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CONTENT

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Preface

Several years ago, we have realized that existing opportunities in communication and networking of the international scientific community were no longer adequate and even insufficient. Given such a global vision, we could take decisions for ourselves and with a view to the needs of his own surroundings with reasonable certainty that they were compatible and effective in reaching objectives and valid values for oneself and at the same time in keeping with a shared own context that could eventually be globally extended and realized together. Therefore we have signed multilayer Agreement between Miskolc University, Tomsk State University and Institute of Strength Physics and Material Sciences SB RAS.

In accordance with a mutual wish to promote international scientific and technological exchange, Tomsk State University, Institute of Strength Physics and Material Sciences SB RAS and Miskolc University join in an agreement in order to further promote mutual cooperation in education and scientific research. Within fields that are mutually acceptable, the following general forms of cooperation were pursued: exchange of undergraduate and/or graduate students; exchange of faculty members and/or research scholars; joint research activities in nanomaterials, nanotechnology, living systems areas; exchange of scientific materials and information. The program was co-ordinated by Prof. Dr. S. Kulkov for TSU and ISPMS RAS for the Russian part and by Prof. Dr. L. Gömze for the Hungarian part.

The present issue of **építőanyag** – Journal of Silicate Based and Composite Materials, therefore, is a special issue that includes several papers on ceramic materials for different applications which were prepared by both Russian and Hungarian sides.

Several interesting topics were included in this issue.

Designing and developing highly-effective materials that remain stable under extreme conditions are among the primary tasks of modern materials science. One potential solution for this challenge lies in the development of composite materials with appropriate matrix and filler. The use of ceramics as matrix is reasonable as ceramics possess high mechanical strength, hardness and wear resistance while retaining their properties under high temperatures. However, ceramics are known to display low toughness making them brittle enough for specific applications. Therefore, the introduction of internal stresses at the filler/matrix interface allows strengthening of the overall composite structure. Such internal stresses can be introduced through a filler that has negative thermal expansion behavior due to the opposite thermal expansion values of the source filler and matrix materials.

A promising method for creating permeable ceramic materials with high porosity is the mixing large-fractured and ultrafine powders, and the geometry of the pores obtained in such a way is determined by the size and shape of large-fractured powder particles. Porous ceramic materials have been successfully used in various fields, including heat-insulating building materials, since they are durable, corrosion resistant and possess stable thermal features. The combination of these characteristics is especially important for construction in seismic regions.

Ceramics based on partially stabilized zirconium are the most interesting materials among the variety of ceramics due to their inherent high fracture toughness, as a result of their inherent transformational conversion. It is known that the characteristics are determined by the quality of the source ceramic powder (particle shape, particle size distribution), the conditions of compacting and sintering modes and any features that are presented in each phase, and how these phases, including pores, are arranged in relation to each other. The most important factor in the successful application of materials understands the features of a structure emerging in them on their behavior under mechanical impact.

It is well known that the porosity of brittle materials can have significant influence on their physical (mechanical, thermal, electrical) properties. Young's modulus, shear modulus and Poisson's ratio are essential parameters in the studies of advanced material mechanics. In addition, the macroscopic behavior of ceramics can vary from brittle to quasi-plastic, depending on the pore space volume. That is why the investigation of the evolution of deterioration in a brittle porous material at different levels of scale and the subsequent damage depending on the deformation rate, constraint, etc. is of considerable interest in terms of the emergence of a structural hierarchy of deformation and destruction in similar brittle materials (ceramics, natural stones etc.).

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Investigation of ceramic brick rods with blackened materials inside

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Abstract

In this work the authors have studied the blackened materials inside of the ceramic rods after their sintering in a laboratory chamber kiln. The samples were extruded from conventional brick clays of mined moistures after mixing with additives of sawdust and sunflower husk in 2.91 m% and 3.85 m%. During the investigation they found a considerable influence of vegetable origin additives on chemical, physical and mechanical properties of sintered materials including color, microstructure, mineral and chemical compositions as well as mechanical strength, drying and firing shrinkages. The mineralogical compositions and morphological structures of the "fired out" sawdust and sunflower husks were also determined inside of the blackened parts of specimens. Thanking to the heat generated by fired out vegetable origin additives a remarkable quantity of glass phase components was also formed in the blackened parts of the sintered rods.

Keywords: material structures, ceramic, composites, hercynite, minerals, mineralization, sawdust, sunflower husk

1. Introduction

The clay minerals are one of the oldest materials which were used by humanity [1]. Clays are used also more than 7,000 years [2] to prepare building materials. In spite of the clay minerals are used by thousand years their study and examination are in the focus of research in several segments of science [3-10] and industry [11-18] until today. In our days the brick and ceramic roof tiles industries are the largest user of the conventional brick clays [19-29]. In spite of the large production volume of brick and ceramic roof tile industries and intensive research of the conventional brick clays the drying sensitivity and material structure inhomogeneity can be reason of the scrap formations and quality defaults.

The goals of this research are to understand the influence of vegetable organic additives on chemical, physical and mechanical properties of conventional brick products including their colors, microstructures, mineral and chemical compositions, mechanical strengths as well as drying and firing shrinkages.

2. Materials and methods

During the experiment the authors have used conventional brick clays with moistures of 21-23 m% of relative humidity and sawdust or sunflower husks and mixed them in a pan mill type planetary rotary mixture at 90rpm through 10 minutes (Table 1). From each mixture cylindrical shape rods were extruded with diameter of 25 mm on a KEMA-PVP 5/S extruder. After extrusions the rods were cut by 14 specimens, 6 from them with 50 mm for pressure strength test and 8 from them with 150 mm lengths for bending strength test. The so prepared specimens were dried in a laboratory chamber-dryer at 50°C during 72 hours.

Clay	Sawdust	Sunflower husk
97.09	2.91	-
96.15	3.85	-
97.09	-	2.91
96.15	-	3.85

Table 1. Mixture composition in m%
1. táblázat A keverékek összetétele tömegszázalékban [m%]

The produced and dried cylindrical rod specimens were sintered in a laboratory chamber kiln at a heating rate of 60°C/hour up to 950°C and keep at this temperature through 2 hours to generate the required solid phase transformations of the clay minerals and mineral components of sawdust and sunflower husk. After these 2 hours keeping at maximum temperature the kiln heating system was switched off and cooled down freely at closed door.

3. Results and discussion

During the experiments the authors have determined the linearly and volumetrically drying and sintering shrinkages together with the mass losses. After the sintering the specimens with 50 mm green length were subjected under compressive strength and the specimens with 150 mm green length under bending strength. The average values of volume shrinkages, weight losses, bending and compressive strengths are shown in Table 2.

After the fractures it was surprising that the sintered ceramic materials inside of each specimen became black colors meanwhile they were covered with the red-brown material shells (Figure 1) with thickness of 1.5-2mm. One of the reasons of this phenomenon can be the very fine grain structure of the used clay minerals with large volumes of submicron and nano

	Additive, m%		Volume shrinkage, %	Weight loss, %	3 point bending strength, MPa	Compressive strength, MPa
Sawdust	Sunflower husk					
2.91	-		12.25	23.75	9.28	30.26
3.85	-		12.34	23.83	9.48	32.09
-	2.91		9.54	23.42	8.67	29.90
-	3.85		10.25	22.73	13.08	34.22

Table 2. Characteristics of specimens made from mixtures of different compositions
2. táblázat A különböző keverékekből készült minták jellemzői

particles. In this case the sawdust and sunflower husk additives could not get oxygen enough to turn into gas phase and fire out. At 950°C temperature the firing sawdust and sunflower husk additives could reduce the 3 valence iron-oxide atoms and promote formations of **hercynite** minerals, thanking to the deficiency of atmosphere air and oxygen.

Fig. 1. The cross-section of fired and cracked specimens
1. ábra A kiégetett és eltört próbatestek keresztmetszete

The material structure and morphology of the cracked specimens were examined by Hitachi TM-1000 scanning electron microscopy. The SEM pictures show briefly that the used sawdust particles have saved their cell type microstructures and morphologies (Figure 2 and 3) in spite of their transformation into ceramics during the heat treatment and sintering. In Figure 3 the mineralization of sawdust cell structure is very similar to the material structures of the remnants of organic pore-forming additives in conventional clay brick materials which were described by F Kristály and L A Gömze [3] in 2008.

(a)   (b)
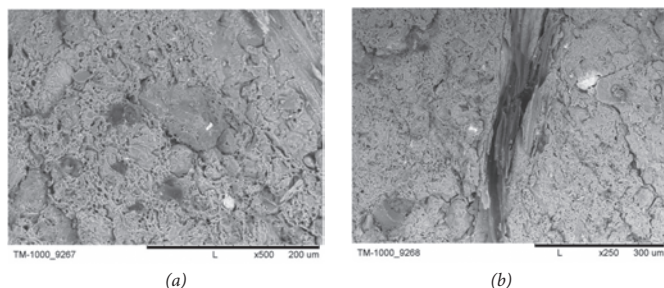
Fig. 2. The fracture surface of sintered specimens with sawdust
2. ábra Fűrészpor tartalmú szinterelt próbatest töretfelülete

(a)   (b)
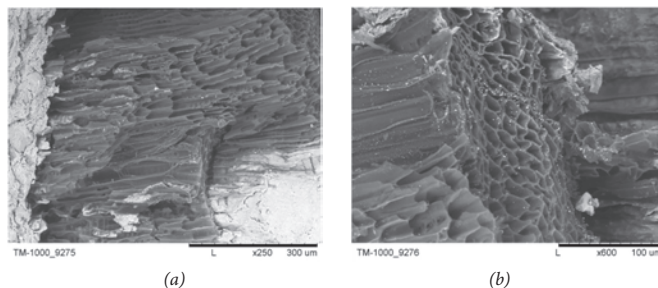
Fig. 3. The sawdust transformed into ceramics inside of the specimens
3. ábra A keramizálódott fűrészpor a minta belsejében

To determine the elementary chemical compositions the specimens were further examined on scanning electron microscope ZEISS EVO MA10 serviced with energy dispersive microswitch (EDAX). The microstructure and material composition of the red-brown cylindrical shell are shown in Figure 4 and the microstructure and material composition of the blackened surfaces inside of the rods are shown in Figure 5. It is seen very well in Figure 5 how the dense and dark quartz particles are bonded in the "ceramic matrix" of the sintered clay minerals.

