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Influence of Sintering Temperature on Raw and Beneficiated Clay "Klokoti"

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Abstract:
The raw clay "Klokoti" from middle Bosnia was beneficiated by method of wet separation which results in removing fraction over 20 µm. The raw clay was characterized by chemical composition, grain size distribution and characteristic temperatures on heating microscope. The beneficiated clay was characterized by chemical composition and characteristic temperatures. The phase composition of raw and beneficiated clay was observed by RDA while the microstructure was monitored on scanning electron microscope (SEM). The sintering process was performed at 1100ºC, 1250ºC, 1320ºC and 1400ºC with two hours holding time at the highest temperature. The obtained results indicate a big content of coarse quartz in raw clay and gradually increase of crystalline mullite content with increasing temperature of sintering. Beneficiated clay at higher temperature of sintering produces larger glassy phase content, which is result of larger fluxing content in its composition. It is also observed that from beneficiated clay by sintering at 1250°C crystallize the most mullite along with minimum porosity and the lowest glassy phase content.
Keywords: *Raw clay; Beneficiated clay, Phase composition, Sintering temperature*

1. Introduction

Clays, like most mineral raw materials, often do not comply with the physical, chemical or technical requirements for certain production. They usually require some processing operation or beneficiation to prepare them for further processing [1]. The most common processing techniques for clay beneficiation are:

- wet method,
- dry method,
- electromagnetic method and
- combined method.

The usually aim of these methods is to decrease the content of quartz and ferrous minerals in clay [2].

The wet method is the most frequent method of beneficiation of clay. It consists of following steps: mixing clay with water to make slurry, settling of coarse grains, separation of suspension with fine grains from sediment and dewatering of suspension. The theoretical basis for this process is the Stokes' Law, which defines the speed of the falling ball through fluid:

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$$v = \frac{d^2 g(\rho_2 - \rho_1)}{18\eta} \quad (1)$$

Where:
v – speed of the falling ball (cm/s)
d – diameter of ball (cm)
g – gravitational constant 981 cm/s^2
ρ_1 – fluid density (g/cm^3)
ρ_2 – ball density (g/cm^3)
η - fluid viscosity (g/cm·s)

Stokes law applies to the ball diameter 0.2 to 200 μm [3].

2. Materials and experimental procedure

The paper deals with clay "Klokoti" situated on 15th kilometre of the local road R-442, direction Kaonik – Kiseljak, about 600 meter on the left side of the road. Beneficiation of clay was done on the following way: The raw clay has dried and crushed up. Distillate water with 0.74 g/l sodium pyrophosphate was added into it and one hour stirring. According the Stokes law and experimental conditions, the sedimentation time of grains over 20 μm was calculated. After that time the suspension with clay component bellow 20 μm was decanted and dried.

Chemical composition was determined by following methods: SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MgO, CaO and MnO were determined by XRF (X-ray fluorescence), while Na_2O, K_2O and ZnO were determined by AAS (atomic absorption spectroscopy). Refractoriness (softening point) was determined in criptol furnace according to EN 993-13:1995. Grain size distribution was carried out using laser granulometer MICRO SIZER 201C.The characteristic temperatures during heating were determined on the heating microscope "Leitz".

Two plates of raw and two plates of beneficiated clay were sintered at 1100°C, 1250°C, 1320°C and 1400°C in a chamber electric furnace with superkantal heating elements. Sample heating rate was $5°C min^{-1}$, a holding time at sintering temperature two hours.

XRD analysis is performed on the device, Philips X'Pert Pro, Model PW 3040/60 with a source of Cu-Kα radiation, operating voltage 40 kV, current strength 40 mA and the goniometer PW 3050/60. Diffraction images of polycrystalline powder samples of clay were taken in the angle $4° \leq 2\theta \leq 64°$. Quantitative phase analysis was performed using the Rietveld method with assisted program Topas 2.1.

The porosity of the sintered samples are determined by the method of mercury porosimetry. It was used Carlo Erba Mercury Intrusion Porosimeter 2000 WS using a sample mass of about 1 g, and the pressure under which the mercury is injected was 0-2000 atm. Scanning electron microscopy was performed on a scanning electron microscope JOEL JSM – 5800 [6] .

