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## Sintering Behavior of Kaolin with Calcite

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### Abstract

The study of sintering behavior of clay raw materials might be difficult because, as it is well known, these clays have a complex mineralogical composition, which causes a series of phase transformations occurring during sintering. Those processes relate to major and minor clay minerals (such as phyllosilicates, quartz, calcite, dolomite and hematite). Kaolinite is one of the main components of the clay. In this work, we consider sintering of kaolin, with different addition of pure calcite. The following techniques were used: differential thermal analysis (DTA), thermogravimetry (TG/DTG), dilatometry (DIL), heating microscope probe and X-ray diffraction (XRD), and scanning electron microscopy (SEM). In addition, comparisons between the microstructure of the sintered bodies and their physical-mechanical properties have been made.

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*Keywords:* sintering; kaolin; calcite; anorthite; glassy phase.

### 1. Introduction

Calcite is frequently present in clays used for production of bricks [1]. It is one of the clay component. Calcareous clays are used in Polish building ceramic industry. Miocene clays containing naturally up to 15% CaO as carbonates are used for production of brick and tiles. Loesses containing naturally up to 6% of CaO as carbonates are used for production of road clinker [2].

The presence of coarse-grained calcite in the raw material can lead to a destruction of the fired product. As a result of thermal dissociation of the coarse carbonate, calcium oxide in the presence of humidity, rapidly reacts with water and is transformed into portlandite. This reaction causes considerable increase in volume, which can destroy ceramic body [3,4].

Fine carbonate dust has different effect on the properties of ceramic material [5]. In general, the mechanical strength of material sintered with calcium carbonate dust is not reduced. It is known that this mineral has an important role during firing of ceramic building materials, but the results of calcium carbonate influence on the properties of ceramics are divergent. Literature data show that there is a limit of the amount of calcite addition, which enhances properties of ceramic material [6–8]. The presence of calcite in ceramic mass leads to the formation of new phases while sintering, such as gehlenite, anorthite, diopside or wollastonite [9–15]. Upon firing fine calcite acts as fluxing agent [10], [15].

Not only microstructure [16–17] but also linear shrinkage is changed [7] by the addition of calcite into the batch. CaO from decarbonation contributes to reduction in viscosity of aluminosilicate melt [18].

In this work, the influence of calcite on sintering process of clays have been studied. For our research, we selected kaolin, as one of the most defined raw material used in ceramics, and commercially available pure calcite. Kaolin was mixed with calcite to study structural transformation of the material during sintering.

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## 2. Experimental procedure

### 2.1. Raw materials

The ceramic masses were prepared from a mixture of kaolin from Surmin-Kaolin S.A. and pure calcium carbonate from POCH S.A. Kaolin was collected and milled to the fraction <0.12 mm. The chemical composition of the used raw material is given in Table 1. The grain-size distribution of components, determined by SediGraph 5100 from Micromeritics is given in Figure 1.

Table 1. Chemical analysis of kaolinite clay

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	L.O.I.
61.38	26.65	0.81	0.45	0.05	0.24	0.66	0.12	0.11	9.47

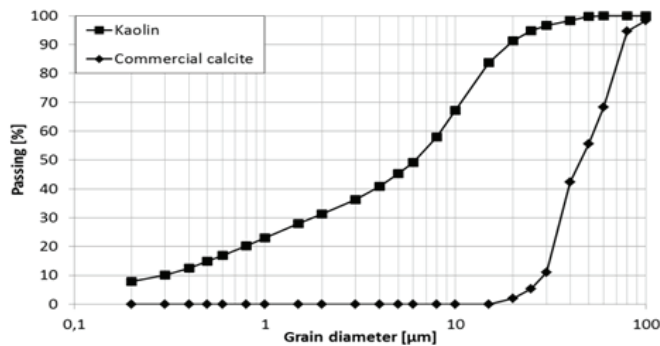


Fig. 1. Cumulative grain size distribution of kaolinite and calcite

The mineralogical composition was determined by X-ray diffraction analysis. The data was obtained with a Phillips PW-1040 diffractometer in Bragg-Brentano geometry, using monochromatic Cu-K $\alpha$  radiation (operation modes:  $\lambda = 0.154\text{nm}$ , 5–60° 2 $\theta$  range, 0.05° step size, 2.995s step time). The X-ray diffraction (XRD) pattern of kaolin is shown in Figure 2. From the XRD analysis it was observed, that kaolin powder consisted of kaolinite, quartz and a small amount of illite phase.