(a)

(b)
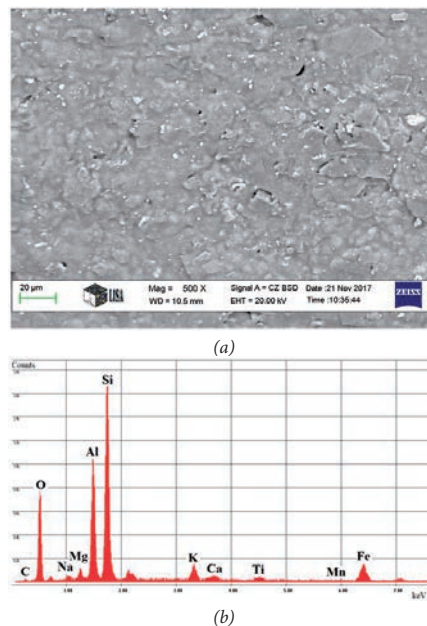
Fig. 4. The microstructure (a) and chemical compositions (b) of specimens with sunflower husks at the red-brown surface
4. ábra A napraforgóhéjjal készült próbatest külső, téglavörös színű felületének a mikrostruktúrája (a) és a kémiai összetétele (b)

The determined by EDAX chemical components of the darkened materials are fixed in the Table 3.
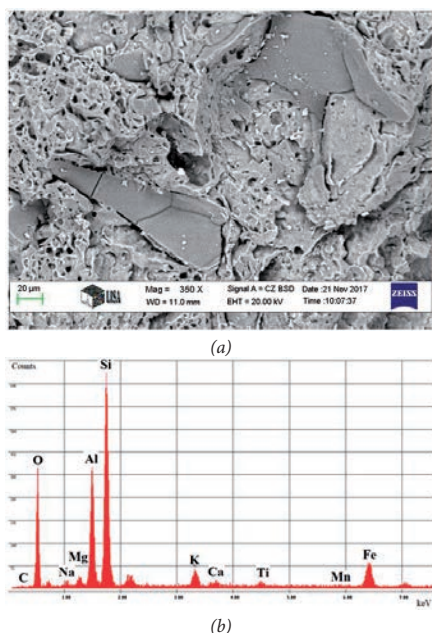
Figure 5. The microstructure (a) and chemical compositions (b) of specimens with
sunflower husks at blackened surface
5. ábra A napraforgóhéjjal készült próbatest belső, fekete színű felületének a
mikrostruktúrája (a) és a kémiai összetétele (b)

Analyzing the data in Table 3 a considerable difference can be seen between carbon (C), oxygen (O), calcium (Ca) and iron (Fe) components depending on their geometrical (outside or inside) positions. This 3.0 m% of carbon (C) can be also the reason of the observed blackening of material particles inside of the rod specimens.
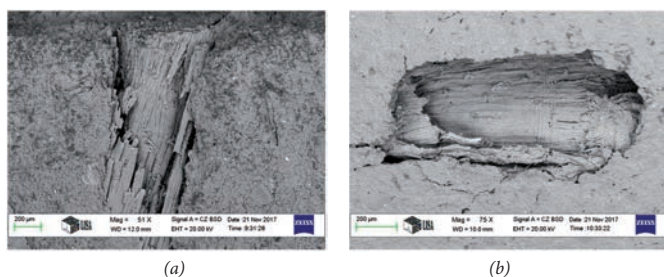
Fig. 6. The sunflower husks transformed into ceramics inside of the specimens (a)
and in an outside surface crack (b)
6. ábra A keramizálódott napraforgóhéj a minta belsejében (a) és egy külső felületi
repedésben (b)

The transformation of sunflower husks into ceramics was examined both in inside and outside surface cracks and they are

shown in Figure 6. The cell structures of the sunflower husk are saved after sintering at 950°C in spite of their transformation into ceramics.

The examined structure of blackened materials inside of the extruded and sintered rod specimens had a wide range but all of them are looking like a sponge. This variety of sponge structures is very well seen in the Figure 7 where the difference (1, 2) in chemical composition of materials (Table 4) influence not only on pore structures but on the darkness also.
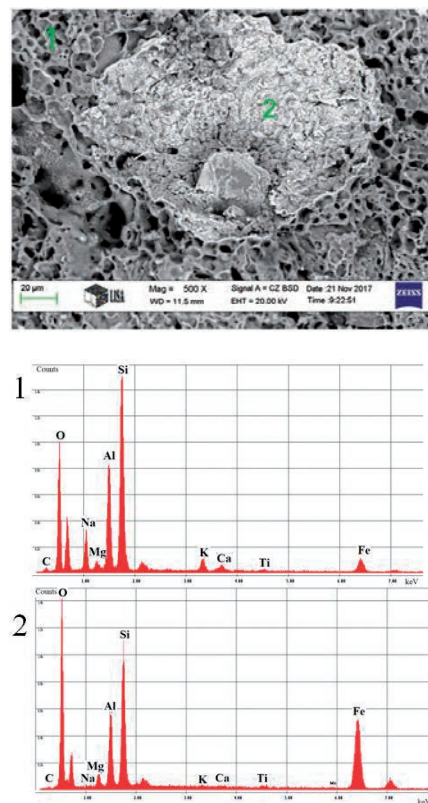
Fig. 7. The sponge structures and chemical compositions of blackened materials
examined by EDAX
7. ábra A fekete anyagra jellemző szivacs struktúra és annak kémiai összetétele
(EDAX)

The mineral and oxide composition of the blackened materials inside of the extruded and sintered ceramic rod samples were determined by XRD examination (Figure 8). The material composition includes minerals and oxides are given in Table 5.

	Chemical elements	C	O	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
Wt %	**The red-brown surface (outside)**	1.7	26.1	0.8	1.4	17.1	34.5	3.5	1.2	1.2	0.3	12.1
	The blackened surface (inside)	3.0	35.5	0.9	1.1	14.2	33.2	2.7	0.8	0.9	0.3	7.4

Table 3. The chemical compositions of the darkened materials examined and determined by EDAX
3. táblázat A minták felületének EDAX segítségével meghatározott kémiai összetétele

	Chemical elements	C	O	Na	Mg	Al	Si	K	Ca	Ti	Fe
Wt %	**1**	3.40	29.97	6.30	1.08	14.38	31.22	2.54	1.54	0.80	8.78
	2	1.37	27.46	0.26	1.99	9.83	18.73	0.29	0.30	0.56	39.20

Table 4. The chemical compositions of the examined by EDAX blackened material with sponge structure
4. táblázat A szivacs struktúrájú fekete anyag EDAX segítségével meghatározott kémiai összetétele

Fig. 8. The XRD diagram of the tested blackened materials with sponge structures
8. ábra A vizsgált megfeketedett szivacs szerkezetű anyag XRD diagramja

	SUM	Quartz SiO_2	Glass (Na, Ca, Mg, Al) Si_2O_5	Microcline $KAlSi_3O_8$	Albite $NaAl-Si_3O_8$	Hercynite $FeAl_2O_4$
Phase %	100,00	45.00	35.00	3.00	5.00	12.00
Fe_2O_3	5.51					5.51
CaO	2.39		2.39			
K_2O	0.51			0.51		
SiO_2	75.98	45.00	25.60	1.94	3.44	
Al_2O_3	9.10		0.54	0.55	0.97	7.04
MgO	0.86		0.86			
Na_2O	6.20		5.61		0.59	
LOI	-0.55					-0.55

Table 5. Minerals and oxides composition determined by X-ray diffraction
5. táblázat A röntgen-diffrakcióval meghatározott ásványi és oxidos összetétel

It is obvious from XRD that the carbons are presented in amorphous phase and they are included in the glass components of X-ray diffraction. The black color of the materials inside of the rods can be understandable thanking to these amorphous carbons and the relatively high value of $FeAl_2O_4$ hercynite mineral which have been built from one molecule FeO and one molecule Al_2O_3.

4. Conclusion

The presented research work has revealed the complexity of influence of sawdust and sunflower husks both on the morphological and material composition and colors of the ceramic items sintered from conventional brick clays. The formed inside of the body sponge structure can increased the thermo isolating properties of walls built from bricks made with pore forming additive like sawdust and sunflower husk [3, 30]. It is necessary underpin that with increasing the portion both of sawdust and sunflower husk up to 3.85 m% the compressive and bending strengths of the sintered products (bricks) will be increased.

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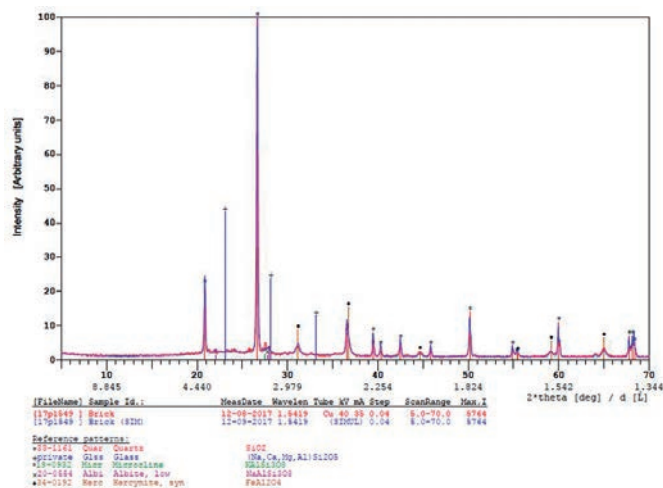
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Belsejében megfeketedett kerámia tégla rudak vizsgálata

Jelen munkában a szerzők olyan kerámia rudakat tanulmányozták, amelyek belsejében fekete anyag jelent meg a laboratóriumi kamrás kemencében történő szinterelés után. A vizsgált mintákat hagyományos bányanedves téglaagyag és adalékanyag (fűrészpor vagy napraforgóhéj, 2,91% és 3,85%-ban) keverése után extrudálták. A vizsgált növényi eredetű adalékanyagoknak jelentős a hatása a termék kémiai, fizikai és mechanikai tulajdonságaira, mint a szín, mikrostruktúra, ásványi és kémiai összetétel, valamint a mechanikai szilárdság, száradási és égetési zsugorodás. A kiégett növényi eredetű adalékanyagok által termelt hőnek köszönhetően figyelemre méltó mennyiségű üvegfázisú amorf komponensek is létrejöttek a szinterelt kerámia rudak belső megfeketedett részében.

