Characterization of phase transformation and thermal behavior of Sedlecky Kaolin

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Érkezett: 2020. 06. 30. ▪ Received: 30. 06. 2020. ▪ https://doi.org/10.14382/epitoanyag-jsbcm.2020.24

Abstract

The authors have examined how the properties are changing using different sintering temperature based on the kaolin. Kaolin powder and a mixture of kaolin and 10 m% alumina was made and measured their sintering properties (TG, DTG, DTA, height). Pellets were compacted from the powders and sintered at 450 °C, 575 °C, 775 °C, 870 °C, 1100 °C temperature. The volume shrinkage, sintering weight losses, microstructure and phase composition of sintered specimens were investigated. In the case of sintering at 450 °C the volume of the samples increased; with a further increase of the temperature a continuous volume decrease can be observed.

Keywords: alumina, derivatograph, kaolin, mullite, XRD

Kulcsszavak: alumínium-oxid, derivatográf, kaolin, mullit, XRD

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1. Introduction

In the case of ceramics, the used drying and sintering methods greatly influences the properties of the product [1-7], so it is important to know the effect of sintering temperature. Because of this both in the traditional and in the technical ceramic industry there are a significant role of selected temperature and the condition (atmosphere) of the heat treatment [8-13]. The heat treatment affects the composition, physical, mechanical and functional properties of the product [10-18]. The phase diagrams can help to plan the composition of the final product from the raw materials. Even the simple materials systems like Al_2O_3 - SiO_2 also has been studied by many researchers. Two phase diagrams of Al_2O_3 - SiO_2 system are shown in *Fig. 1* [19-20]. The alumina-hydro-silicates such as the conventional kaolinite can also study partly with these phase diagrams, because they can show their thermal decomposition [21-22]. Many studies can be read regarding to the thermal properties of kaolin [23-26] and its kinetic analysis [27-28]. Kaolin and other clay minerals are usually raw materials obtained from nature which are widely used in the ceramic industry [29-32]. These materials may contain several contaminants and oxides, which may change the phases formed during heat treatment and their amount compared to what is theoretically expected.

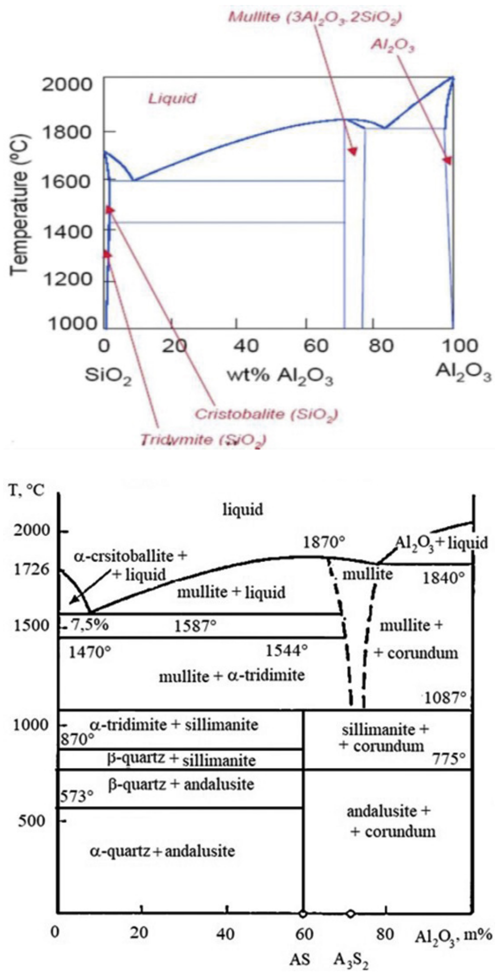
In this research the authors have examined how the Sedlecky ml kaolin and alumina powder mixture behave under heating using a derivatograph and a heating microscope [33]. From the powder mixture ceramic specimens were also made to determine how the volume, weight and phases are changing using different sintering temperatures.