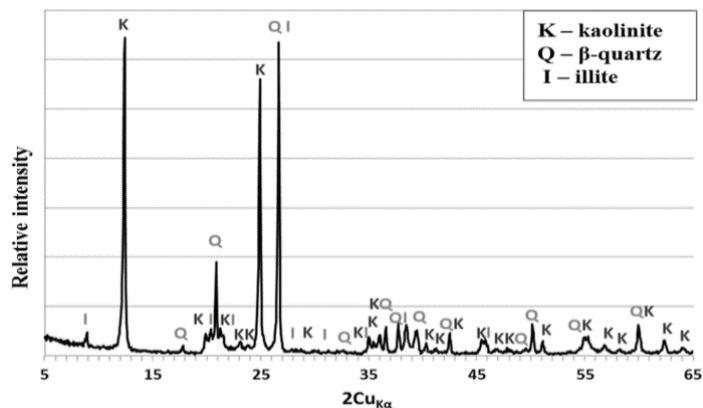


Fig. 2. The XRD pattern of kaolin powder

Simultaneous DTA/TGA/DTG measurements of the components were carried out with Netzsch Jupiter 449F3 analyzer, in air atmosphere, at temperature range 20-1200°C, with heating rate of 10°C/min. The thermal curves of kaolin and pure calcite are shown in Figure 3-4. As it can be seen, the weight loss in the temperature range of 400-800°C [19] indicates that kaolin consists of 66% clay minerals and the weight loss of calcite indicates that is 97% CaCO<sub>3</sub> in this material.

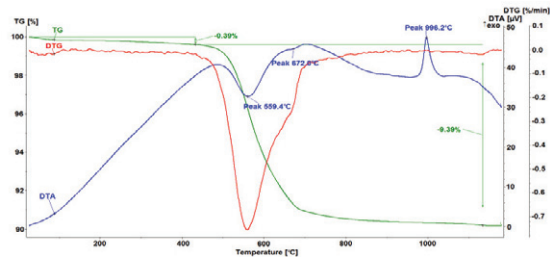


Fig. 3. DTA/TGA/DTG measurements of kaolin

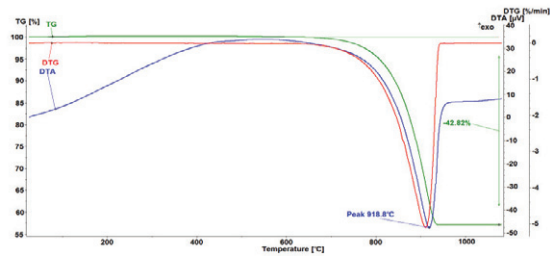


Fig. 4. DTA/TGA/DTG measurements of commercial calcite

## 2.2. Sample preparation

The dry kaolin and calcite were blended and homogenized. The exact composition is presented in Table 2.

Mixtures were blended with the addition of 12% of deionized water in respect to dry material weight and thrice wiped through a sieve. The granules held in sealed containers for 24 hours to homogenize their moisture content. Rectangular ceramic bodies (90×9×5 mm) were formed by uniaxial pressing at 22MPa to render apparent densities of kaolin samples approximately of 1.86 g/cm<sup>3</sup>, upon drying. The green ceramic bodies were dried at 110°C. Mixtures were analysed by dilatometry measurements in DIL802 BÄHR-Thermoanalyse GmbH (heating rate 10°C/min, maximum temperature 1200°C, soaking time 10 min, cooling rate to 400°C was 15°C/min, then free cooling).

Table 2. Compositions of the masses

Mass	Kaolin content [% wt.]	Calcite content [% wt.]
1	100	0
2	95	5
3	92.5	7.5
4	90	10
5	85	15

The samples were sintered in laboratory kiln in the 1220-1350°C maximum temperature (heating range 8°C/min, soaking time 30 min). These temperatures correspond to temperatures used during firing of industrial ceramic tiles and porcelain.

## 2.3. Measurements and analyses

The measurements of sintered ceramic samples included: linear shrinkage, water absorption, apparent density, apparent porosity and flexural strength. In order to appoint apparent density, samples saturated with water were weighted in air and in water. The flexural strength of specimens was determined by a three point bending technique in universal strength machine QC501B1 with spans of 70 mm at a loading rate of 0.1 mm/min.