Kulcsszavak: anyagszerkezet, kerámia, kompozit, hercinit, ásványok, mineralizáció, fűrészpor, napraforgóhéj

Investigation of mineralogical composition and technological properties of conventional brick clays

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Abstract

In this research the layers of a Hungarian conventional brick clay deposit were examined both on material and mineralogical structures and compositions as well as on technological properties. During their examination the authors have found that the volumes of X-ray amorphous submicron and nano particles of the conventional brick clays do not influence on the dry sensitivity of the extruded and formed green products. The authors have found also a strong correlation between the X-ray amorphous nano particles of raw materials and the bending strengths of the sintered ceramics. As more the volumes of submicron and nano particles are in the conventional brick clays as higher are the bending strengths of the produced from them sintered ceramics.
Keywords: bending strength, bricks, clays, drying, minerals, roof tiles, shrinkage, X-ray diffraction

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1. Introduction

In our days the conventional brick clays are playing very important role in production of ceramic bricks and roof tiles [1-14] but they are wildly used also in different segments of industry [15-17]. Their mineralogical composition, grain size distribution, moisture and specific surface are influencing very strong not only on color and quality of the final products but on the technological properties and parameters also [18-20]. There are several authors underpin that the drying sensitivity of the conventional brick clays depends on their grain sizes and specific surfaces, means as smaller the average grain size and higher the specific surface are as stronger the susceptibility of clays is to the drying sensitivity and drying cracks [21-24]. This option is one of the reasons that it is so important to analyze the mine layers before their exploitation to produce building ceramics like large borehole bricks or roof tiles.

It is obvious that the layers of the conventional brick clay deposits have formed during several thousand years. This circumstance is one of the reasons why they may have very different mineralogical, chemical, morphological and grain size structures depending on their position and location inside of the mined deposits and layers.

The aims of this research work to determine the mineral composition of the layers of a new clay deposit and their influence on the technological properties like extruding, drying and firing as well as shrinkages and bending strengths of the sintered products.

2. Materials and experiments

To determine the material structure, specific surface, mineralogical composition, extruding, drying and sintering properties of clay minerals of a new Hungarian quarry 9 mining holes were drilled in a square mesh structure in 15 m depth of each. The drilled out materials from each mined holes were divided by 5m as 0-5m, 6-10m, 11-15m and were crashed and mixed on a laboratory pan mill with 90rpm through 10 minutes. From each mixture by 100g were taken for the material tests as scanning electron microscopy (SEM and EDAX), Langmuir and BET specific surface determination and X-ray diffraction. All the remaining clays were extruded on a KEMA-PVP 5/S extruder into cylindrical shape rods with diameter of 33 mm. After extrusions each rods were cut on 7 specimens by 150 mm green lengths of each before drying, sintering and bending strength tests. In this research work are shown the results of material tests and examinations made on mixes of the 3 different layers taken from the central (5th) drilling hole.
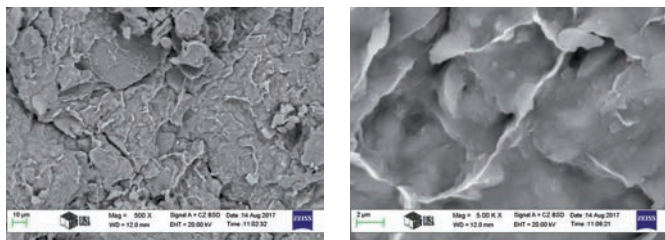
Fig 1.   Material structure of clay mixture from layer 11-15m
1. ábra   A 11-15m-es agyag réteg anyagszerkezete

The typical material structure and chemical composition of clay mixtures investigated with scanning electron microscopy and EDAX are shown in Figure 1 and Figure 2.

Element	O	Na	Mg	Al	Si	K	Ca	Ba	Ti	Fe
Wt %	56.25	0.38	1.37	12.15	25.01	1.27	0.36	0.02	0.34	2.85
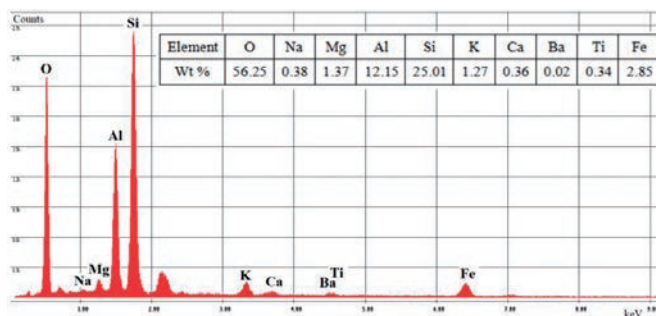
Fig 2.   The surface chemical composition of clay mixture from layer 11-15m
2. ábra   A 11-15m-es agyag réteg kémiai összetétele

3. Results and discussions

The material samples taken from mixtures by 100 g of each were dried in a laboratory chamber-dryer at 85°C during 72 hours. After drying some part of them was used to determine specific surfaces and part of them for determine the mineral and chemical composition through X-ray diffraction. The Langmuir and BET specific surfaces were determined with instrument TriStar 3000 and the results are given in the Table 1.

Layers	Tested mass	Langmuir, m²/g	BET, m²/g	
			single	multi
0-5 m	0.3096 g	28.7347	19.1615	20.3931
		31.7419	21.3475	22.5983
6-10 m	0.4781 g	29.5417	19.6578	20.9726
		32.1277	21.6153	22.9077
11-15 m	0.2686 g	30.7266	20.4658	21.7865
		33.3207	22.4282	23.7279

Table 1.   The specific surfaces of the clay mineral mixtures taken from the 3 different layers of drilling 5
1. táblázat   Az 5. furat 3 különböző rétegéből vett agyagminták fajlagos felülete

The XRD diagrams of the layers are given in Figure 3 and the mineralogical and oxide compositions of the layers are given in Table 2 and Table 3.

0-5 m
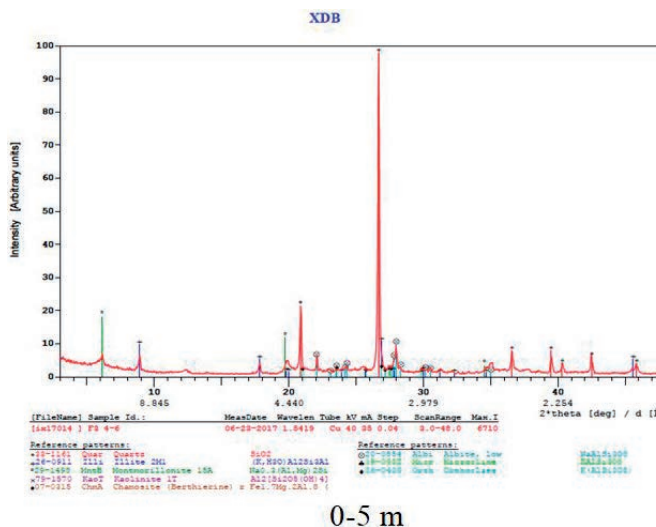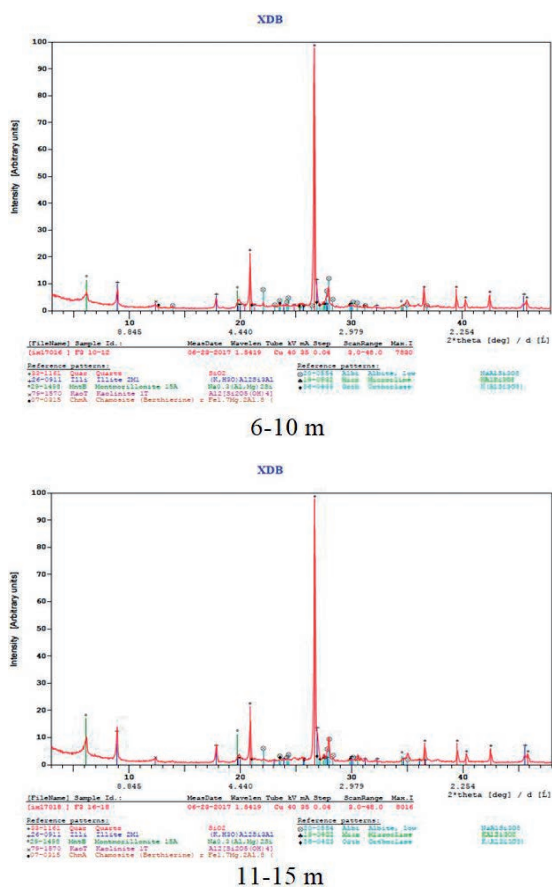
6-10 m

11-15 m

Fig 3. The X-ray diagram of materials taken from the 3 different layers of the drilling 5th
3. ábra Az 5. furat 3 különböző rétegének a röntgendiffraktogramja

	Minerals	0-5 m	6-10 m	11-15 m
quartz	SiO_2	28	30	30
illite	$[K(H_3O)^+]Al_2[SiO_3AlO_{10}](OH)_2$	14	15	18
montmorilonite	$(0,5Ca,Na)_{0,7}(Mg_{0,7}Al_{3,3})$ $[(Si_8O_{20})(OH)_4]$	12	8	12
kaolinite	$Al_2Si_2O_5(OH)_4$	1	3	2
chamosite	$(Fe^{2+},Mg)_5Al(AlSi_3O_{10})(OH)_8$	2	3	2
albite	$NaAlSi_3O_8$	13	16	12
microcline	$KAlSi_3O_8$	2	2	2
orthoclase	$KAlSi_3O_8$	3	3	3
XRD-amorphous	-	25	20	19

Table 2. The mineral composition of the layers from the drilling 5th
2. táblázat Az 5. furat rétegeinek ásványi összetétele

Oxides	0-5 m	6-10 m	11-15 m
Fe_2O_3 %	0.84	1.26	0.84
K_2O %	2.17	2.27	2.55
SiO_2 %	55.08	58.2	58.67
Al_2O_3 %	11.35	12.82	13.08
MgO %	1.32	0.91	1.32
Na_2O %	1.83	2.09	1.71
H_2O %	2.46	2.54	2.87
LOI %	2.41	2.46	2.82

Table 3. The oxides composition of the layers from the drilling 5th
3. táblázat Az 5. furat rétegeinek oxidos összetétele

Analyzing the mineralogical composition determined by X-ray diffraction we can see that total volumes of clay minerals are more than 25 m% which means that this mined raw material is applicable to produce good quality ceramic bricks and roof tiles using plastic forming technology like extrusion. At the same time the ratios of the X-ray amorphous particles are higher than 15 m% in each case. Because of the large volume of the X-ray amorphous submicron and nano particles after the sintering will be formed a nano size porous structure that will make the produced bricks and tiles frost resistant [25].

