Phase composition and microstructure of ceramics made from kaolin mineral, alumina, and corn starch

Emese KUROVICS ▪ Institute of Ceramics and Polymer Engineering, University of Miskolc, Hungary ▪ fememese@uni-miskolc.hu
Jamal-Eldin F. M. IBRAHIM ▪ Institute of Ceramics and Polymer Engineering, University of Miskolc, Hungary
Mohammed TIHTIH ▪ Institute of Ceramics and Polymer Engineering, University of Miskolc, Hungary
Emese SEBE ▪ Institute of Ceramics and Polymer Engineering, University of Miskolc, Hungary
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Abstract
In this work, Sedlecky ml kaolinite, Nabalox No. 315 alumina and corn starch were used. The powder mixtures were milled and uniaxially pressed into pellets. Some properties of the raw materials and mixtures were investigated like TG, DTA, and the gas composition formed during the sintering process. The pellet samples were pre-sintered in the electric kiln under an oxygen-free reduction atmosphere at 1250 °C and then sintered in nitrogen gas at 1450 °C. The composition and microstructure of the produced specimens were tested.

The pyrolysis results show that in reducing pre-sintering 25 wt% of the mass of the corn additive remove from the ceramic body as gas. The remained part of the corn can incorporate into the material structure, and it may affect the further heat treatment processes. The mullite content of the ceramic samples increased from 43 wt% to 70 wt% because of high-temperature sintering in nitrogen gas. The mullite crystal structure has also changed. The increase in the amount of mullite phase is a consequence of the sintering process since the free SiO_2 and Al_2O_3 formed mullite crystals.
Keywords: alumina, free SiO_2, mullite, pyrolysis, sintering process
Kulcsszavak: alumínium-oxid, szabad SiO_2, mullit, pirolízis, szinterelési folyamat

Emese KUROVICS
is received her PhD degree in 2022 at the University of Miskolc. Where she is working as an assistant research fellow at the Institute of Ceramics and Polymer Engineering.

Jamal Eldin F. M. IBRAHIM
is a lecturer in the University of Bahri, Khartoum, Sudan, he graduated from University of Marmara, Istanbul, Turkey, Institute of Pure and Applied Sciences, Department of Metallurgical and Materials Engineering, for the time being, he is a PhD student in the University of Miskolc, Institute of Polymer and Ceramics Engineering, under supervision of Dr. István Kocserha.

Mohammed TIHTIH
is a lecturer in the Sidi Mohamed Ben Abdellah University, Morocco, he graduated from Faculty of sciences Dhar El Mahraz, Fez, Morocco, Department of Physics, for the time being, he is a PhD student in the University of Miskolc, Institute of Ceramics and Polymer Engineering, under supervision of Dr. István Kocserha.

Emese SEBE
is a PhD student at Institute of Energy and Quality, University of Miskolc, Hungary.

1. Introduction

Nowadays, a growing number of research works are carried out on the production of high-value-added products using waste or plant-origin renewable materials, which can also be observed in the case of research and development of new ceramic materials and products [1-14].

The authors in their previous works [15-19] have already shown the role of the plant origin additive in the production of ceramics. Usually, kaolin or zeolite rocks were used as raw minerals [17-19] because the goal was to produce ceramics with high mechanical strength using natural raw materials. The research and applications of clay-based composite materials have drawn a great deal of attention in recent years [20-22]. The mullite phase is formed during the thermal decomposition of clay minerals at above 1000 °C. During the sintering process of the ceramic products, different kiln atmospheres or temperatures can be used. Changing these parameters can produce different products with different properties. For example, the carbothermal reduction (CR) or the carbothermal reduction and nitridation (CRN) reactions of different clay minerals are well known. During the CR or CRN reactions, high-tech ceramic powders (SiC, Si_2ON_2, Si_3N_4, SiAlON) can be produced from traditional raw materials [20-27].

The authors have studied the possibilities of manufacturing advanced ceramics from traditional, relatively inexpensive raw materials and plant-origin additives by using the CR and CRN sintering processes.