The composition of crystalline phases present in sintered samples was assigned by XRD method, using CuK $\alpha$  radiation and the microstructure was observed by FEI Nova NanoSEM 200 scanning electron microscope.

## 1. Results

Sintering observations of components and mixtures were made in a heating microscope Hesse Instruments with automatic recording of changes in the sample volume. Cylindrical samples ( $d = h = 3$  mm) were made from particulated materials ( $<0.063 \mu\text{m}$ ). Heating rate was  $10^\circ\text{C}/\text{min}$ . Maximum temperature was  $1400^\circ\text{C}$ . Characteristic temperatures were determined during the study.

In the heating microscope, kaolin wetting by glassy phase formed during heating cylindrical samples of calcite based on kaolin was also observed. The measurements were carried out under the conditions described above.

The results of heating microscope measurements are presented in Fig. 5 and in Table 3. A small decrease in volume at  $900\text{--}1050^\circ\text{C}$  is caused by decarbonation of calcite and Si-Al spinel phase formation. Above  $1160^\circ\text{C}$  sintering begins.

The addition of calcite to kaolin up to 15% wt. reduces the difference between initial and maximum sintering temperature. CaO produced during calcite decomposition acts as fluxing agents, but in this work, initial sintering temperature was not decreased. Only maximum sintering temperature was decreased. Fig. 5 indicates that samples with calcite addition do not exhibit significant changes in the volume, excluding the sample with 15%  $\text{CaCO}_3$  which expands above  $1300^\circ\text{C}$ . It is due to a high content of liquid phase which closes pores hindering the escape of gas outside the specimen.

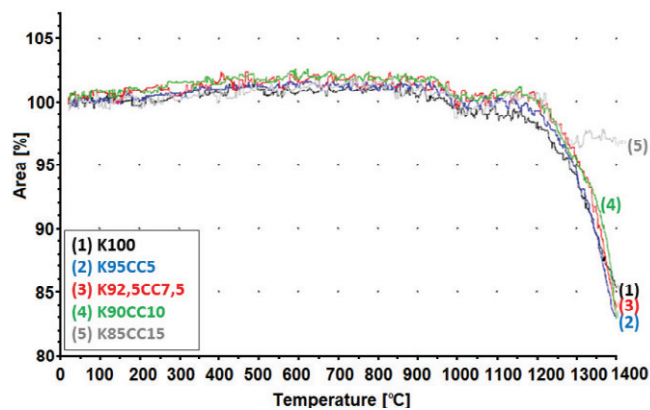


Fig. 5. Heating microscope curve of specimens area change

Table 3. Characteristic temperatures determined by heating microscopy (T1- initial sintering temperature, T2- maximum sintering temperature, T3- deformation temperature, n.d. – not determined)

Sample	Characteristic temperature [ $^\circ\text{C}$ ]			Temperature intervals	
	T1	T2	T3	T2-T1	T3-T2
1	1160	>1400	n.d.	>240	n.d.
2	1190	>1400	n.d.	>210	n.d.
3	1195	>1400	n.d.	>205	n.d.
4	1200	>1400	n.d.	>200	n.d.
5	1225	1310	n.d.	85	n.d.
CC	1355	1370	1375	15	5

Heating microscope measurements of pure commercial calcite have also been made. The decomposition of calcite started at  $830^\circ\text{C}$ . CaO thus formed, began to sinter at  $1355^\circ\text{C}$ . Maximum sintering of CaO was observed at  $1370^\circ\text{C}$  and at  $1375^\circ\text{C}$  sample started to soften.

Wetting sample probe (Fig. 6-7) indicated that at  $1345^\circ\text{C}$  high amount of liquid phase begins to form. Calcite reacts with dehydrated kaolin matrix components. The amount of glassy phase between CaO cylinder and transformed kaolin base is high. It is located around the CaO cylinder. High amount of glassy phase during sintering