3. Results and discussion

The results of chemical analysis of raw and beneficiated clays are given in Tab. I. By removing the coarse particles it has been increased the content of Al_2O_3 and loss of ignition, indicating the increase of clay minerals in the beneficiated clay. The reduction of SiO_2 in beneficiated clay indicates that raw clay contains coarse particles of quartz that are removed by beneficiation. Increasing the content of alkali and alkaline earth elements in beneficiated clay indicates the presence of fine granular muscovite or sericite and illite.

Tab. I. Chemical composition of clay

Component	**Chemical composition (%)**	
	Raw clay	**Beneficiated clay**
Al_2O_3	17.8	30.7
SiO_2	70.7	52.1
Fe_2O_3	1.4	2.03
TiO_2	1.27	0.87
CaO	0.03	0.19
MgO	0.48	0.55
Na_2O	0.30	0.97
K_2O	3.65	4.23
MnO	0.08	<0,01
ZnO	0.019	0.021
LOI	4.11	7.63

Tab. II. Grain size distribution of raw clay

Grain size (μm)	< 1	1-2	2-5	5-10	10-20	20-45	45-80	80-100	100-150	150-300
Weight percent (%)	2.5	4.1	12.4	16.5	19.9	22.1	14.2	3.7	3.5	1.1

Tab. III. Characteristic temperatures and refractoriness

State of clay	**Characteristic temperatures (°C)**						
	Shrinkage start	Shrinkage end	Expanding start	Max expanding	Sintering	Melting	Refractoriness
Raw	1180	1320	1380	1500	1530	1560	1540/1560
Beneficiated	1140	1300	1380	1600	1630	1650	1580/1600

Granulometric composition of raw clay (Tab. II) shows that it is coarse granular clay with a small percentage of particles below 2 microns, which suggests that the clay contains little amount of clay minerals.

Refractoriness of raw clay is relative high compared to the relative low content of Al_2O_3. High content of quartz contributions increased refractoriness. The process of beneficiation of clay increases the temperatures of sintering and melting, and refractoriness (Tab. III).

Fig. 1 shows decreased reflections of quartz and increased reflections of kaolinite, muscovite and illite in beneficiated clay by comparasion with raw clay.

Samples of sintered raw clay “Klokoti”, according to the results of XRD (Table 4), show in its composition: mullite, low-temperature or β-quartz, corundum and amorphous phase. Besides above mentioned phases, at lower temperatures, rutil and other phase, which is not exact determined is it a γ-Al_2O_3 or Al-Si spinel, are present. Cristobalite is present at the highest temperature.

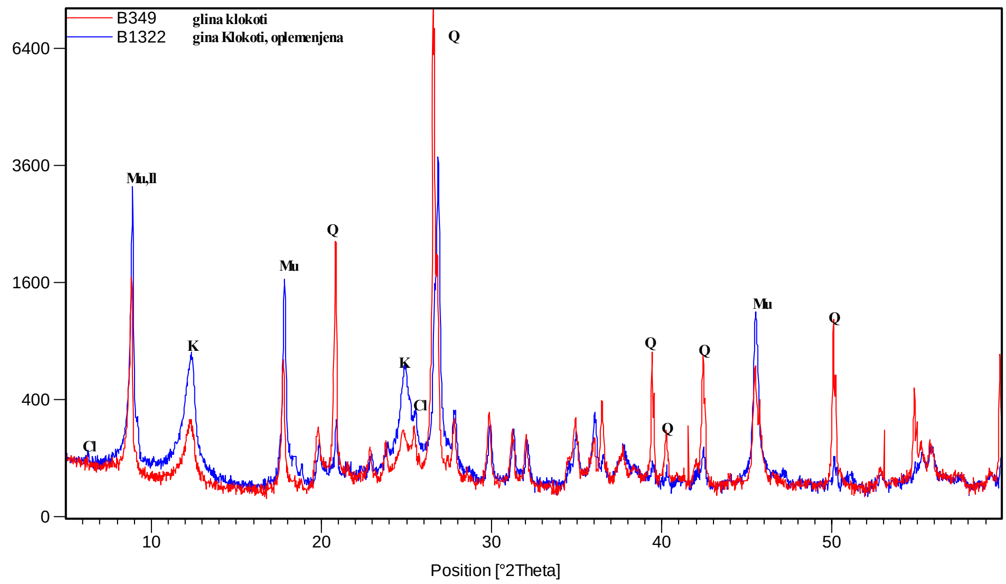


Fig. 1. XRD patterns of raw and beneficiated clay “Klokoti”Q – quartz, K – kaolinite, Mu-muscovite, Il – illite, Cl - chlorite

Samples of sintered beneficiated clay “Klokoti”, according to the results of XRD (Table 5), show in its composition: mullite, corundum and amorphous phase. There are no rutile and cristobalite. Quartz and the γ-Al_2O_3 or Al-Si spinel are present at lower temperatures of heat treatment.