2. Materials and experiments

For the tests, kaolin and a mixture of kaolin and 10 m% alumina was milled in Retsch PM 400 planetary ball mill for 20 min at 150 rpm. The sintering behavior of powders were measured with a Camar Elettronica heating microscope and a MOM Derivatograph-C. During the tests, the furnaces were heated up to 1200 °C at a heating rate of 12 °C/min. The heating microscope took photos every 5 °C.

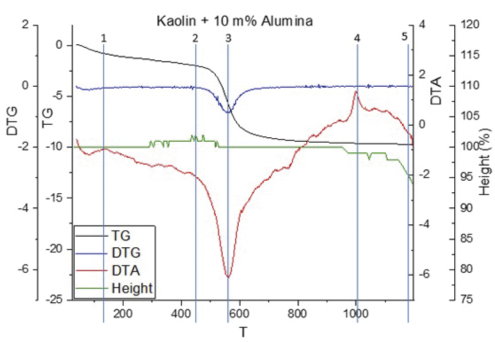
Specimens were made from the mixtures with uniaxially pressing method using a 100 kN mechanical pull-press machine. The pressed specimens were sintered in an electrical chamber kiln using different maximum kiln temperature and were kept at this temperature for 3 hours (*Fig. 2*).

The maximum temperature for sintering was chosen based on the SiO_2-Al_2O_3 phase diagram [20], waiting for the following phase transitions: 450 °C – kaolinite–metakaolinite;



1. ábra *SiO_2-Al_2O_3 rendszer normál körülmények között (átvéve L. Gömze A., 2001 [16] N M Bobkova 2007 [17])*
Fig. 1 *SiO_2-Al_2O_3 system at normal (Taken from L. A. Gömze, 2001 [19] N M Bobkova 2007 [20])*

2. ábra *A 450 °C, 575 °C, 775 °C, 870 °C és 1100 °C hőmérsékleten szinterelt minták*
Fig. 2 *The specimens sintered at 450 °C, 575 °C, 775 °C, 870 °C, 1100 °C temperature*



3. ábra *Kaolin és alumínium-oxid keverék termoanalitikai görbéi*
Fig. 3 *Thermo-analytical curves of kaolin and alumina mixture*

575 °C – α-quartz–β-quartz; 775 °C – andalusite–sillimanite; 870 °C – β-quartz–tridymite; 1100 °C – metakaolinite–mullite transitions. As the sintering temperature increases, the color of the specimens changes continuously. When the sintering temperature achieved 1100 °C the specimens became white. The change in color may indicate that the expected phase transitions have occurred. The properties of sintered specimens were measured, like volume shrinkage, sintering weight losses, microstructure, phase composition. The microstructures were examined by Hitachi TM-1000 scanning electron microscopy and XRD pattern were recorded with a Rigaku MiniFlex II X-ray diffractometer.

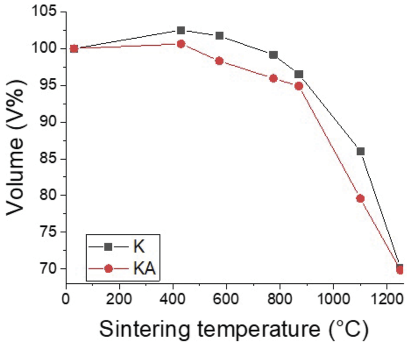
3. Results and discussions

The results of the thermo-analytical test of the kaolin-alumina mixture are shown in *Fig. 3*. From the achieved curves can be distinguish between drying 1, thermal degradation of kaolin 2-3 (conversion to metakaolin), formation of mullite 4 and sintering point 5 (where by the Camar Electronic the height of the sample compared to the original is 95%).