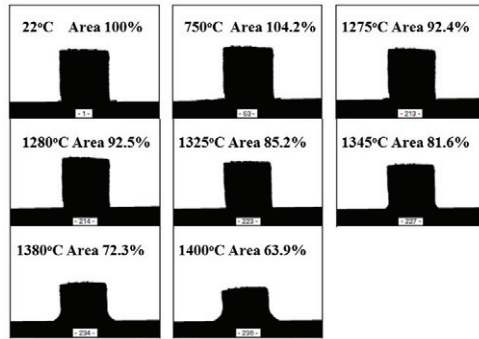


Fig. 6. Heating of commercial calcite on kaolin base at various stages of the heating cycle (wetting probe in heating microscope)

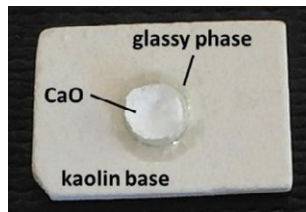


Fig. 7. Sample after wetting measurements

The thermal linear shrinkage of samples is shown in Fig. 8 and in Table 4. Dilatometric measurements show that calcite reduces shrinkage upon firing. The final shrinkage is the highest for pure kaolin. The samples with calcite addition have low final shrinkage but there are no significant differences. An increasing addition of calcite leads to greater final linear shrinkage measured during cooling. It happens, as the viscosity of glassy phase is lowered by a larger amount of CaO. If glassy phase has low viscosity, it is easier for CO<sub>2</sub> escape from pores and sintering has higher intensity.

Bulk density, open porosity and flexural strength as a function of calcite content and firing temperature in the 1220-1350°C temperature range is shown in Fig. 9-11.

Apparent density of samples decreases with addition of calcite. The highest decrease in density with addition of calcite is at 1350°C. With temperature raise apparent density increases which is due to intensification of sintering. These results indicate that the total porosity increase with the addition of calcite.

Open porosity of samples with different content of calcite, fired in different temperatures is shown in Fig. 10. The porosity is significantly decreased for samples fired at 1350°C. Samples with 10% content of calcite have higher closed porosity than those with 15% CaCO<sub>3</sub>, what is due to relation between apparent density and open porosity of these samples.

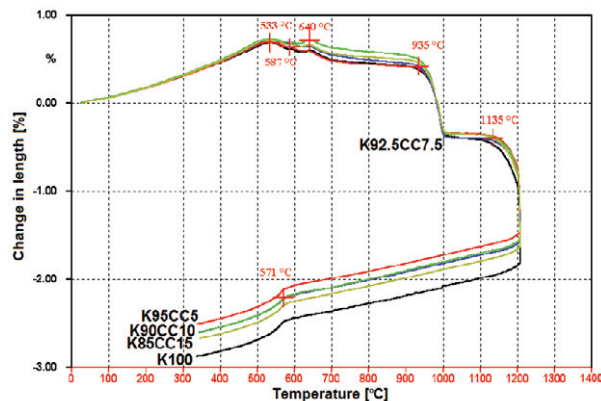


Fig. 8. Dilatometry measurements of ceramic bodies

Table 4. Dilatometry linear shrinkage of samples measurements

Temperature [°C]	1	2	3	4	5	CC
heating						
100	0,06	0,06	0,06	0,07	0,06	0,0
200	0,17	0,17	0,18	0,18	0,17	0,2
300	0,31	0,31	0,32	0,32	0,32	0,0
400	0,47	0,47	0,48	0,49	0,48	0,2
500	0,68	0,66	0,68	0,70	0,69	0,5
600	0,64	0,62	0,67	0,68	0,66	0,4
700	0,50	0,49	0,55	0,63	0,56	0,2
800	0,46	0,44	0,49	0,58	0,53	-0,1
900	0,43	0,42	0,46	0,54	0,50	-1,4
1000	-0,29	-0,29	-0,35	-0,31	-0,30	-2,0
1100	-0,37	-0,35	-0,40	-0,36	-0,36	-3,1
1200	-0,82	-0,75	-0,93	-0,9	-0,82	-5,2
1200 <sub>(after 10 min soaking time)</sub>	-1,67	-1,46	-1,53	-1,56	-1,62	-8,0
cooling						
600	-2,30	-2,07	-2,17	-2,17	-2,25	-9,8
500	-2,55	-2,31	-2,41	-2,41	-2,49	-10,0
400	-2,69	-2,45	-2,54	-2,54	-2,62	-10,1
Apparent linear shrinkage during 10-minutes holding time (1200°C)						
Δl [%]	-0,85	-0,71	-0,60	-0,66	-0,80	-2,8

All the specimens showed an increase in flexural strength (Fig. 11) with increasing firing temperature. All samples with calcite have higher flexural strength than pure kaolin material. Flexural strength reaches maximum value for samples with addition of 10% of calcite in samples fired in 1220 and 1250°C and with the addition of 7.5% of calcite in samples fired in 1350°C.