2. Materials and experiments

During this research work, the authors used Sedlecky ml kaolin, Nabalox 315 alumina, and corn starch to make two mixtures. Corn starch was used as the carbon source additive that is necessary for the carbothermal processes. The composition of the mixtures was: mixture A – 90 wt% kaolin, 10 wt% alumina and mixture B – 64 wt% kaolin, 7 wt% alumina and 29 wt% corn starch. The raw materials were mixed in a planetary ball mill for 25 minutes at 150 rpm. Cylindrical samples were prepared with a diameter of 25 mm from the powder by the compression process. The pressed samples were first sintered at 1250 °C in a reduction atmosphere. This sintering method was partly the same as the carbothermal reduction, because of this the CR abridgment was used as a sign for the samples which were sintered in a reduction way. Later the samples were sintered at a higher temperature (1450 °C) using flowing nitrogen gas, like in the carbothermal reduction and nitridation process (CRN) of clay minerals. The use of higher amounts of corn starch in the described processes already significantly deteriorates the stability of the ceramic specimen during the heat treatment processes and therefore, in the present work was maximized the amount of corn starch to 29 wt%.

Before the heat treatments, the powders and mixtures were studied with a Derivatograph-C equipment to get the thermogravimetry (TG) and differential thermal

analysis (DTA) curves of the samples. In a pyrolysis study, the authors observed in advance the evolution of the gases during the heat treatment process in the case of the corn starch used, their evolution temperature, and the variation in the volume fraction of the gas components. In this way, for the carbothermic reactions important parameters were studied in advance: formation of CO and CO_2, residual liquid, and solid matter. The duration of the pyrolysis test was 2 hours using a heating rate of 10 °C/min. The test was performed in an electric tube furnace up to 900 °C. Composition of the formed gases was determined with a DANI 500 gas chromatograph.

The phase compositions of the sintered ceramics were determined by an X-ray diffractometer (XRD). To perform the phase composition analysis, the specimens were ground in a mortar into a sufficiently fine-grained powder. In this way, the average phase compositions were determined. The amorphous content was determined indirectly: the sum of all the crystalline phases considered to be 100% with the amorphous content. Test parameters: Cu Kα irradiation, accelerating voltage 40 kV, current 30 mA, step scanning mode, and the measurement range is 3-70° (2Θ). The microstructures were studied by Scanning Electron Microscopy (SEM) and Plasma-Focused-Ion-Beam Scanning Electron Microscopy (PFIB-SEM).

3. Results and discussions

In order to design the carbothermic reactions, the formation of CO and CO_2 gases was investigation in the case of corn starch additives. The specified total gas composition of the synthesis gas is summarized in *Table 1*, which clearly shows that the measured composition of the synthesis gas produced during the study is almost identical for the starch and mixture B (64 wt% kaolin, 7 wt% alumina and 29 wt% corn starch).

Tested samples	Gas composition, V/V%					
	CO_2	H_2	CO	CH_4	C_2-C_4	H_2S
Corn starch	32.91	31.58	23.23	10.31	1.97	<0.1
Mixture B	30.45	38.13	20.70	8.78	1.94	<0.1

Table 1 Total gas composition measured in the pyrolysis test
1. táblázat A pirolízisvizsgálat során mért teljes gázösszetétel

The study shows that combustible carbonaceous gases start to evolve, and volatile substances and hydrocarbons are released from the sample at temperatures above 350 °C in oxygen-depleted media (*Fig. 1*). In the test of the corn starch, more than 25 % of its original mass retained as pyrolysis coke and more than 50 % as pyrolysis oil. It shows that when using oxygen-depleted pre-sintering (CR), it expects that 25% of the mass of the plant additive (starch) will be removed from the ceramic samples as gas, and the remainder can incorporate into the material structure of the pre-sintered ceramic. Conversely, if this test was performed under conventional oxidation conditions, most of the starch would be removed as gas, as can be seen in the case of the thermogravimetry (TG) of the raw material (*Fig. 2*).

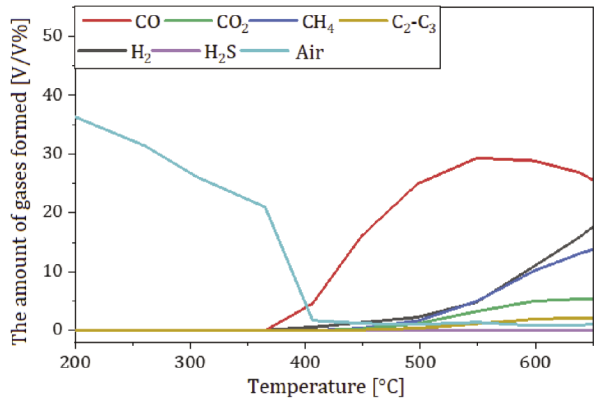


Fig. 1 Variation of gas composition during the pyrolysis test of corn starch
1. ábra A gázösszetétel változása a kukoricakeményítő pirolízisének vizsgálata során