After the extrusion the 21 pieces of cylindrical rods with green lengths of 150 mm were dried in open air at room temperature of about 25-30°C and their diameters, lengths and weights were measured by 1 hour in the first 3 hours and after by 2 hours. The results of mass and volume losses are presented in Bourry diagrams in Figure 4.

0-5 m

6-10 m

11-15 m
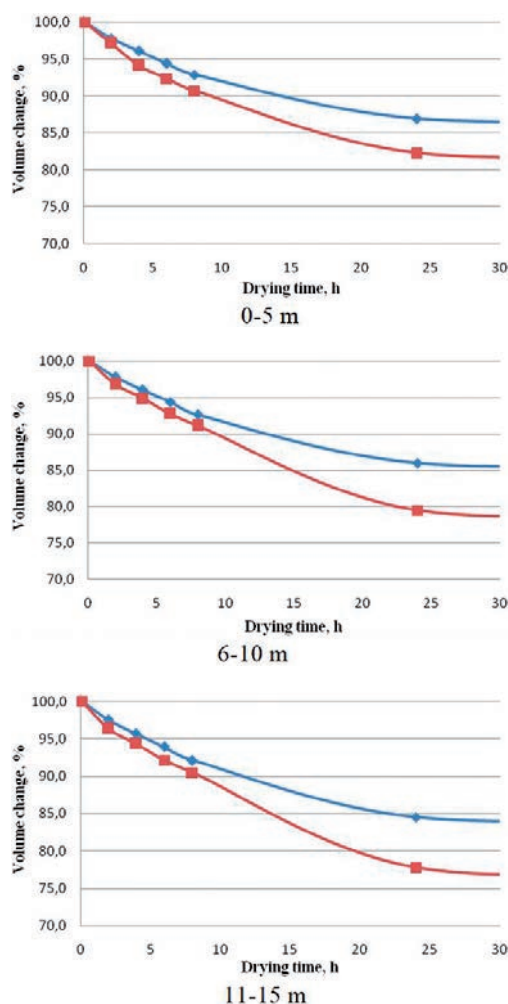
Fig 4. Bourry diagrams (volume and mass losses) during drying of the raw material mixtures of the 3 different layers
4. ábra A 3 különböző agyagréteg keverék száradási Bourry diagramja (térfogat és tömegveszteség)

There are huge number of literature which are studied and described the drying properties and drying shrinkage of the conventional brick clays. Most of them [1-4, 21-24 and 26-29] underpin that when in conventional brick clays the particles with 2 mm or less diameters are more than 15-20 m% the extruded products will be inclined to formation of drying

cracks because of the too fine grain structure. During the drying we did not find any cracks or microcraks not on the surfaces and nor in the cross-section of the extruded ceramic rods in spite that the studied brick clays have 19-25 m% of particles with nano sizes. This means that increment of fine particles in the conventional brick clays does not increase the drying sensitivity of the extruded and plastic formed ceramic items. So the appearances of cracks during drying must be explained with incorrect forming pressures and residual stresses inside of the body after extrusion and pressing and not with the fine grain size structures.

After drying the 21 pieces of the cylindrical rod specimens were sintered in an electrical chamber kiln with heating rate of 60°C/hour up to 950°C and kept at this temperature during 2 hours and after the heating system was switched off. The volumetric and mass losses of drying and firing together are shown in Fig. 5 and Table 4.
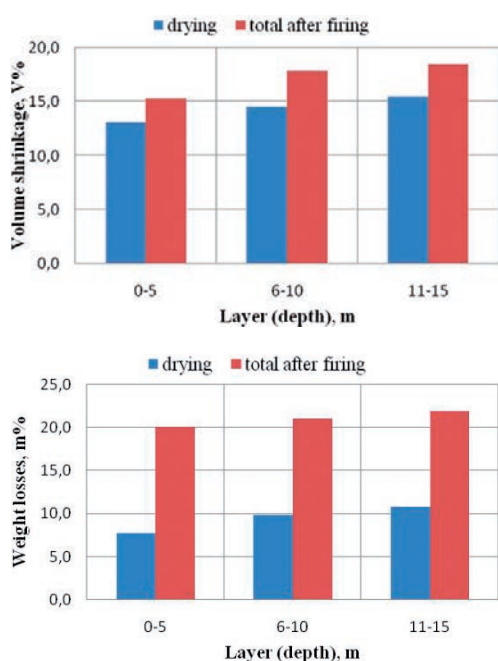
Fig. 5. The volumetric and mass losses of drying and total after firing
5. ábra A száradás és az égetés utáni teljes térfogat- és a tömegváltozás

Generally the ceramics produced from conventional brick clays and sintered at less than 950-1000°C which is relatively low temperature for formation mullite and other mechanically strength crystals. Because of this circumstance the sintered cylindrical rod specimens were tested also on 3 point bending strength (Table 4).

Depth of drilling, m	Volume shrinkage, %		The weight loss, %		3 point bending strength, MPa
	drying	total after firing	dry	total after firing	
0-5	13.07	15.32	7.80	20.11	15.87
6-10	14.54	17.85	9.90	21.10	12.05
11-15	15.51	18.45	10.79	21.92	12.07

Table 4. The volumetric and mass losses of drying and total after firing and the 3 point bending strength of specimens
4. táblázat A száradás és az égetés utáni teljes térfogat- illetve tömegváltozás és a próbatestek hárompontos hajlítószilárdsága

The 3 point bending strength test gave relatively high values which means that the conventional clay minerals from this new mine can be perfectly used for production ceramic roof tiles with high quality. Analyzing the reasons of this relatively good mechanical bending strength the authors could not find a convincing correlation between the bending strength and quartz content but a very good correlation have been found between the bending strength and volumes of XRD amorphous fine particles in the conventional brick clay raw material (Figure 6). So it can be stated that using conventional brick clays the bending strength of the sintered products will as higher as more X-ray amorphous nano particles are in the minerals.
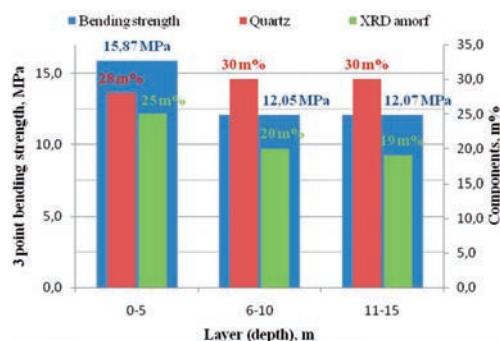
Fig 6. Bending strength [MPa], quartz and X-ray amorphous nano particles ratio [m%] of specimens made and sintered from the clays of the different layers
6. ábra A különböző rétegekből készült, szinterelt próbatestek hajlítószilárdsága [MPa], kvarc és röntgen amorf aránya [m%]

4. Conclusion

The most important conclusion of the present research work is that the examined clay deposit is applicable for production building ceramic items like wall bricks and roof tiles. At the same time submicron and nano particles of the conventional clays are not reason of the micro and macro cracks on surface and in body during drying the extruded and pressed from them products.

The strong correlation was founded between the bending strength of the sintered cylindrical ceramic rods and the volume of the X-ray amorphous submicron and nano particles. As more the volumes of submicron and nano particles are in the conventional brick clays as higher are the bending strengths of the produced from them sintered ceramics.

Acknowledgements

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Hagyományos téglaagyagok ásványi összetételének és technológiai tulajdonságainak vizsgálata
Jelen kutatás során hagyományos, magyarországi agyagbánya furat rétegeit vizsgálták a technológiai tulajdonságok, valamint az anyag-, és ásványi szerkezet alapján. A szerzők megállapították, hogy a hagyományos téglaagyagok röntgenamorf, szubmikron és nanoméretű részecskéinek mennyisége nincs hatással az extrudált nyers termékek repedésérzékenységére. A szerzők erős kapcsolatot találtak a nyersanyag röntgenamorf tartalma és a szinterelt kerámia hajlítószilárdsága között. Minél nagyobb arányban tartalmaz a hagyományos téglaagyag szubmikron és nanoméretű részecskéket, annál magasabb lesz a belőle készült, égetett kerámia termék hajlítószilárdsága.
Kulcsszavak: agyag, ásványok, cserép, hajlítószilárdság, száradás, tégla, XRD, zsugorodás

Development ceramic floor tiles with increased shear and pressure strengths

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Abstract

In the present research work is studied and described the influence of alumina and zirconia powders on physical and mechanical properties of the conventional ceramic floor tiles. After testing several different raw material compositions the authors have found that adding 5 m% commercial ZrO_2 powders the shear strengths and pressure strengths of these floor tiles can be considerable increased. These new floor tiles with increased mechanical strengths may be suitable for use in dairy, meat, food and other industries.
Keywords: alumina, ceramics, compacting, density, floor tiles, mixtures, powders, zirconia

1. Introduction

The ceramic floor tiles are widely used as building materials both for interior architectural purposes in the living and public buildings and for hygiene purposes in the dairy, meat, food and other industries [1-2]. Because of this circumstance there are several research works which are studying, analyzing and describing the physical, chemical, thermal, acoustic and morphological properties both of the used raw materials and the sintered glazed or unglazed floor tiles [3-12]. Generally the production lines of wall and floor tiles industry are used fast drying and sintering technology with roller furnaces of less than 50 minutes cold to cold firing cycle. Because of this fast heating and cooling the green bodies of tiles are very sensitive to the diffusion of water vapor and heating curve in the beginning part of the fast firing roller kilns.

