of kaolin and 1750°C sintering temperature have the largest shrinkage (about 24%).

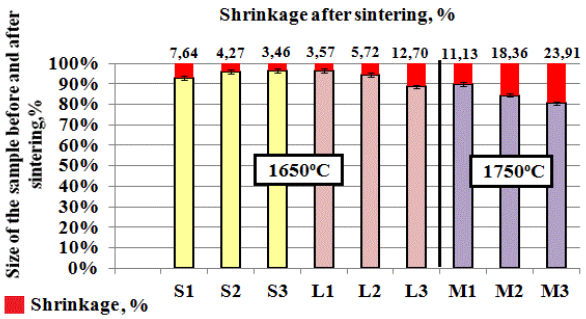

Fig. 7 Shrinkage of samples after sintering at the 1650°C and 1750°C

The increase of shrinkage is linearly proportional to the amount of kaolin. The shrinkage increases in about 2 times when quantity of kaolin increases by each 10 wt%. The shrinkage of samples also increases with increasing of sintering temperature. The dependence of shrinkage on amount of kaolin is explained by processes that occurred at the time of kaolin heating. The metakaolin is the intermediate stage at the phase transformation from kaolinite to the mullite. The layered structure is saved at the heating above 550°C. The phase dehydroxylates at this temperature and metakaolin forms at this time. The metakaolin is with higher density than kaolinite. The observed structure becomes denser with further heating (Fig. 8). That is explained with progressive entrance of two oxygen atoms of the unit cell in the cavity of Si-O layer, forming a more compressed consecution. This also explains that bulk density of samples increases with increasing of kaolin quantity. The increase of bulk density is linearly proportional to the amount of kaolin, because this parameter increases in about two times when quantity of kaolin increases by each 10 wt%. The α-Al_2O_3 increases the bulk density of samples, because it is with larger density and simultaneously with smallest activity than γ-Al_2O_3. The α-Al_2O_3 slowly reacts with remaining raw materials and does not form mullite.

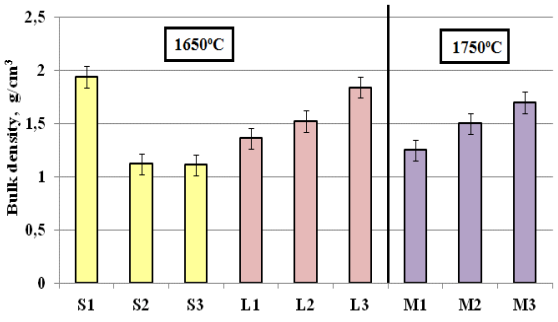

Fig. 8 The bulk density of samples after sintering

The Young's modulus describes the ceramics resistance to elastic deformation. Fig. 8 and Fig. 9 show that Young's modulus is proportional to the bending strength of samples. The samples that are sintered at the 1650°C are with lower bending strength, than samples sintered at the temperature of 1750°C.

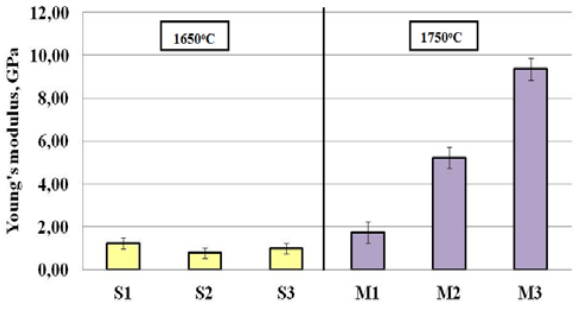

Fig. 9 The Young's modulus of samples

The bending strength is largest with increasing kaolin quantity. The bending strength is depending on kaolin quantity as well as on bulk density and on mullite intensities in the samples. This depends on the sintering process, temperatures and raw materials (Fig. 10).