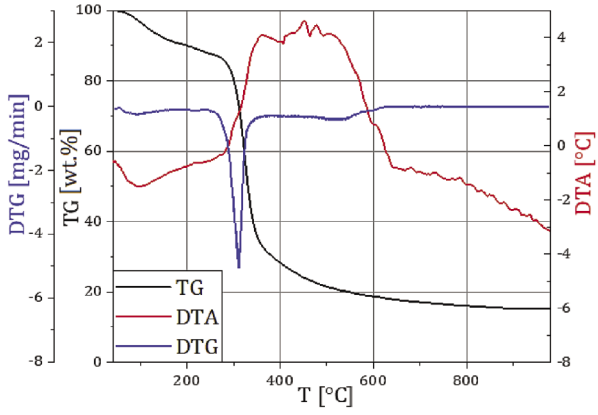


Fig. 2 Thermo-analytical curves of the corn starch
2. ábra A kukoricakeményítő termoanalitikai görbéi

After pyrolysis, the remaining high carbon content of the corn starch can play an important role as a carbon source during sintering in a nitrogen gas and can also contribute to the formation of a new pore structure during the second heat treatment (CRN sintering). The color of the samples changed depending on the used mixture and heat treatment (*Fig. 3*).

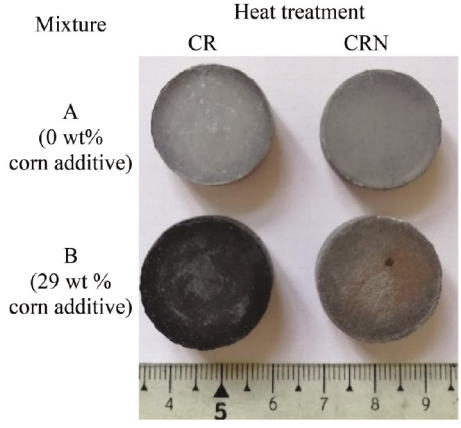


Fig. 3 The heat-treated samples
3. ábra A hőkezelt minták

As a result of CR sintering, the corn additive could not burn out from the ceramic matrix through the formation of CO or CO_2 gases. The skeletal structure of the corn particles remained in the ceramic body to increase the carbon content of the pre-

sintered (CR) samples (*Fig. 4*). This remained carbon content can help to incorporate nitrogen into the aluminosilicate ceramic structure [11].

The average results of the XRD measurements can be seen in *Table 2*. Based on the amount of phases, the mullite content of the ceramic samples increased from 43 wt% to 70 wt% as a result of high-temperature CRN sintering. The type of mullite transformed, and new mullite crystals formed by the reaction of free SiO_2 in the ceramic samples with the alumina, so the amount of mullite phase increased. The results show that a relatively high amorphous content was formed in the samples B (64 wt% kaolin, 7 wt% alumina and 29 wt% corn starch), while any nitrogen-containing crystalline phase was not detected. I.e., the residual carbon content from the corn starch proved to be insufficient to allow the formation of significant amounts of crystalline SiO_2N_2, Si_3N_4, or SiAlON phases in the material structure.

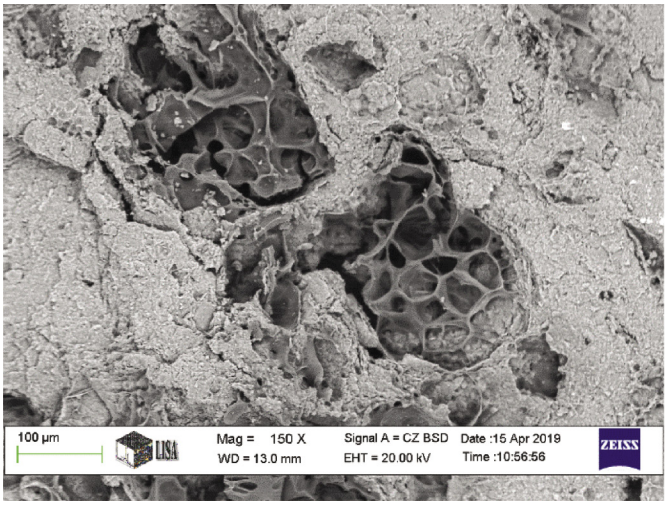
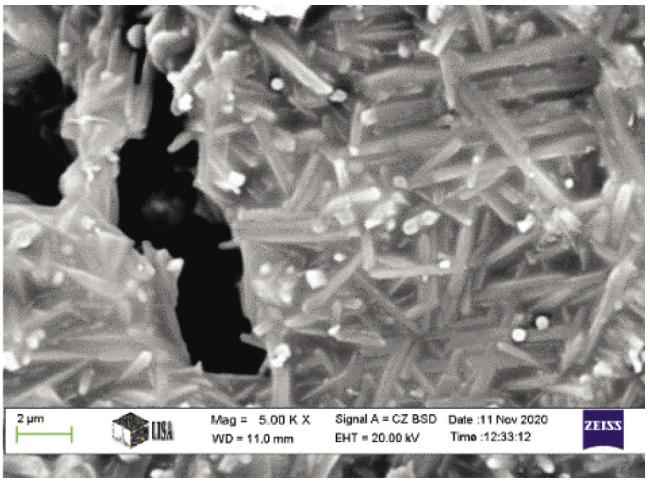