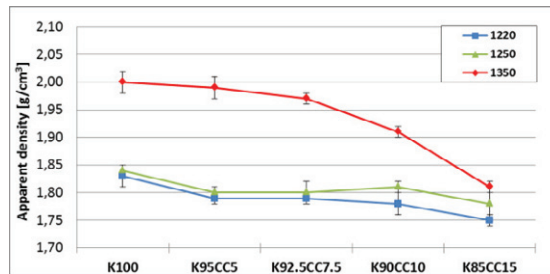


Fig. 9. Apparent density of specimens with different addition of calcite from 1220, 1250 and 1350°C

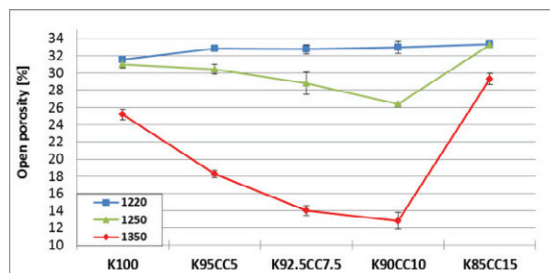


Fig.10. Open porosity of specimens with different addition of calcite from 1220, 1250 and 1350°C

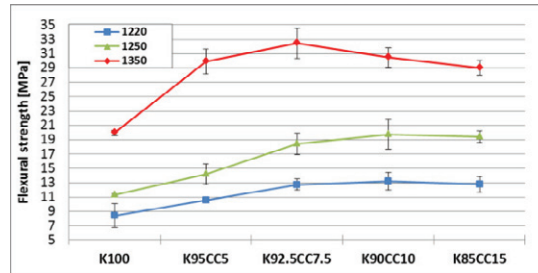


Fig. 11. Flexural strength of specimens with different addition of calcite from 1220, 1250 and 1350°C

Formation of new phases during firing at temperatures 1220, 1250 and 1350°C was studied based on the results of XRD analysis, see Fig. 12. Each sample contained mullite and quartz as the main crystalline phase and also trydymite after firing at 1250°C. In samples with calcite anorthite was present. Peaks from trydymite was registered for samples with calcite fired at 1250°C. At these temperature trydymite was not observed in sample of pure kaolin. The obtained data suggest that CaO present during sintering of ceramic masses stabilizes high temperature polymorph of quartz – trydymite, which is consistent with [20]. The higher temperature of the firing and the higher the amount of calcite, lead to an increase in amount of anorthite created in the samples. Lower content of mullite in the samples with calcite is not only due to „the dilution effect” but also due to other reactions taking place simultaneously in the same time as the formation of mullite, for example anorthite production. Peaks from calcium oxide or calcium hydroxide were not observed.

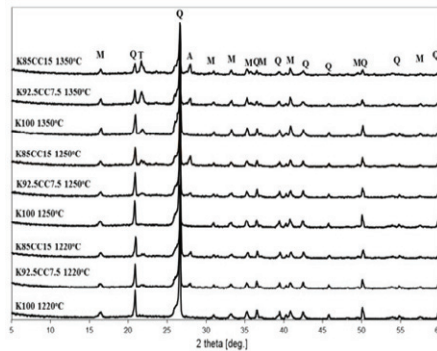


Fig. 12. XRD pattern of specimens with different addition of calcite from 1220, 1250 and 1350°C

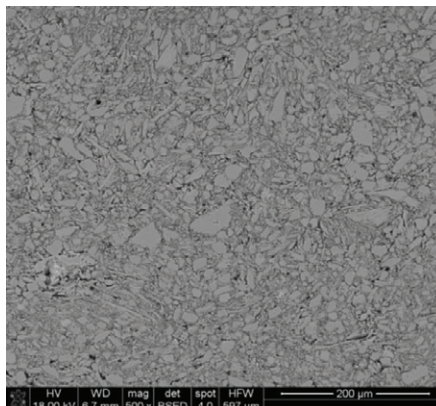


Fig. 13. SEM micrographs of kaolin samples without addition of calcite sintered in 1250°C



