

THE INFLUENCE OF THE MINERAL CONTENT OF CLAY FROM THE WHITE BAUXITE MINE ON THE PROPERTIES OF THE SINTERED PRODUCT

VPLIV VSEBNOSTI MINERALA GLINE IZ RUDNIKA BELEGA BOKSITA NA LASTNOSTI SINTRANEGA PROIZVODA

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An investigation of the influence of the mineral content of clay from the White Bauxite Mine on the properties of the sintered product is presented. The whole area of the white bauxite deposit (the "Bijele Poljane" mine) is characterized by the presence of clays. To investigate the properties of the sintered product, two of the most present types of clays were used (marked as "B" and "C"). The investigations of the properties of the sintered products on the basis of these clays involved the linear and volume shrinkage, the total porosity and the compression strength. The sintering process was conducted at temperatures of 1000 °C, 1100 °C, 1200 °C, 1300 °C and 1400 °C.

Key words: clay, linear shrinkage, total shrinkage, compression strength, sintering, porosity

Raziskava vpliva vsebnosti minerala glin iz Rudnika belega boksita je predstavljena v tem delu. Karakteristična za celotno področje ležišča belega boksita (rudnik Bele Poljane) je prisotnost glin. Lastnosti sintranega proizvoda so bile izvršene pri dveh največ prisotnih vrstah glin (označbi B in C). Določene so bile naslednje lastnosti sintranih proizvodov teh glin: linearno in volumensko krčenje, celotna poroznost in tlačna trdnost. Sintranje je bilo izvršeno pri temperaturah (1000, 1100, 1200, 1300 in 1400) °C.

Ključne besede: glina, linearno krčenje, skupno krčenje, tlačna trdnost, sintranje, poroznost

1 INTRODUCTION

The investigated clay types from the White Bauxite Mine appear in layers and have different mineral contents:

- clays with bauxite minerals,
- illite-kaolinite clays,
- clays with a very heterogeneous mineral content.

This mineral content gives us the possibility to obtain different ceramic products ¹. The most important differences in the mineral content are related mostly to the content of bauxite minerals, clay minerals, iron compounds, quartz and calcite ². Depending on the sintering temperature, this mineral content of the clays influences the solid-state reactions, the polymorphic transformations of the quartz and the liquid-phase formation³. Apart from the degree of the sintering of the ceramic mass, i.e., the firing regime, the mineral content of the raw material also has an important influence on the relations between particular microstructural elements. ⁴ The new crystal phases, i.e., the compounds formed within the solid-state reactions during sintering, are determined by the mineral content of the clays, as well as by the previously mentioned factors. ^{5,6} It causes important differences in the mineral content of the sintered products. The content of bauxite minerals

(boehmite, gibbsite), iron compounds (hematite), clay minerals (kaolinite, illite) in the investigated clay types primarily determines the properties of the sintered products.^{7,8} According to their refractoriness, the investigated clay types are refractory (the refractoriness is over 1500 °C).^{1,9} Neither flux, as a component that decreases shrinkage, nor electrolytes were used for the raw-material mixture formation, because the aim of the investigation was to determine the influence of the mineral content of the investigated clays on the properties of the sintered product.

2 EXPERIMENTAL

The samples were formed by shaping of a plastic mass in a mould corresponding to a parallelepiped with dimensions of 7.7 cm × 3.9 cm × 1.6 cm. The characterization of the investigated clays was made by a determination of the mineral content, the chemical content, the density, the humidity and the granulometry. The chemical content was determined with a Perkin Elmer 4000 atomic absorption spectrophotometer. The granulometry of the clays was determined on a "Microsizer 201C" VA INSTALT instrument. For the raw, non-sintered products the linear and volume shrinkage during the drying in air and in a dryer, to a constant

Table 1: Chemical composition of clay "B" and "C" in mass fractions, w/%

Tabela 1: Kemična sestava glin "A" in "B" v masnih deležih, w/%

Oxides	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	lg. loss
Clay "B"	63,2	2,2	25,2	1,2	1,3	0,9	0,8	4,1
Clay "C"	64,2	2,3	24,8	1,3	1,4	1,0	0,7	3,8

mass, at a temperature of 110 °C was determined. The samples were sintered at (1000, 1100, 1200, 1300 and 1400) °C.

For the sintered products the linear and volume shrinkage during sintering, the total porosity and the compression strength were determined. The volume shrinkage was determined using the following equation:

$$C_v = \frac{V_0 - V_i}{V_0} \cdot 100(\%)$$

V_0/m^3 – the volume before shrinkage

V_i/m^3 – the volume after shrinkage

The total porosity was determined using the following equation:

$$TP = \frac{\rho_0 - \rho_v}{\rho_0} \cdot 100(\%)$$

$\rho/(kg\ m^{-3})$ – the sample's density

$\rho_v/(kg\ m^{-3})$ – the sample's volume mass

The compression strength was determined on a novopress HPM 400 and the X-ray analysis was performed on a Diffractometer PHILIPS PW 1710. The microscopic analysis of the sintered products was made by scanning electron microscopy on a JEOL-JSM 6460LV-DEU (BAL-TEC SCD 005-SPVTTTER COATER).