Tab. IV. The phase composition of raw clay “Klokoti”

Phase content (%)	**Sintering temperature (°C)**			
	1100	**1250**	**1320**	**1400**
Mullite	14.93	14.6	19.81	21.5
Quartz	53.24	38.3	36.0	31.5
Corundum	1.01	2.3	1.58	1.9
γ-Al_2O_3 or Al,Si-spinel	5.68	0	0	0
Rutile	0.97	Trace	0	0
Cristobalite	0	0	0	5.6
Glassy phase	24.17	44.8	42.61	39.5

Tab. V. The phase composition of beneficiated clay “Klokoti”

Phase content (%)	**Sintering temperature (°C)**			
	1100	**1250**	**1320**	**1400**
Mullite	29.49	46.6	39.76	42.2
Quartz	8.72	2.0	0	Trace
Corundum	1.45	3.3	1.56	2.4
γ-Al_2O_3 or Al,Si-spinel	8.57	0	0	0
Glassy phase	51.77	48.1	58.68	55.4

Change of porosity is shown in Tab. VI. Only at 1100°C beneficiated clay has a higher porosity than the raw clay.

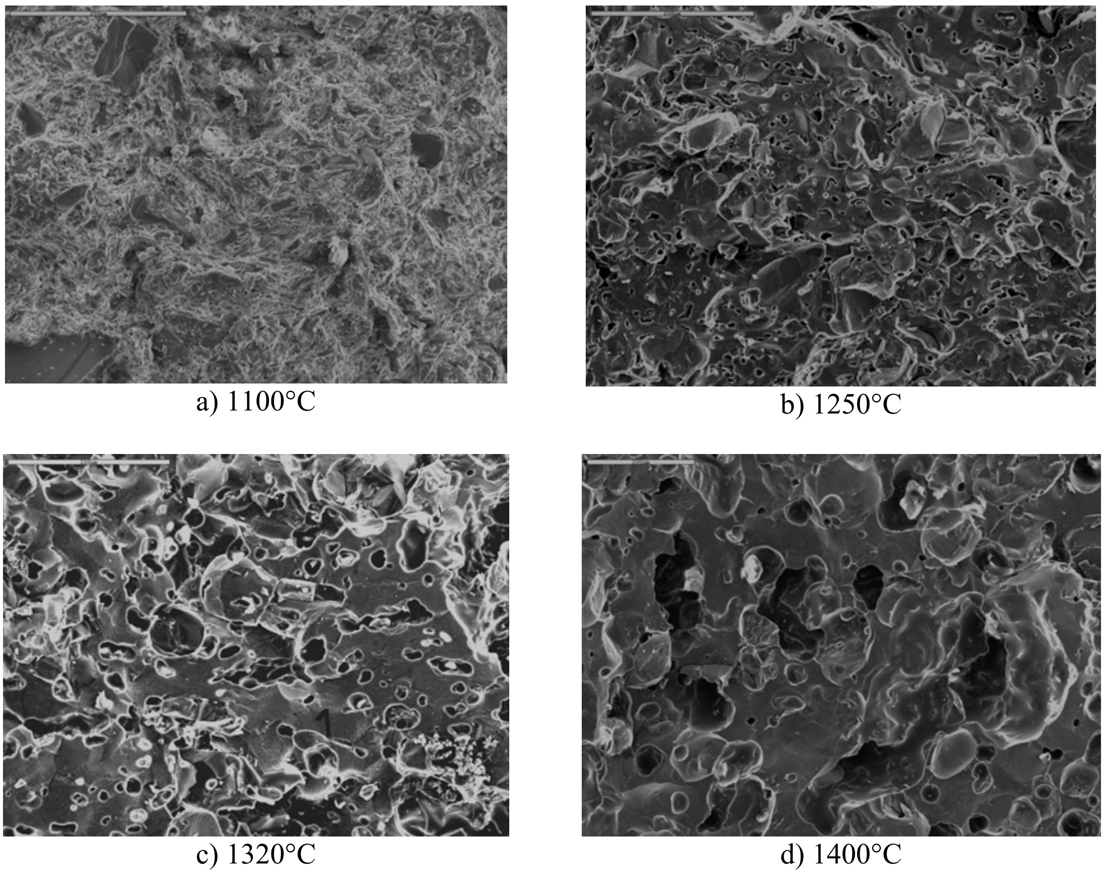
Tab. VI. Porosity of sintered clay “Klokoti”