Fig. 4 The remained part of the corn starch in the ceramic body after sintering reduction atmosphere (CR)
4. ábra A kukoricakeményítő maradék része a kerámia testben a szinterezés után redukciós atmoszférában (CR)

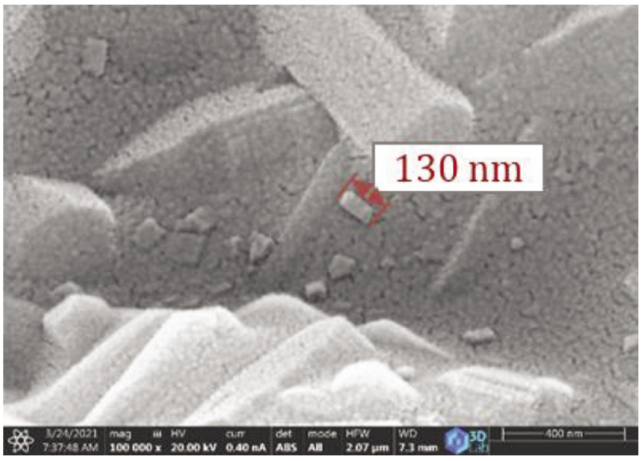
Mixture sign (wt% corn)		A (0)		B (29)	
	Heat treatment	CR	CRN	CR	CRN
The detected phases, wt%	Amorphous	22	24	37	30
	Mullite	43	70	43	70
	Corundum	9	-	14	-
	Cristobalite	25	5.5	4	-
	Quartz	1	0.5	2	-

Table 2 The average phase compositions of the samples
2. táblázat A minták átlagos fázisösszetétele

The microstructure of the sintered samples shows needle-like mullite crystals with nanocrystals whose feature size is smaller than 200 nm. Large amount of amorphous phase which also includes these nanocrystals was stated by the X-ray measurement. Based on the PFIB-SEM studies of the sample B (64 wt% kaolin, 7 wt% alumina and 29 wt% corn starch) (*Fig. 5*), these nanocrystals are mullite crystals therefore the mullite content is even higher than the XRD results show.



a)



b)

Fig. 5 The microstructure of the CRN sintered sample B by SEM (a) and PFIB-SEM (b)
5. ábra A szinterezett B minta mikroszerkezete SEM (a) és PFIB-SEM (b) segítségével.

4. Conclusions

Based on the pyrolysis study of the reducing pre-sintering (CR) of ceramic samples containing corn starch additive, some part of the additive remained in the structure. 25% of the mass of the plant additive was removed from the ceramic samples in gaseous form, and the remained part can incorporate into the material structure. As a consequence, plant origin additive (corn starch) can play an important role as a carbon source and contribute to form new phase composition and to the formation of a different pore structure during the second heat treatment (CRN).

Based on the phase composition investigations it can be stated, that the mullite content of the ceramic samples increased during the CRN heat-treatment. Sintering at 1450 °C (CRN) changed the morphology of mullite particles from plates to needle-like crystals. The amount of mullite phase boosted from 43 wt% to 70 wt% by reason of high-temperature sintering in nitrogen gas (CRN). This way, mullite ceramics with higher purity were produced, compared with CR sintered specimens due to the amount of mullite phase increased by 27 wt%. This increase in the amount of mullite phase is a consequence of the sintering process since the free SiO_2 and Al_2O_3 were able to form mullite crystals.

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