3 RESULTS AND DISCUSSION

The results of the chemical analysis (**Table 1**) show a slightly higher content of oxides, i.e., CaO and MgO, in the clay "C" as a consequence of the higher content of carbonates. The clay "C" contains more Fe₂O₃ in the mass fraction, w ($w = 2.3\%$), with respect to the clay

"B" ($w = 2.2\%$). The content of TiO₂ in clay "B" is slightly higher ($w = 0.8\%$) compared to the clay "C" ($w = 0.7\%$).

The mineral content of the clay "B", determined by the X-ray analysis (**Figure 1**), shows the presence of kaolinite, gibbsite, boehmite and anatase. The X-ray analysis shows the presence of the following minerals in the clay "C" (**Figure 2**): kaolinite, gibbsite, boehmite, anatase, hematite, illite and clinochlore.

The results of the granulometric analysis show an average grain size of 69.32 μm in the samples on the basis of clay "B", while in the samples on the basis of clay "C" the average grain size is 63.25 μm, under the same milling conditions. The clay "B" has a higher average grain size with respect to the clay "C" under the same milling conditions, which is a consequence of the mineral content of the clays.

The volume shrinkage of the products during sintering (**Figure 3**) grows with the increase of the temperature as a consequence of solid-state reactions, polymorphic transformations of the quartz, the carbonates' dissolution, the glass-phase formation and the closure of pores during sintering. The content of K₂O in clay "C" is slightly higher (1.0 %) with respect to clay "B" (0.9 %) and it can be concluded that it does not have an important influence on the differences in the liquid-phase content, which accelerates the solid-state reactions (the diffusion coefficient increases).

The granulometric content of clays "B" and "C" also has an important influence on the volume shrinkage. The average grain size is greater in clay "B".

The content of Fe₂O₃ also has an influence on the volume shrinkage during sintering, and the content of Fe₂O₃ in the clay „C" (2.3 %) is slightly higher compared to the clay "B" (2.2 %).

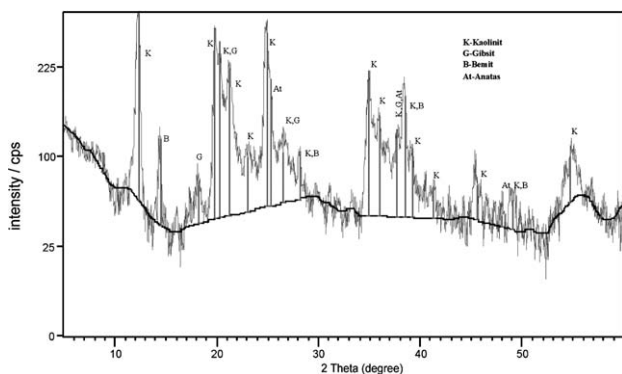


Figure 1: X-ray diffractogram of "B" clay
Slika 1: Rentgenski difraktogram gline "B"

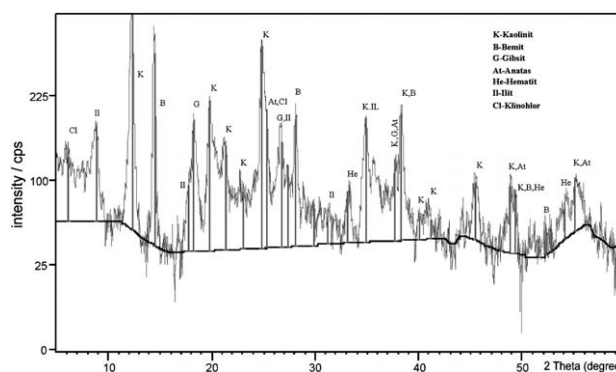


Figure 2: X-ray diffractogram of "C" clay
Slika 2: Rentgenski difraktogram gline "C"

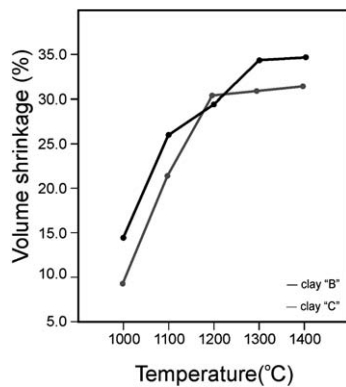


Figure 3: Volume shrinkage of product during sintering (clay "B" and clay "C")

Slika 3: Volumensko krčenje med sintranjem (glina "B" in "C")

The volume shrinkage increases with the increase of the sintering temperature and the growth is more evident in samples on the basis of clay "B" at higher temperatures (1300 °C and 1400 °C), which can be explained by the differences in the mineral and granulometric contents of the clays and solid-state reactions (X-ray analysis of sintered product at $T = 1300$ °C and 1400 °C, see **Figure 6** and **Figure 7**).