Sintering temperature (°C)	**Porosity (%)**	
	Raw clay	**Beneficiated clay**
1100	32.76	42.87
1250	15.18	15.42
1320	31.02	19.05
1400	22.81	16.46

The flow of raw clay morphology changes with temperature heat treatment is shown in Fig. 2. Structure obtained at 1100°C (Fig. 2 a)) contains large quartz grains. These large quartz grains have not started to melt in a glassy matrix at this temperature. At the higher temperature, 1250 ºC (Fig. 2 b)) significant dissolution of quartz grains in the glassy matrix and significantly different structure is observed. At the same temperature it can be seen larger porosity, with larger pore diameter. These pores are probably closed pores and their presence could be explained by entrapment of water molecules arising from the residual hydroxyl groups [5].

The same phenomenon is characteristic for raw clay sintered at 1320°C (Fig. 2 c)). Increasing the temperature of heat treatment leads to increased pore diameter which is caused by enlargement of pores, as it could be observed at 1400°C (Fig. 2 d)).

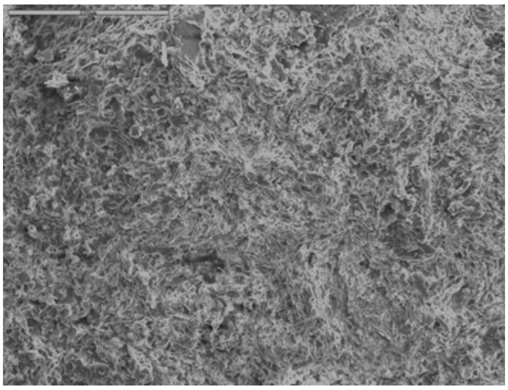
The flow of beneficiated clay morphology changes is shown in Fig. 3. The changes are similar to those of the raw clay, with strong influence of grain size on the structure.

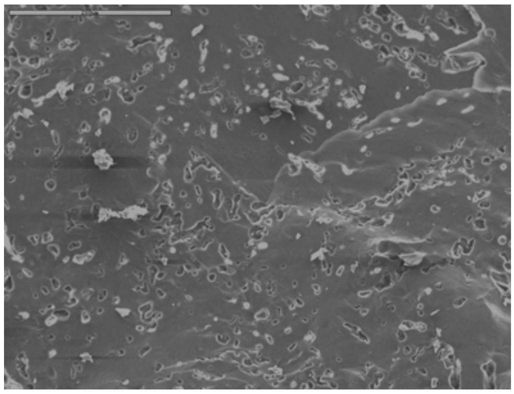


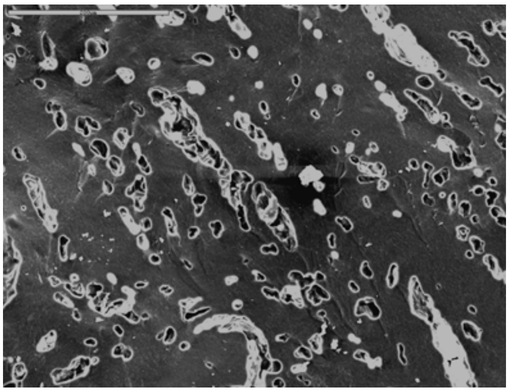
a) 1100°C b) 1250°C

c) 1320°C d) 1400°C

Fig. 2. Morphology changes of raw clay “Klokoti” versus temperature (bar length is 200 μm)


a) 1100°C


b) 1250°C


c) 1320°C

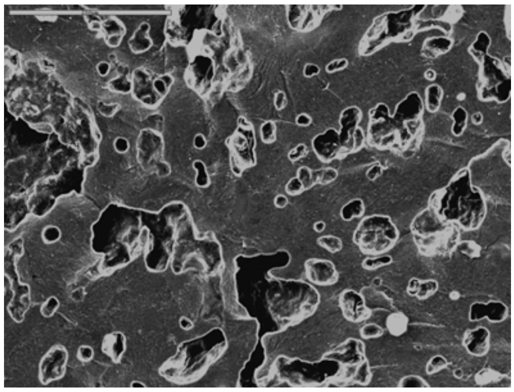

d) 1400°C

Fig. 3. Morphology changes of beneficiated clay "Klokoti" versus temperature (bar length is 200 μm)

4. Conclusion

Raw and beneficiated clay "Klokoti" were subjected to sintering at 1100°, 1250°, 1320° and 1400°C with the retention time at the highest temperature for two hours.