The beautiful designed wall and floor tiles which are excellent in the living and public buildings usually cannot be used in the industrial workshops, storage pools, silos and reservoirs because of the shortages of their durability and mechanical strengths. It can be possible to increase the mechanical strengths through increment of sintering temperature [13] but this is not so easy because of the low melting temperature of

some of the components of the used pulverized powder-mix raw materials. Generally it is possible to get ceramic products with increased mechanical strengths trough composite material structures [14-18]. Our aims are to increase the mechanical properties and durability of the ceramic floor tiles used in food and chemical industries by creating a new ceramic composite structure adding ceramic powders with increased mechanical

strengths, hardness and durability to the conventional raw materials as pulverized floor tile powders.

2. Materials and experiments

In the last 10-15 years ceramics and ceramic matrix composite materials (CMC) are widely used because of their low density and excellent wear resistance, hardness, toughness and mechanical strength [19-24]. Really the most widely used and popular technical ceramics [25-33] have relatively low density and very competitive mechanical properties (Table 1).

Type of ceramics	Density g/cm³	Tensile strength MPa	Bending strength MPa	Compressive strength MPa	Young Modulus GPa	Fracture toughness MPam¹ᐟ²
Al₂O₃	3.98	210	560	2800	392	5.5
SiC sintered	3.1	175	560	3920	420	4.4
Si₃N₄ reactively bound	2.5	140	245	1050	210	3.3
Si₃N₄ hot pressed	3.2	560	910	3500	315	5.5
SiAlON	3.24	420	980	3500	315	9.9
ZrO₂ partially stabilized zirconia (PSZ)	5.8	455	700	1890	210	11.0
ZrO₂ transformation toughened zirconia (TTZ)	5.8	350	806	1750	203	12.1

Table 1.   The mechanical properties of the most widely used technical ceramics
1. táblázat   A leggyakrabban alkalmazott műszaki kerámiák mechanikai tulajdonságai

In the laboratory experiments were used conventional pulverized powder mixtures of floor tiles which were prepared from the following raw materials: clay Petény I and II, clay Teplicsány, rhyolite, conventional clay Kisőrs, GVZ and phonolite. The mineralogical composition of these powder mixtures is described in the Table 2 and the typical microstructure and chemical components are shown in Figure 1.

Minerals	Chemical composition	Quantity, m%
β-quartz	SiO₂	22.51
α-quartz	SiO₂	37.31
tridimite	SiO₂	7.35
orthoclase	K(Al, Fe)Si₂O₈	0.3
nepheline	3Na₂O K₂O 4Al₂O₃ 9 SiO₂	5.37
albite	NaAl₃Si₃O₁₁	4.55
microcline	K Al₃Si₃O₁₁	5
illite	2K₂O 3MgO Al₂O₃ 24 SiO₂ 12H₂O	3.69
sanidine	(Na, K)(Si₃Al)O₈	2.89
glauconit-1	K(Fe, Al)₂(Si, Al)₄O₁₀(OH)₂	3.32
sodium aluminum silicate	Na₂O SiO₂ Al₂O₃	6.83
sodium iron oxid	Na₄FeO₃	0.93

Table 2.   The mineralogical composition of the used floor tile powder mixtures
2. táblázat   A hagyományos padlólap porkeverék ásványi összetétele
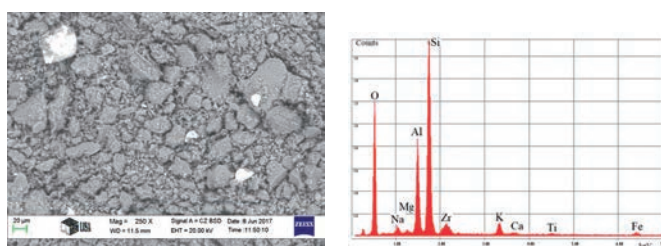
Fig. 1.   Micrograph and chemical composition of the conventional pulverized powder of traditional floor tiles
1. ábra   A hagyományos padlólap atomizer por mikroszerkezete és kémiai összetétel

On the basis of the earlier experiments with alumina [34-37] and zirconia [38-40] of the authors in this research to the conventional floor tiles powder Martoxid KMS-94 alumina (Figure 2) and TZP zircon-dioxide (Figure 3) powders were added in different ratios.
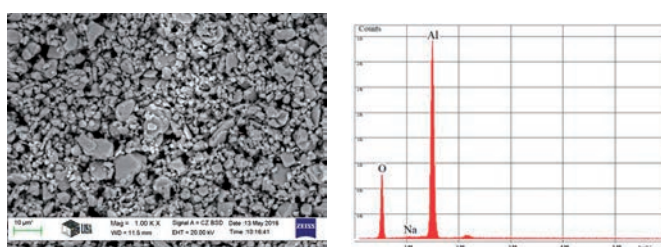
Fig. 2.   Micrograph and chemical composition of the Martoxid KMS-94 alumina
2. ábra   Martoxid KMS-94 alumínium-oxid mikroszerkezete és kémiai összetétel
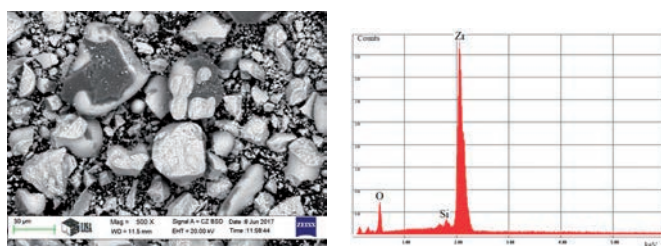
Fig. 3.   Micrograph and chemical composition of the TZP zircon-dioxide
3. ábra   TZP cirkon-dioxid mikroszerkezete és kémiai összetétel

To increase the mechanical properties to the conventional pulverized floor tiles powders Al₂O₃ (A) and commercial ZrO₂ (Z) powders were added in portion of 5m%, 10m%, 15m% and 20m% as they are shown in Table 3.

Mixture sign	Pulverized powder	Martoxid KMS-94 alumina	TZP zircon-dioxide
A5	95	5	-
A10	90	10	-
A15	85	15	-
A20	80	20	-
Z5	95	-	5
Z10	90	-	10
Z15	85	-	15
Z20	80	-	20
ZA5	95	2.5	2.5
ZA10	90	5	5
ZA15	85	7.5	7.5
ZA20	80	10	10

Table 3.   The composition of prepared new mixtures by m%
3. táblázat   A készített keverékek összetétele tömegszázalékban [m%]

From each mixture of the powders were taken out by 200g weights and milled and mixed in a Retch PM 400 planetary ball mill at 200rpm trough 5, 10 and 15 minutes. The so prepared powder mixtures were divided by 10g and compacted through one-sided pressing to discs in a cylindrical die cavity with 20mm diameter and filling depth of 50mm on uniaxial mechanical press at compressing pressures of 158MPa, 196MPa, 234MPa, 274MPa and 312MPa. After compacting the geometrical parameters of the discs were measured and determined the "green" density of the specimens. Further these discs were sintered in an electrical laboratory kiln heating up to 1250°C. When the kiln achieved this temperature the current was switched off and the kiln cooled down freely. The influence of the material composition on the color of the sintered specimens is very well seen in the Figure 4.

Fig. 4. The sintered at 1250°C ceramic disc specimens with different volumes of Al_2O_3 and ZrO_2 powders in the raw material mixtures
4. ábra A különböző mennyiségű Al_2O_3 és ZrO_2 port tartalmazó keverékekből préselt, majd szinterelt próbatestek

3. Result and discussions

During the experiments the green density of the pressed specimens were determined depending on the quantity (portion) of the zirconia and on milling times as function of the compaction pressure. It is obvious from Table 1 that density of zirconia is 5.8 g/cm³ which is much higher than the density of conventional floor tiles after sintering. So with increasing the portion of TZP powders in the mixtures will increase the green density of the pressed specimens. At the same time the densities of the pressed specimens are increased also with increments the values of compression pressures (Figure 5).
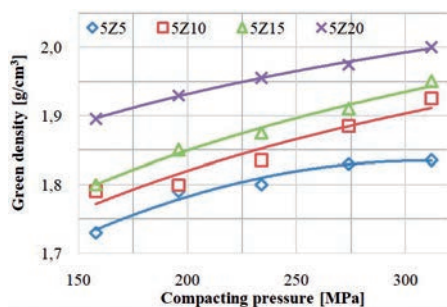
Fig. 5. Influence of volume of ZrO_2 powders and compacting pressure on the density of the pressed "green" specimens
5. ábra A ZrO_2 por mennyiségének és a présnyomás hatása a préselt nyers próbatest sűrűségére

The influence of milling times also was studied at different compacting pressures (Figure 6). For these 2 different mixtures

were prepared with 5m% of zirconia (a) and 5m% of alumina (b) and milled and mixed in a Retch PM 400 planetary ball mill at 200rpm trough 5, 10 and 15 minutes. In both cases there is no remarkable different between the pressed green densities after 5 min and 10 min milling but after 15 minutes of milling the densities of the pressed green specimens have decreased considerable. This phenomenon can be explained with intensive mechanochemical processes taking place during fine comminution of the ceramic powders. Thanking to this mechanochemical processes the powder mixtures have very fine grain and pore structures and the submicron particles are electro statically repel each others in the compacting die cavity during and after pressing.