The total porosity during sintering decreases with the increase of the temperature (**Figure 4**). Apart from the intense solid-state reactions at higher temperatures (liquid-phase formation, diffusion coefficient increase), the decisive factors for the decrease of the porosity at higher temperatures are the chemical, mineral and granulometric contents of the raw material. The granulometric analysis shows that clay "B" has a larger average grain size with respect to the clay "C".

Considering the small difference in the content of alkali, they do not decisively influence the total porosity. The total porosity at 1400 °C has smaller values in the samples on the basis of clay "C", which is probably a consequence of the grain fraction (smaller average grain size) and the relations between the microstructural elements.

Clay "B" has a higher average grain size with respect to clay "C", which increases the total porosity and in this

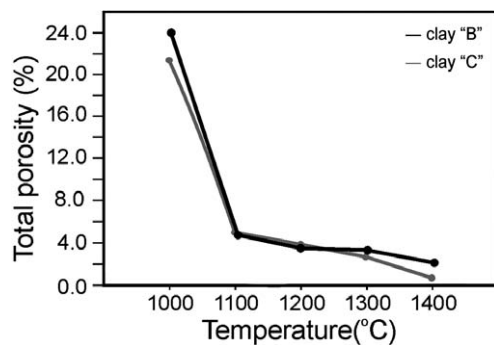


Figure 4: Total porosity of products during sintering (clay "B" and clay "C")

Slika 4: Skupna poroznost med sintranjem (glina "B" in "C")

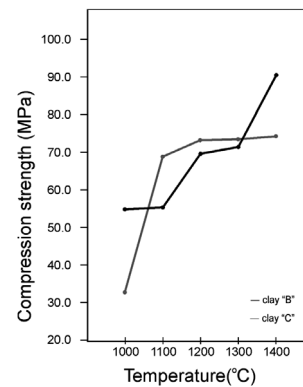


Figure 5: Compression strength of product during sintering (clay "B" and clay "C")

Slika 5: Tlačna trdnost sintranca med sintranjem (glina "B" in "C")

way the granulometric content of the clays influences indirectly on the compression strength. For the samples on the basis of clay "B" at (1100, 1200, 1300 and 1400) °C it is evident that there is an almost linear dependence of the compression strength of the sintering temperature, while in samples on the basis of clay "C" the compression strength value at temperatures of (1100, 1200, 1300 and 1400) °C (**Figure 5**) increases only slightly, which can be explained by the mineral content . In the samples on the basis of clay "B" with an increase

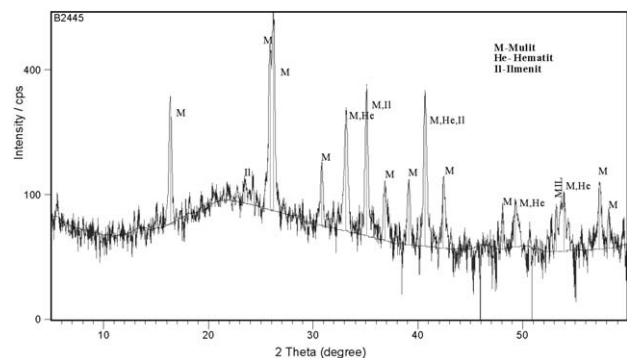


Figure 6: X-ray diffractogram of sintered product (clay "B", $T = 1300$ °C)

Slika 6: Rengenski difraktogram sintranca (glina "B", $T = 1300$ °C)

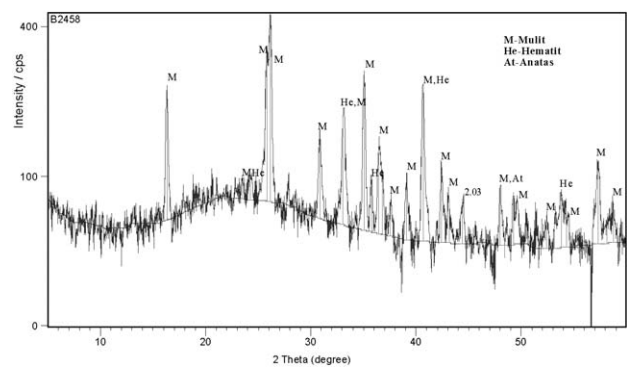


Figure 7: X-ray diffractogram of sintered product (clay "C", $T = 1300$ °C)