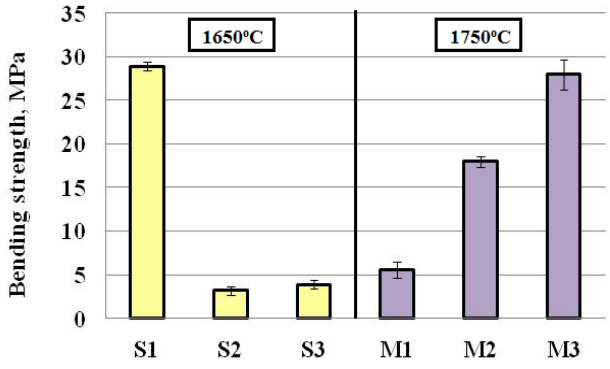

Fig. 10 The bending strength of samples

The increase of strength of alumina-silica ceramic from kaolin, alumina and silica oxides is observed after 1000°C of sintering temperature, when spinel phase arises. Then mullite arises at the 1050°C of temperature and its crystallization increases at the further moment of sintering. With this SiO_2 continues to exude and parameter of crystal lattice corresponds to the composition of mullite $3Al_2O_3 \cdot 2SiO_2$ (structure of sillimanite). Bending strength of samples increases with increasing of quantity of mullite. The lower bending strength (3.2 MPa) is in S2 series samples with α-: γ-Al_2O_3 (1:1), sintered at the 1650°C. The highest bending strength (30.59 MPa) is in M3 samples with α-: γ-Al_2O_3 (1:3) and 30 wt% of kaolin, that are sintered at the 1750°C.

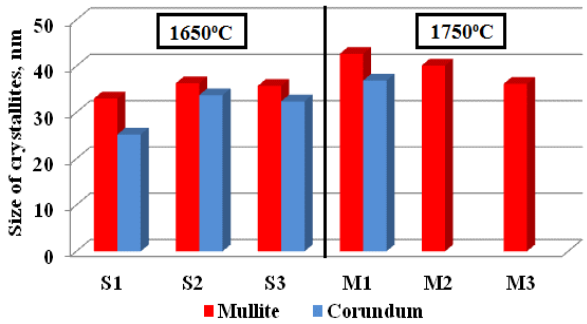

Fig. 11 Sizes of mullite and corundum crystallites, (nanometer)

Mechanical properties of samples can be explained with phases of mullite and corundum, and with sizes of its crystallites. The characteristics of mullite crystallites size from raw material are determined by X-ray powder diffractometry from diffraction line by Selyakov-Scherrer's method. Results from Fig. 11 show that the crystallites size of mullite decreases with increase of kaolin quantity. Mechanical strength of ceramics increases with decreasing of crystallites size. This is observed from Fig. 10 and Fig.11, where bending strength is inversely proportional to the crystallites sizes of mullite and corundum phases. Mechanical strength of samples can be explained with difference between the thermal expansion coefficients of two dominant phases of samples. For corundum it is about $8 \cdot 10^{-6.0} C^{-1}$, but thermal expansion coefficient of mullite is about $5.3 \cdot 10^{-6.0} C^{-1}$ [8], therefore large corundum crystallites with largest change of thermal expansion produce highest microstresses in structure of the samples. These microstresses influence on the bending strength and decrease mechanical properties of the samples with corundum phase. Compare with this bending strength is highest in the samples only with mullite phase. Therefore, mechanical properties increase with increasing of mullite quantity and decreasing of corundum phase.Porosity of the sample influences on bending strength strongly and inversely [9], [10]. Porosity of samples decreases with kaolin quantity increasing in raw materials suspension. The type of pores is important for mechanical properties of ceramics. If samples are more with open pores, rather than with closed pores, its bending strength is smaller.