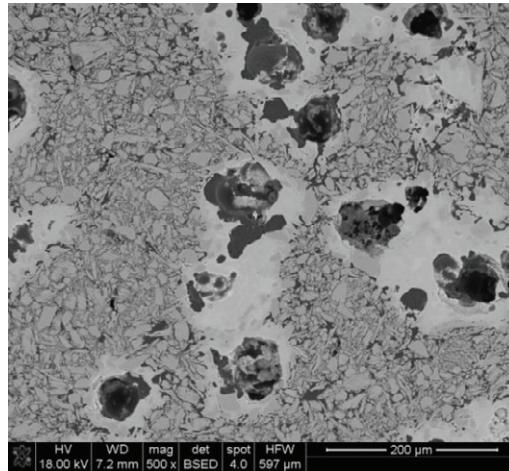


Fig. 14. BSE micrographs of kaolin polished section with 15% addition of calcite sintered in 1250°C

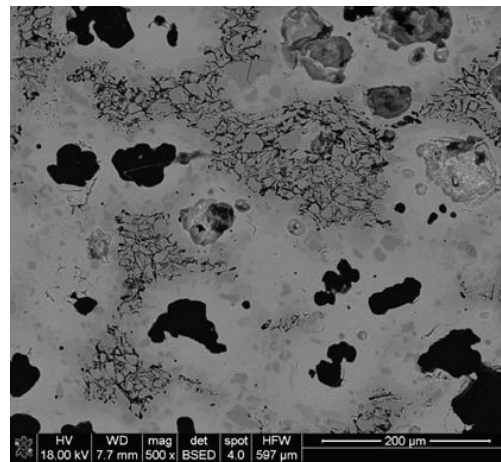


Fig. 15. BSE micrographs of kaolin polished section with 15% addition of calcite sintered in 1350°C

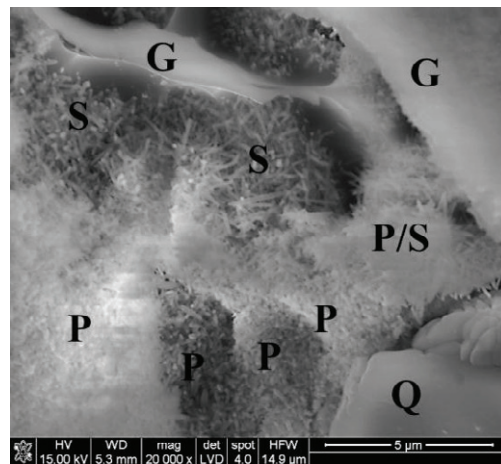


Fig. 16. SEM micrographs of kaolin samples with 15% addition of calcite sintered in 1350°C  
(P – primary mullite crystals, S – secondary mullite crystals, G – glass melt, Q – quartz)



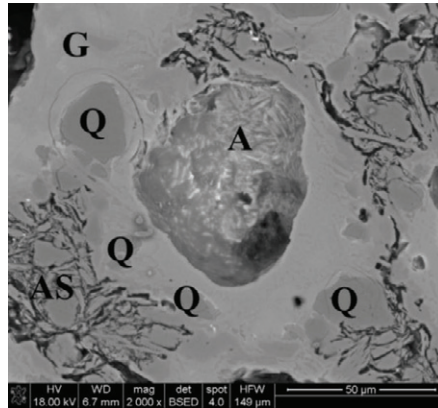


Fig. 17. SEM micrographs of kaolin samples with 15% addition of calcite sintered in 1350°C (A – anorthite crystals, AS – alumino-silicate matrix, G – glass melt, Q – quartz).

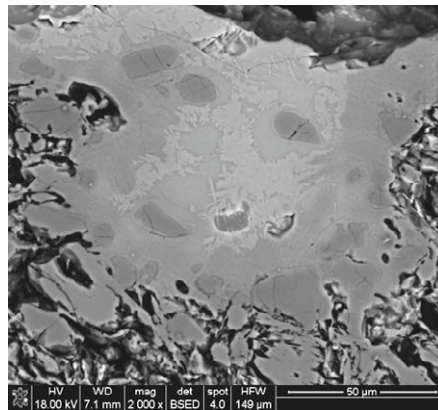


Fig. 18. BSE micrographs of kaolin polished section with 7.5% addition of calcite sintered in 1350°C – view of glass melt

Fig. 13 presents a backscattered SEM image of kaolin sample without calcite addition sintered at 1250°C for 30 min.