Slika 7: Rentgenski difraktogram sintranca (glina "C", $T = 1300$ °C)

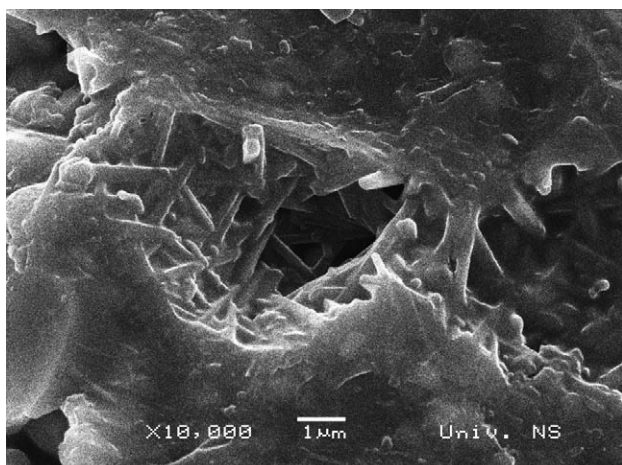


Figure 8: Microstructure of sintered product (clay "B", $T = 1300\text{ }^{\circ}\text{C}$, magn. 10 000-times)

Slika 8: Mikrostruktura sintranca (gline "B", $T = 1300\text{ }^{\circ}\text{C}$, pov. 10 000-kratna)

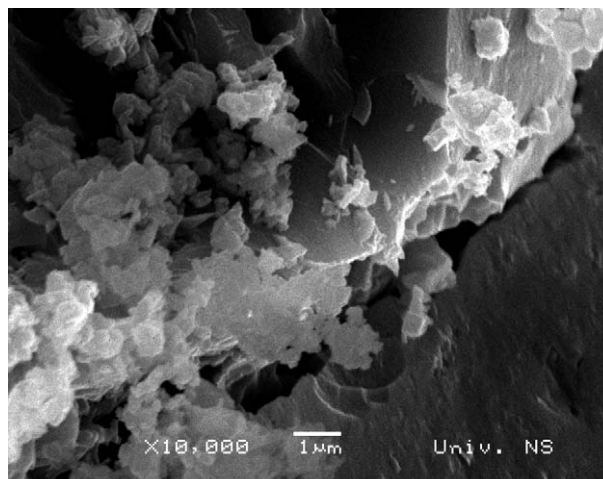


Figure 9: Microstructure of sintered product (clay "C", $T = 1300\text{ }^{\circ}\text{C}$, magn. 10 000-times)

Slika 9: Mikrostruktura sintranca (gline "C", $T = 1300\text{ }^{\circ}\text{C}$, pov. 10 000-kratna)

of the temperature up to $1400\text{ }^{\circ}\text{C}$ a high compression strength can be obtained (above 90 MPa). With an increase of the sintering temperature in samples on the basis of clay "C" above $1200\text{ }^{\circ}\text{C}$ the compression strength increases slightly.

The X-ray structure analyses of the sintered products in the samples on the basis of clay "B" and "C" show important differences in the mineral content (**Figure 6 and Figure 7**). The crystal phases at the temperature of $1300\text{ }^{\circ}\text{C}$ for samples on the basis of clay "B" are mullite, hematite and ilmenite, while for samples on the basis of clay "C" they are mullite, hematite and anatase. Mullite and hematite, as crystal phases, are present in sintered products even at temperatures of (1100 , 1200 and 1400) $^{\circ}\text{C}$. The presence of the crystal phases is a consequence of the solid-state reactions at these temperatures. The microstructural analysis of the sintered products (**Figure 8 and Figure 9**, $10,000\times$ magnification) shows the complexity of the structure (glass phase, crystal phase, unreacted grains and pores).

4 CONCLUSIONS

On the basis of the performed investigations of the influence of the mineral content of clays from the White Bauxite Mine it is concluded that:

- The investigated clay types are very different for in terms of their mineral and chemical compositions,
- the volume shrinkage is greater for samples on the basis of clay "B" and this is explained by the difference in mineral and granulometric content of the clays and the solid-state reactions,
- the differences in the total porosity of the sintered products on the basis of the investigated clays are not significant,
- the values of the compression strengths of the sintered products are very different: in the samples

on basis of clay "B", important values of the compression strength are noted only at temperatures above $1300\text{ }^{\circ}\text{C}$, while in samples on the basis of clay "C" this is already above $1100\text{ }^{\circ}\text{C}$.

On the basis of the volume shrinkage, the total porosity and the compression strength it is concluded that a quality ceramic product can be obtained by sintering clays from the White Bauxite Mine.

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