(a)

(b)
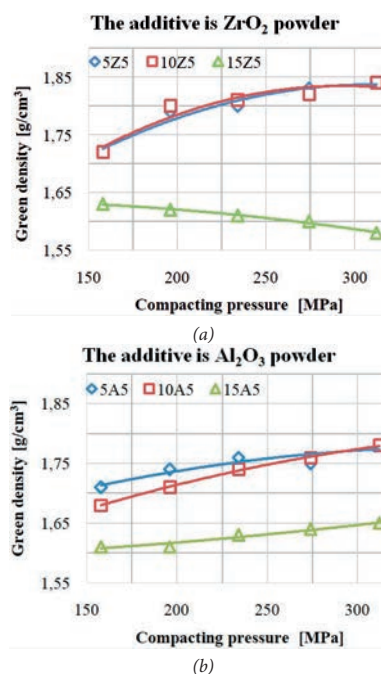
Fig. 6. Influence of the milling time on density of the pressed specimens depending on compacting pressure
6. ábra Az őrlési idő hatása a préselt nyers próbatest sűrűségére az alkalmazott présnyomás függvényében

While the green densities of the pressed specimens are followed the densities of the used high-tech ceramics powders after sintering the specimens with TZP zirconia additives had the smallest densities, meanwhile the $ZrO_2+Al_2O_3$ mixed additives have generated the highest sintered densities (Figure 7).
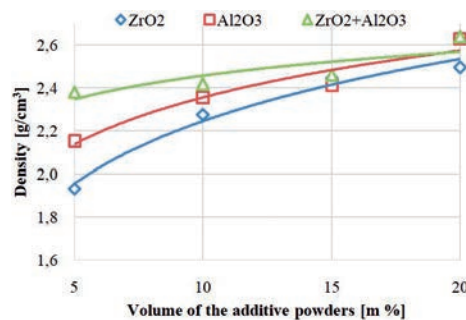
Fig. 7. Influence of volume of Al_2O_3 and ZrO_2 additive powders on density of the sintered specimens
7. ábra Az Al_2O_3 és ZrO_2 por adalékanyag mennyiségének a hatása a szinterelt próbatestek sűrűségére

After the sintering the cylindrical disc specimens were tested on shear strength and pressure strength depending on the containments of zirconia (ZrO$_2$) and alumina (Al$_2$O$_3$) powders in the raw material mixtures. The typical destruction and fracture surfaces of the cracked specimens are shown in Figure 8 and the average values of the shear strengths and pressure strengths are shown in Figure 9.

(a)

(b)
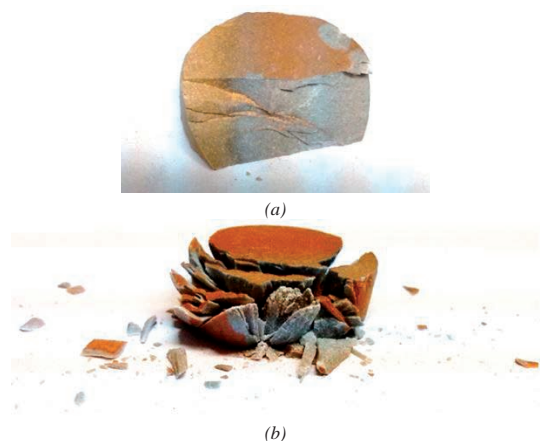
Fig. 8.   *Typical fracture surfaces of specimens after shear test (a) and pressure test (b)*
8. ábra   *A próbatestek tipikus törés felületei a nyíró- (a) és a nyomószilárdság vizsgálatok (b) után*

It is obvious from the Figure 9 that the volumes of Al$_2$O$_3$ and ZrO$_2$ raw materials very strong influence both on the shear strengths (a) and pressure strengths (b) of the floor tile specimens sintered at 1250°C. The highest values of shear strengths were achieved when 5m% zirconia powder was mixed into raw materials and the smallest when 15m% of (Al$_2$O$_3$+ZrO$_2$) mixed powders were added. The pressure strengths are also minimum when 15m% of Al$_2$O$_3$ itself and 15m% of (Al$_2$O$_3$+ZrO$_2$) additives are mixed into the conventional floor tile pulverized powders.

(a)

(b)

Fig. 9.   *The shear strengths (a) and pressure strengths (b) of the sintered specimens made from new raw material compositions*
9. ábra   *A szinterelt próbatestek nyírószilárdsága (a) és nyomószilárdsága (b)*

In cases when only alumina powder additives are used the shear strengths of the sintered specimens are higher in each case than their pressure strengths a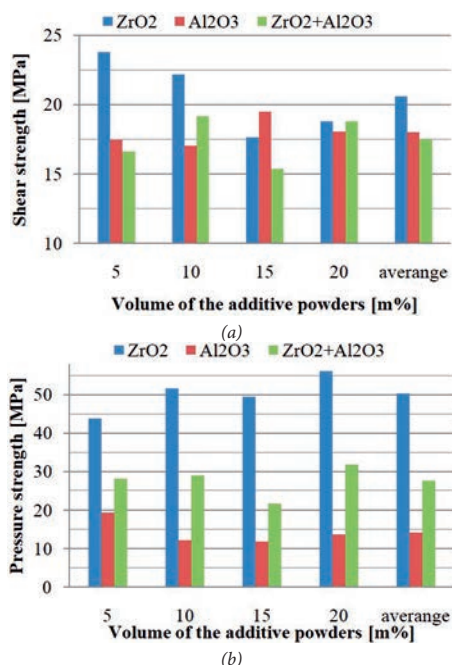t 10m%, 15m% and 20m%. This phenomenon can be explained that the used 1250°C sintering temperature is not high enough when the volume of Al$_2$O$_3$ is higher than 5 m%. At the same time the largest pressure strengths of the floor tile specimens made from the new powder mixtures were achieved at volume of 20m% ZrO$_2$ but at 5m% ZrO$_2$ also very good pressure strengths were achieved with average values about 45MPa.

4. Conclusion

It is obvious from the realizes experiments that the traditional raw material composition can be used to produce ceramic floor tiles with increased mechanical shear and pressure strengths just adding to its 5m% commercial ZrO$_2$ powders and sintering it at 1250°C.

Acknowledgements

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Növelt nyíró- és nyomószilárdságú kerámia padlólapok fejlesztése

Jelen kutatás során tanulmányozták és leírták az alumínium-oxid és a cirkon-dioxid hatását a hagyományos kerámia padlólapok fizikai és mechanikai tulajdonságaira. Különböző nyersanyag összetételek vizsgálata után a szerzők megállapították, hogy a kereskedelmi forgalomban levő ZrO_2 por 5 m%-ban történő hozzáadásával jelentősen növelhető a padlólapok nyíró- és nyomószilárdsága. Az ilyen új, megnövelt mechanikai szilárdsággal rendelkező padlólapok alkalmasak lehetnek a tej-, hús-, élelmiszer- és más iparágakban történő felhasználásra.

Kulcsszavak: alumínium-oxid, kerámiák, préselés, sűrűség, padlólapok, keverékek, porok, cirkon-dioxid

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Deformation and fracture of alumina ceramics with hierarchical porosity

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Abstract

The compression behavior of Al2O3 ceramics with a hierarchical pore structure was studied. The hierarchical pore structure included the pores of three types: coarse porosity with a size of 80 to 100 μm, fine porosity with a size of 14 to 15 μm, and intermediate interblock porosity comprised of elongated (110–120 μm) porous microchannels formed as a result of zonal isolation during sintering.

It is shown that the obtained hierarchical porous structure causes the formation of a hierarchical deformation structure in the volume of ceramics and leads to a decrease in the extent of destruction processes from the macroscopic scale in the case of unimodal ceramics to the microscale destruction comparable with the sizes of the blocks formed during sintering. At fixed values of the pore space, the studied ceramics with hierarchical pore structure shows a noticeably higher compressive strength as compared to the ceramics with a unimodal porosity.

Keywords: deformation, fracture, pore ceramic, alumina.

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1. Introduction

Deformation behavior of porous brittle media, in particular, ceramics, geological materials, etc., is currently studied in detail primarily for ceramic with unimodal pore-size distribution (unimodal porosity), made by the method of partial sintering [1–7]. At the same time, it has been shown that threshold values of the pore-space volume exist for such materials at which both the deformation and subsequent fracture modes change substantially. The macroscopic strain-induced behavior of high-porosity ceramics is depicted by characteristic stress-strain curves that exhibit a fairly long portion corresponding to inelastic strain due to microcracking. The latter contribute to accumulation and movement of local volumes of the material into the pore space in addition to a portion describing linear elastic strain seen at low stresses. Such deformation behavior is called pseudo-plastic because of the shape of the stress-strain curve similar to plastic metallic and elastic polymeric materials [5, 6, 8]. Moreover, it has been shown that the character of deformation depends on the mean pore size as well [5, 6, 9].

It was shown in [5] that the mechanism of micromechanical instability of rod or cellular structures formed during sintering in high-porosity ceramics can be manifested. Meanwhile, the study of the evolution of defects in the volume of such brittle materials is of considerable interest in terms of generation of hierarchies of the deformation structure and subsequent destruction. The synthesis of ceramics having a hierarchical porous structure with spatial and interpenetrating structures of different configurations (cells, channels, shells, etc. [1, 2, 10]) is considered to be a very most promising means for creation of porous ceramic materials, as similar elements in the structure can give rise to unusual deformation modes of hierarchically

organized structures as compared with conventional brittle materials [1, 2, 11]. Nevertheless, there is a lack of such studies because of difficulties arising upon the synthesis of such systems. Typically, a system of pores with sizes commensurate with the grain size, or with larger pore sizes when pore-forming agents are added, develops upon sintering ceramics. These methods include the methods of chemical pore formation, the methods of burnable additives, the foaming methods, etc. [1, 2]. On the other hand, the effect of "zonal segregation" as a consequence of the active shrinkage of samples upon sintering is known [11], which consists in the partition of a sintered sample into regions (blocks) that are significantly larger than the mean particle size of the sintered material. Typically, the following two types of pore structures can be formed: one is determined by the interparticle porosity and the other by the porosity between blocks. Usually, these structures are formed randomly; however, the zonal segregation effect during sintering can be achieved by the addition of relatively large particles of pore-forming agents, which will be removed in the initial stage of sintering.

The study of the difference in the damage evolution in the volume of porous ceramics with unimodal and hierarchical porosity on different structural scales and their subsequent fracture depending on the strain rate, degree of constrained strain, etc., are of considerable academic interest in the hierarchical deformation and fracture structures formed in ceramics and rocks.

The present paper undertakes to investigate the deformation and fracture of porous alumina ceramics with unimodal and hierarchical porosity.