Fig. 14 shows a back scattered SEM image of kaolin sample with 15% calcite sintered at 1250°C, 30 min. This picture indicates that addition of calcite to kaolin results in high porosity. Glass melt is created around pores. Its amount is higher at higher temperature (Fig. 15). Pores and formed around glassy envelope are very big compared to the matrix components. Envelopes are products of reactions between CaO and aluminosilicate matrix. Near envelopes mullite crystals were observed, Fig. 16. Anorthite crystals occurs in pores and glassy melt what is observed on SEM/EDS pictures (Fig. 17) and XRD pattern. These are present only in samples with added calcite and all firing temperatures. Analysis of the microstructure is consistent with [21].

### 3. Discussion

Upon firing mix of calcite and kaolin overlap following processes: sintering, decarbonation (formation of porosity as a result of CO<sub>2</sub> exhaust) and formation of new phases, for example anorthite (which can lead to an increase or decrease in volume). Each of this process has influence on final properties of ceramic material. Sintering process causes the fusion of individual grains, what leads to creation a durable ceramic material. Decarbonation, occurred during firing, gives high porosity, so material has lower apparent density. High density area of glassy phase is visible around the pores. The new phases, in this case, anorthite and mullite, causes strengthening of the material and growth of flexural strength. Characteristic phase distribution in material: glassy melt around the pores strengthened by anorthite crystals and mullite in alumino-silicate matrix inhibit propagation of cracking in material during bending of the samples.

Reduction of sintering temperature interval are due to the presence of increased amount of liquid phase during sintering. Calcium oxide formed during calcite decarbonation acts as a flux agent. Reduction of open porosity together with a decrease in density implies that liquid phase, appeared during sintering, converts open pores into closed ones.

Linear changes depend on amount of calcite added to mixture and temperature of firing. These factors have influence on viscosity of liquid phase. If viscosity is low, CO<sub>2</sub> can escape outside the sample. If viscosity is high, CO<sub>2</sub> is stopped in pores and raising pressure causes expansion.

Referring to BSE pictures we conclude that there are two regions in sintering sample: low density alumino-silicate matrix and high density glassy phase. There are also regions with other mechanisms of sintering: low density matrix - solid state sintering and for surroundings the pores initially filled with CaO - liquid phase sintering. With increasing firing temperature and CaCO<sub>3</sub> content in the composition of raw materials, liquid phase sintering region is dominated. Alumino-silicate matrix is continuous phase at 1250°C, but in 1350°C glass melt is continuous phase.

Distribution of calcium isn't uniform. The amount of calcium decreases with increasing distance from the open pores. This indicates that in the vicinity of pores resulting from decarbonation of CaCO<sub>3</sub> locates glassy phase with a higher calcium content. This is due to the diffusion of Ca<sup>2+</sup> to matrix during the sintering. BSE, SEM, XRD give information that anorthite can be crystallized in glass melt (Fig. 18) and in closed pores (Fig. 19). Mullite also crystallized from glassy melt. Referring to [22] work there are two types of mullite in samples fired at 1350°C: primary – type I and secondary – type II (Fig. 18). In samples with higher content of CaO, mullite have longer crystals than samples with low content of CaO. This results from higher amount of melt during firing of samples. Secondary mullite crystallized near glassy phase by dissolution-crystallization mechanism. Although long mullite crystals in samples bending strength decreases because of high porosity.

#### 4. Conclusions

In this study, we investigated the sintering of kaolin with addition of calcite. Properties of fired ceramic body were examined.

It was determined that calcite addition to kaolin decreases the temperature of maximum sintering of mixture. High content of glassy phase was observed during sintering. There are two sintering regions in samples observed on SEM micrographs: solid-state sintered and liquid phase sintered. Flexural strength increase is due to specific microstructure and phase composition. The main phases were: anorthite, mullite, quartz and tridymite.

Similar processes can be considered in the calcareous clays sintering, which are used in production of building ceramics. Clays have complex mineralogical composition. Some behavior of the mixture of kaolin and calcite during sintering does not give full explanation of the issue. For a full explanation of the calcite impact on the sintering, behavior of major and minor clay minerals in the presence of calcite must be considered. This work is an introduction to further research.

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