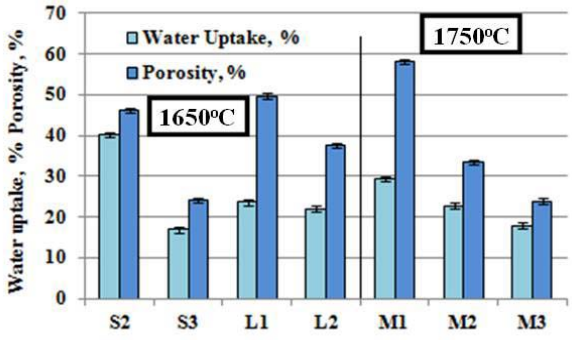

Fig. 12 Water uptake and porosity of samples

When quantity of kaolin increases, quantity of water uptake decreases, because quantity of open pores decreases, but quantity of closed pores oppositely increases (Fig. 12). Application of α- and γ- Al_2O_3 (ratio 1:3), with 10 wt% of kaolin, increase the porosity of samples about 45-58% (L1, M1 samples). Increase of firing temperature influences on sintering of samples, therefore porosity decreases after sintering at the highest temperatures.

Fig. 13 and Fig. 14 show the comparison of pores sizes distribution by Hg porosimetry of samples from alumina and silica oxides with samples from these oxides and kaolin. One or two diapasons of pore sizes are achieved in materials.

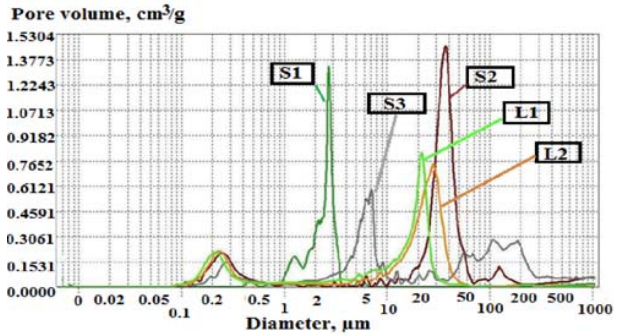

Fig. 13 Compare of pore size distribution of S series samples with L series samples

The quantity of micropores with size 0.1-0.5µm decreases in samples with temperature increasing from 1650°C to 1750°C (L and M series of samples Fig. 13, Fig. 14). Pores with this diameter are in samples of first and second series, but they cannot be observed in samples of third series, that sintered at the temperature of 1750°C.

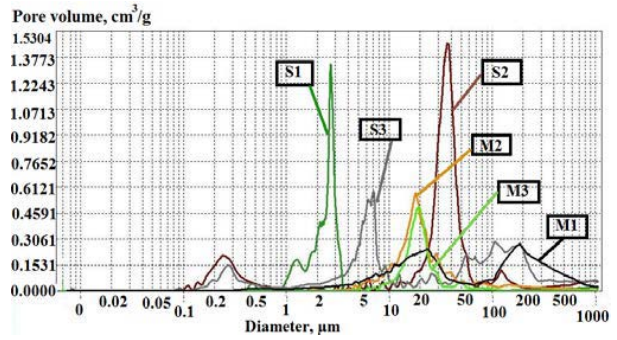

Fig. 14 Compare of pore size distribution of S series samples with M series samples

α-Al_2O_3 reduces the size of pores (range: 1-4 µm, S1 sample), whereas γ-Al_2O_3 influences on formation of pores with larger size (range: 4-10; 10-50 µm, another samples).

The pore size distribution with 10-40 µm diameter is observed in samples (L1 and L2) of second series, that are with 10 and 20 wt% of kaolin and firing at 1650°C temperature, and it is similar in samples of third series (M1, M2, M3).

Pore volume with 10-40 μm diameter decreases in samples that sintered at the temperature of 1750°C. This can be explained with increasing of bulk density and that pores become more closed with increase of quantity of kaolin and as well as with increase of firing temperature.

IV. Conclusions

The application of α- and γ-Al_2O_3 (ratio 1:3) with 10 wt% kaolin increases the porosity of samples about 45-58%. α-Al_2O_3 reduces the size of pores, but it is necessary for mechanical strength of materials. At the higher temperature of sintering pores become more closed and bigger, because micropores vanish during the sintering process of the material samples. Phase of mullite is achieved in materials of all compositions. The increase of amount of kaolin and temperature of sintering raises the quantity of mullite phase. It begins to dominate over the corundum phase. The decreasing of crystallites size of mullite phase and decreasing of corundum phase's quantity increase mechanical strength of samples.

Acknowledgments

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