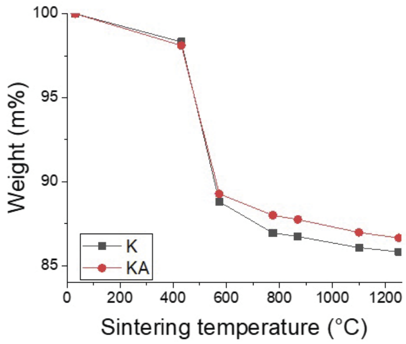
Sintering at 450 °C increases the volume of specimens while decreasing their mass. At 575 °C, a weight loss of more than 10% is observed, which is because of the kaolinite-metakaolinite conversion is complete. The kaolinite mineral loses its crystalline water content (kaolinite mineral composition: 39.52 m% Al_2O_3, 46.52 m% SiO_2, 13.96 m% H_2O). The change in mass from 575 °C was already slightly influenced by the added Al_2O_3 content. The initial volume of specimens and the volume of specimens sintered at 1250 °C were approximately the same for both mixtures (*Fig. 4*).

Some fracture samples were taken from the sintered specimens to examine the microstructure changes depending on the used maximum temperature. The fracture surface of the KA samples can be seen in the *Fig. 5* where the characteristics structure of the clay minerals and the added fine-grained alumina are well observable.

The mineral composition was not significantly affected by the addition of Al_2O_3 and is present throughout the corundum phase in the samples due to the low sintering temperatures. The XRD pattern shown in the *Fig. 6*. The mineral composition of the samples from the used kaolin sintered at 450 °C contain α-quartz and clay minerals like kaolinite and muscovite. In the experiment as the sintering temperature increased, the phase transitions took place as expected. Thus, the XRD pattern of the samples prepared during the research confirm the Al_2O_3-SiO_2 phase diagram found in Bobkova's book [20]. During the sintering at 1100 °C, the mullite phase was formed (*Table 1*). The proportion of crystalline phase is higher due to the addition of Al_2O_3 in the KA mixture. The ratio of mullite to tridymite was the same for both mixtures (mullite/tridymite ~ 10.6).

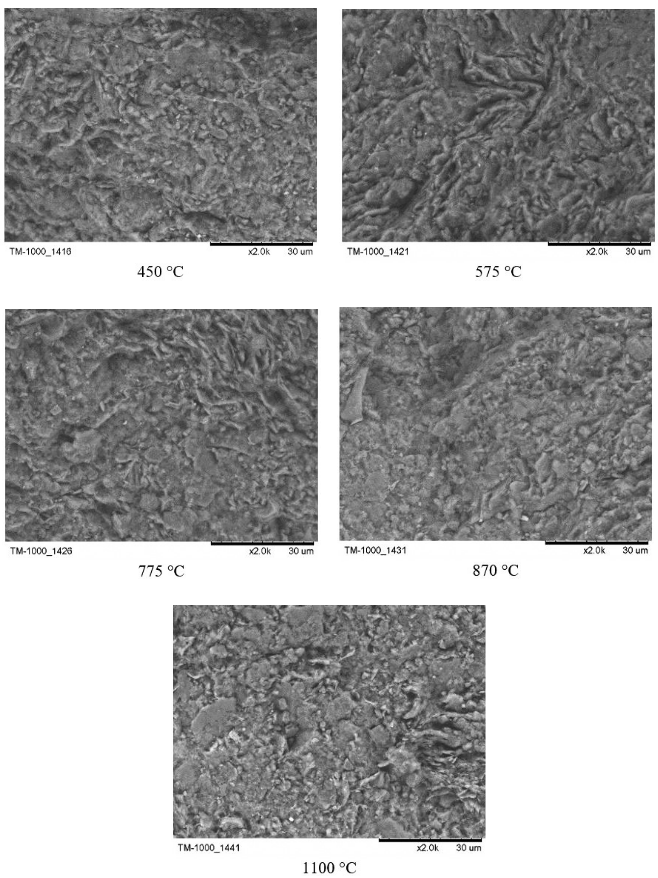


a)