The results of investigation show that due to beneficiation process conditions of mullitization are significantly changed as well as the quantity and composition of the glassy phase, which lead to large differences in the structural and phase composition of the clay. Test results of the phase composition, porosity and structure indicate the following effects of sintering:

- Raw clay contains a large proportion of coarse grain quartz which is difficult to dissolve in a glassy phase.
- The amount of mullite is significantly higher in the beneficiated clay, due to reduced amount of quartz and increased amount of kaolinite.
- The amount and stability of the glassy phase is higher in the beneficiated clay due to a larger content of impurities.
- Raw and beneficiated clay at all temperatures have a certain proportion of corundum.
- γ-Al_2O_3 or Al,Si-spinel occurs only at 1100°C, while at higher temperatures transforms into α-Al_2O_3 and glassy phase.
- The beneficiated clay contains no cristobalite, while in raw clay it only appears at 1400°C.

- The most of rutile content is eliminated by beneficiation process.
- The correlation between the amounts of glassy phase with the open porosity could not be established.
- The raw clay at temperatures above 1250°C carried out the process of creating secondary mullite by recrystallization of glassy phase.
- In the beneficiated clay the maximum mullite content and minimum porosity are achieved at 1250°C.
- The raw clay at 1250°C was determined by the lowest porosity and highest glassy phase, but minimum mullite.
- Structure of beneficiated clay is more uniform and dispersed.
- For the raw clay "Klokoti" the best results of mullitization are achieved at 1400°C. To determine the optimum temperature for this clay it would be necessary to perform heat treatment at higher temperature than 1400˘C.
- For beneficiated clay the optimum plateau temperature for the heat treatment is 1250°C, because at that temperature most of mullite crystallizes with minimum amorphous phase and porosity.

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References

1. W. Lorenz, Mineral Raw Materials, Symposium on Mineral Construction Raw Materials, BGR, Hannover 2000., 41-55.
2. S. Drljević, Teoretske i tehnološke osnove proizvodnje vatrostalnog materijala, Fakultet za metalurgiju i materijale, Zenica, 1999.
3. A. Ahmić, F. Rahić, Primarna prerada nemetaličnih mineralnih sirovina, Fakultet za metalurgiju i materijale u Zenici, Zenica, 2005.
4. W. E. Worrall, Clays and ceramic raw materials, Applied Science Publishers Ltd., London 1975.
5. S. Ferrari, A. F. Gualtieri, Applied Clay Science 32 (2006) 73-81
6. S. Martinović, J. Majstorović, V. Vidojković, and T. Volkov-Husović, Science of Sintering, 42(2010)2. 211-219

Садржај: *Сирова глина "Клокоти" из средње Босне је оплемењена методом мокре сепарације, чиме је уклоњена фракција испод 20 μm. Карактеризација сирове глине је вршена преко хемијског и гранулометријског састава, и карактеристичних температура коришћењем загревног микроскопа. Оплемењена глина је карактерисана преко хемијског састава и карактеристичних температура. Фазни састав сирове и оплемењене глине је одређен преко РДА, док је микроструктура одређена коришћењем скенинг електронског микроскопа (СЕМ). Процес синтеровања је се одвијао на 1100°, 1250°, 1320° и 1400°C у трајању од два часа задржавања на највишој температури. Добијени резултати указују на висок садржај крупно зрнастог кварца у сировој глини и постепено повећање кристалног мулита са повишењем температуре синтеровања. Код оплемењене глине, на вишим темпетарурама синтеровања, ствара се већа* *количина стакласте фазе, што је последица већег удела топитеља у њеном саставу. Такође је уочено да из те глине, при синтеровању на 1250°C, кристалише највише мулита уз најнижу порозност и најмању количину стакласте фазе.*

Кључне речи: *сирова глина, оплемењена глина, фазни састав, температуре синтеровања*