2. Experimental procedure

Two types of samples were obtained: unimodal porosity, obtained due to the partial sintering of ceramic powders, and with a hierarchically organized pore structure obtained by introducing a pore-forming agent into the mixture.

Samples with unimodal distribution of pores and different values of porosity 17 and 70% were produced from Al_2O_3 powder by thermal decomposition of water solutions of metal nitrates in high-frequency discharge plasma [3]. Electron microscopic examination under scanning and transmission electron microscopes revealed that the powders were largely composed of hollow spherical particles in sizes of about several micrometers. The size of the crystallites constituting the powders was ~20–50 nm.

A 3% polyvinyl alcohol solution was added to the initial powders. The mixture was pressed in steel die molds at a pressure of 100 MPa, using a hydraulic press. The resultant specimens were cylindrical (10 mm in diameter and 15 mm in height) in shape. Sintering was performed in air in the temperature range from 1000 to 1600 °C for an isothermal annealing time of 1 h. The heating and cooling rates were 240 °C/h.

Samples with a hierarchically organized pore structure were obtained using the method of slip casting of Al_2O_3 powder, to which spherical particles of high-density ultra-high molecular weight polyethylene (UHMWPE) with a mean particle size of 100 μm in amounts of 15, 20, and 25 wt. % were injected with the subsequent removal of the polymer bond and sintering in air at temperatures of 1400, 1500, and 1600 °C by isothermal exposure.

The density of the sintered specimens was measured by a geometric method. The residual porosity was calculated from theoretical-to-measured density ratio. The structure of the samples after sintering was studied by the methods of optical and scanning electron microscopy. The size of pores and the distance between them in the ceramics after sintering and after compression tests were measured by means of a scanning electron microscope. Several micro images and at least 400 pores were measured for each sample. The two- dimensional pore-size distribution obtained in such a way was transformed into a three-dimensional distribution using Saltykov's main stereo metric equation [12].

Cylindrical samples were subjected to mechanical-compression tests on a Devotrans universal testing machine at a loading rate of $2 \times 10^4 \, s^{-1}$. The stiffness of the loading system was determined before testing. A rectilinear portion corresponding to the elastic strain of the specimens was identified in the stress (σ)- strain (ε) curves. The effective elastic moduli were found from the initial rectilinear portions of the σ–ε curves plotted upon the compression testing of the specimens.

3. Results and discussion

After sintering, the ceramics with unimodal porosity had a porosity of 17 - 70%. The pore structure of Al_2O_3 ceramics with unimodal porosity sintered at 1400°C and 1600°C is shown in Fig. 1.a,b. With an increase in sintering temperature, along with decrease in pore space volume, an increase in the average pore size was observed due to the consolidation of fine pores into larger ones.

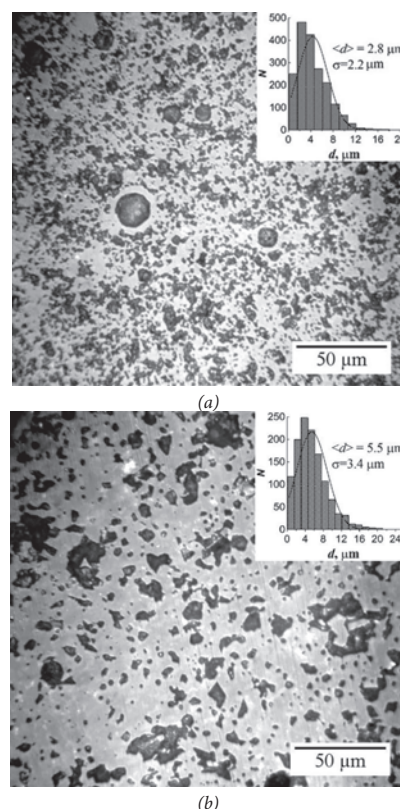*(a)*

(b)

Fig. 1. The pore structure of Al_2O_3 ceramics with unimodal porosity sintered at (a) 1400°C and (b) 1600°C.

1. ábra Egyszerű porozitású Al2O3 kerámiák pórusszerkezete (a) 1400°C-on és (b) 1600°C-on történő szinterelés után.

After sintering, the ceramics with hierarchical porosity had a porosity of 35 - 60%. The inter grain fine porosity appeared in the sample volume as a result of the diffusion and recrystallization processes during sintering and is determined by the sintering temperature. The UHMWPE particles played the role of pore-forming agents promoting the production of coarse porosity in the sintered ceramic samples. The ratio between coarse and fine porosity was changed by selection of the process parameters (temperature and the number of pore- forming agent particles), which made it possible to achieve the "zonal-segregation" effect upon the shrinkage of the samples. The mean size of large pores was about 80 - 100 μm (Fig. 2,a), and the size of small pores was 10 - 15 μm on average (Fig. 2b). The inter- group porosity resulting from the "zonal segregation" effect in the volume of sintered ceramics was present in the form of elongated pore channels connecting large pores with each other and forming a block structure thereby (Fig. 2, a). The mean size of blocks of the sintered material was determined by the distance between the large pores and was in the range from 110 to 120 μm.
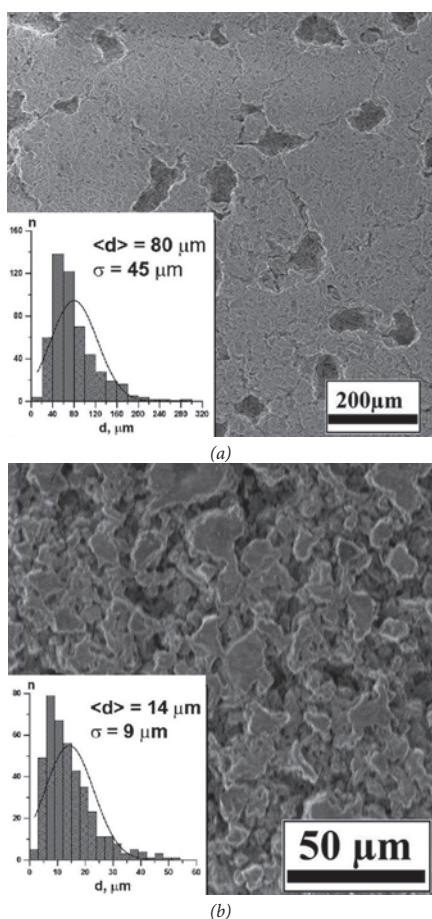

(a)

(b)

Fig. 2.　Typical images of the Al_2O_3 ceramics with hierarchical porosity: (a) "coarse" and "interblock" porosity, and (b) "fine" porosity. The inserts show the typical size distributions of (a) "large" and (b) "small" pores.

2. ábra　Hierarchikus porozitással rendelkező Al_2O_3 kerámia (a) durva és interblock porozitással illetve finom porozitással (b). A jellemző pórus-méreteloszlás (a) durva és (b) finom pórusok esetén.

The appearance of the stress-strain curves and the fracture behavior of the ceramic samples with the unimodal and hierarchical porosity depended on the porosity level. For the Al_2O_3 ceramics with unimodal porosity with porosity varying between 10 and 30%, the stress-strain curves exhibited a linear relationship up to multiple fracture of the material (Fig. 3, a, curve 1). An increase in the porosity more than 30% leads to a deviation from linearity in the pre-fracture stage (Fig. 3, a, curves 2 and 3).
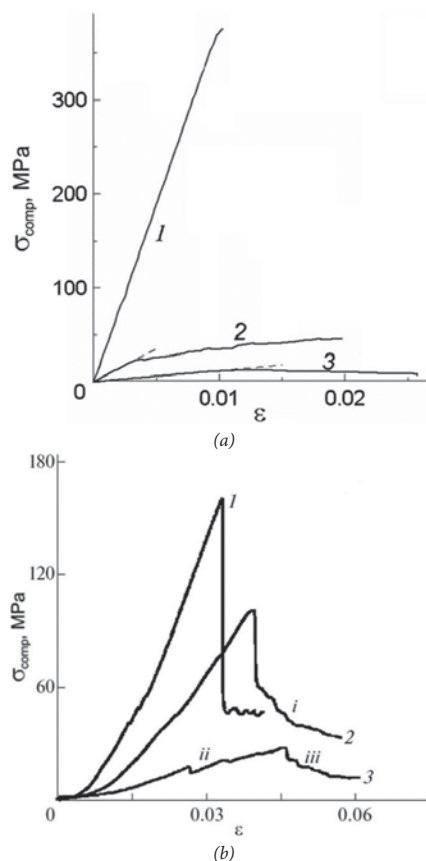

(a)

(b)

Fig. 3.　Stress-strain curves obtained after the compression tests of Al_2O_3 ceramics with: (a) unimodal porosity 20 (1), 50 (2), and 65% (3) and (b) hierarchical porosity (1) 35, (2) 48, and (3) 58%.

3. ábra　Az Al_2O_3 kerámiák préselése során kapott erő-deformáció görbék (a) egyszerű porozitás 20 (1), 50 (2) és 65% (3) és (b) hierarchikus porozitás 35 (1), 48 (2) és 58% (3) esetén.

The ceramic samples with a hierarchical porosity of up to 40% show stress-strain curves characterized by the elastic behavior until the breakdown (Fig. 3, b, curve 1). The samples with porosity of 40 - 50% are characterized by an increase in the microdamage accumulation region after a solitary macroscopic fracture (Fig. 3, b, curve 2, section i). In the samples with a porosity of more than 50%, microdamage appears already at the active stage of loading (Fig. 3, b, curve 3, section ii), and the stress smoothly drops at the final section of the stress-strain curves after reaching the ultimate tensile strength (maximum loading) (Fig. 3, a, curve 3, section iii).

The dependence of effective elastic modulus (E_{eff}) and compressive strength values (σ_{comp}) and on the pore-space volume for alumina ceramics with unimodal and hierarchical porosity illustrated in Fig. 4. The values of the compressive strength and effective elastic modulus of the ceramics decrease exponentially upon an increase in the pore-space volume of the samples. At fixed values of the pore-space volume, the studied ceramics with hierarchical pore structure shows a noticeably higher compressive strength as compared to the ceramics with a unimodal porosity.