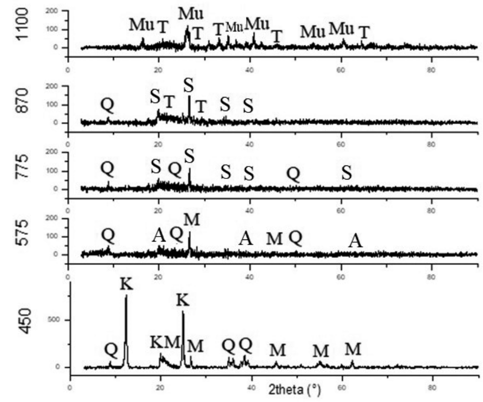


b)

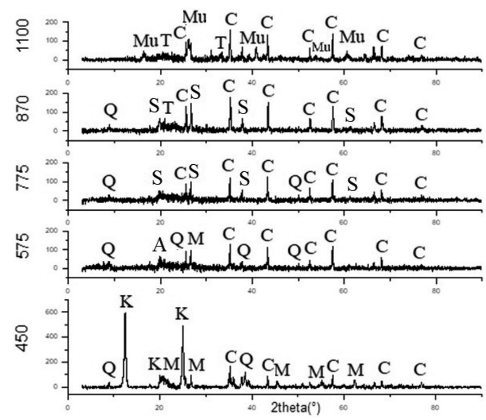
4. ábra Az (a) térfogat és a (b) tömeg változása különböző hőmérsékleten
Fig. 4 The changing of volume (a) and weight (b) using different temperature



5. ábra A különböző hőmérsékleten szinterelt KA minták töretfelületének mikroszerkezete
Fig. 5 The microstructure of the fracture surface of the KA specimens sintered at different temperature



a)



b)

6. ábra A K (a) és KA (b) minta XRD mintája különböző szinterezési hőmérsékleten (A-andalúzit, C-korund, K-kaolinit, M-muszkovit, Mu-mullit, S-szillimanit, T-tridimit, Q-kvarc)
Fig. 6 The XRD pattern for sample K (a) and KA (b) at different sintering temperature. (A-andalusite, C-corundum, K-kaolinite, M-muscovite, Mu-mullite, S-sillimanite, T-tridymite, Q-quartz)

Sign of the mixture		K	KA
Phase content, m%	Amorph	61.4	47
	Crystalline	38.6	53
	mullite	91.45	63.13
	tridymite	8.55	5.97
	corundum	-	30.9

1. táblázat 1100 °C-on szinterelt minták fázisaránya
Table 1 Phase ratio for samples sintered at 1100 °C

4. Conclusions

In this research work the Sedlecky ml kaolin as a traditional ceramic raw material were studied. The authors investigated how the microstructure, the phase composition changes depending on the used sintering temperature and how they will be changing when a small amount (10 m%) alumina were added to the kaolin raw mineral. From the experiments of derivatograph and heating microscopy investigation it can be concluded that both kaolin (K) and mixed (KA) powders shown the characteristic thermal curve of kaolin. The SEM and XRD results of the sintered specimens also confirm that 10 m% alumina has no significant effect on the sintering properties compering the pure kaolin when low sintering temperatures are used but it can be seen that at 1100 °C the proportion of crystalline fraction is significantly higher in the case of the alumina-containing mixture due to the corundum phase. The added alumina affects the functional properties of the ceramic products.

Acknowledgements

The described article was carried out as part of the EFOP-3.6.1-16-00011 "Younger and Renewing University – Innovative Knowledge City – institutional development of the University of Miskolc aiming at intelligent specialisation" project implemented in the framework of the Széchenyi 2020 program. The realization of this project is supported by the European Union, co-financed by the European Social Fund.

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Ref.:

Kurovics, Emese – **Kotova**, Olga B. – **Ibrahim**, Jamal Eldin F. M. – **Tihtih**, Mohammed – **Sun**, Shiyong – **Pala**, Péter – **Gömze**, László A.: *Characterization of phase transformation and thermal behavior of Sedlecky Kaolin*
Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 72, No. 4 (2020), 144–147. p.
https://doi.org/10.14382/epitoanyag-jsbcm.2020.24