After compression tests, the structure of the ceramic with unimodal porosity and low porosity values contained macrocracks. The structure of the high-porosity specimens exhibits multiple microcracking.
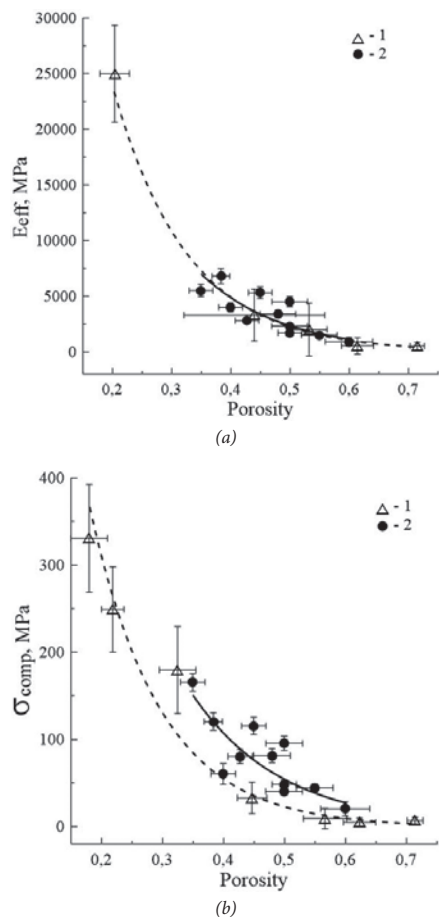

Fig. 4. The dependence of effective elastic modulus (E_{eff}) and compressive strength values (σ_{comp}) and on the pore-space volume for alumina ceramics with (1) unimodal and (2) hierarchical porosity.

4. ábra Az effektív rugalmassági modulus változása a nyomószilárdság és az Al_2O_3 kerámia pórustérfogata szerint (1) egyszerű és (2) hierarchikus porozitásnál.

The study of the microstructure of the Al_2O_3 ceramics with hierarchical porosity after compression tests showed that blocks formed during sintering are separated from each other by mesoscopic fractures and discontinuities (Fig. 5, a) that are formed at the boundaries between adjacent blocks owing to the deformation localization in the process of loading. The block structure formed during sintering collapses along the block boundaries because of the destruction of brittle bridges connecting the blocks with each other, forming, as a result of the fracture, fragments comparable in size with a mean size of grains (10 - 20 μm, Fig. 5, b), which leads to broadening of the fracture zones between blocks up to 40 to 50 μm (Fig. 5, b). Such a destruction mechanism reduces the extent of destruction, enhancing the capability of totally brittle ceramics to efficiently resist an applied load, which is evidenced by the increased compressive strength values.

Thus, analysis of the stress-strain curves for the porous alumina ceramics with unimodal and hierarchical porosity has revealed a transition from characteristically brittle fracture of low-porosity specimens attendant with formation of the main

crack to the development of multiple fracture sites configured as microcracks in high-porosity specimens. The macroscopic deformation behavior of ceramics exposed to loading is referred to as pseudo-plastic and is similar to that observed in plastic materials. The obtained hierarchical structure of porous ceramics exerts a significant influence on the character of damage produced in the material under compression, bringing about a transition from a brittle state to quasi-plastic failure due to the formation of numerous focal areas of destruction, and the formation of hierarchical deformation structures in the ceramics volume leads to the effect of reducing the destruction processes from the macroscopic scale, in the case of unimodal ceramics, to a mesoscale fracture comparable with the size of blocks formed during sintering. A separate study should be devoted to a more detailed analysis of the mechanisms of formation of such deformation structures.
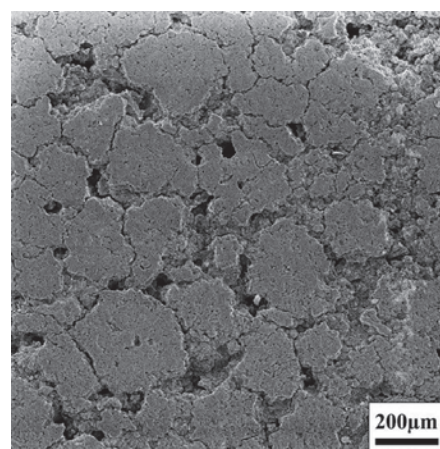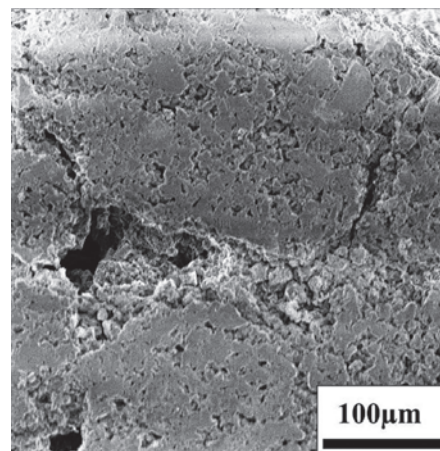
Fig. 5. Structure of porous ceramics with a hierarchical porosity of 60% after the compression tests.

5. ábra Porózus kerámiák mikroszerkezete 60% hierarchikus porozitással a tömörítés után.

4. Conclusion

The analysis of stress-strain curves of porous alumina ceramics are shown that during deformation in compression tests; there was a transition from a typically brittle state for dense ceramics to a pseudo-plastic state with a high porosity level.

It is shown that the obtained hierarchical porous structure causes the formation of a hierarchical deformation structure in the volume of ceramics and leads to a decrease in the extent of destruction processes from the macroscopic scale in the case of unimodal ceramics to the microscale destruction comparable with the sizes of the blocks formed during sintering.

At fixed values of the pore space, the studied ceramics with hierarchical pore structure shows a noticeably higher compressive strength as compared to the ceramics with a unimodal porosity.

Acknowledgement

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Hierarchikus porozitású alumínium-oxid kerámiák deformációja és törése
Jelen munkában a szerzők a porózus alumínium-oxid kerámiák tömörödési tulajdonságait és viselkedését tanulmányozták. A hierarchikus pórusszerkezetet háromféle pórus típus alkotta: durva porozitás 80-110 μm, finom porozitás 14-15 μm és köztes „interblock" porozitás, amely hosszúkás (110-120 μm) mikrocsatornákból áll és a szinterelés során a zónaszűrés eredményeként alakul ki. Mechanikai terhelések során az ilyen hierarchikus porózus szerkezetű kerámiában hierarchikus deformációs struktúra jön létre. A vizsgált hierarchikus pórusszerkezettel rendelkező kerámiák jelentősen nagyobb nyomószilárdságot mutattak, mint az egyszerű vagy hagyományos porozitású kerámiák.
Kulcsszavak: deformáció, törés, póruskerámia, alumínium-oxid.

Effect of mechanical treatment on properties of Si-Al-O zeolites

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Abstract

In the work the results influence of mechanical treatment on morphology, specific surface area, and phase composition of natural zeolite of Tokaj Mountain deposits, synthetic zeolites SAPO-34, SCT-323 are presented. Specific surface area of the synthetic zeolites decreases during the mechanical activation in a planetary ball mill. The changes of the specific surface area of the natural zeolites corresponds to the curve of the developed specific surface as function of the milling time (rittinger-zone, aggregation-zone and agglomeration-zone). During the mechanical activation, it was observed an increase of system amorphisation by 8-10% for synthetic zeolites, by 40-45% for natural zeolite. Results obtained represent scientific and practical interest, which can be used for further studies zeolites.

Keywords: crystal structure, mechanical activation, morphology, X-ray diffraction, zeolite

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1. Introduction

Zeolites are crystalline aluminosilicate materials having microporous (zeolite pore) in their structure. They are made of various compounds of TO4 (T = Si or Al) tetrahedral which result in the various zeolite pore sizes and structures [1]. The interest of researchers towards zeolites is connected with their unique properties: an extremely high adsorption capacity, catalyzing action, thermal stability and resistance in different chemical environments [2].

The results of the study of structural, physicochemical properties of zeolites allow developing the theoretical bases for the directed change of useful properties of natural minerals that are required for sorption materials [3].

The specific surface area is a dominant parameter for zeolites [4]. Obtain the necessary magnitude of specific surfaces of materials depends not only on their chemical and mineralogical composition, but also on physical, mechanical and rheological parameters of the used materials [5,6]. It is known that mechanical processing in activator mills can change the structure, specific surface area, crystal composition of zeolite containing materials and occasionally improve their processing properties [7]. In spite of the numerous publications, the physicochemical properties of natural zeolites are still not sufficiently studied.

The objective of this work was to study changes induced by mechanical activation on morphology, specific surface area, and phase composition of the zeolites.

2. Materials and Experimental Procedure

We used natural zeolite from the Tokaj Mountain deposits, and two commercial zeoliteSAPO-34 and SCT-323 which are chabazite's structural analog from the silicoaluminophosphate group samples of chabazite, differing in elemental composition.

Mechanical activation of the zeolites was performed in a planetary ball mill for 600 minutes. The acceleration in planetary mill was 26.8 g. Ceramic grinding balls were used in planetary mill [8].

The crystal structure and phase composition of the zeolite before and after the mechanical activation were determined by X-ray diffraction analysis (XRD) using diffractometer Rigaku MiniFlex II with Cu-Kα (λ= 1.5418 Å) radiation [9]. The phases were determined by search method using powder diffraction data base file PDF2.

The morphology of the powder was analyzed using scanning electron microscopy Zeiss Supra 55VP.

The particle size was determined by using laser diffraction particle size analyzer Horiba LA-950 in the range 0.01 - 3000 µm.

Brunauer, Emmett, Teller (BET) surface area was determined using a micrometrics Tristar 3000 gas adsorption analyzer [10].

3. Results and Discussion

3.1. Initial powders

Zeolite	OK	AlK	SiK	PK	TiK	MgK	CaK	FeK
Natural	48.56	3.76	46.28	-	-	0.25	0.55	0.60
SAPO-34	35.60	48.03	03.06	13.32	-	-	-	-
SCT-323	48.88	23.77	03.84	22.43	01.08	-	-	-

Table 1. Chemical composition of the zeolites (wt %)
1. táblázat A vizsgált zeolitok kémiai összetétele (m%)

The results of elemental analysis (Table 1) showed that the natural zeolite powder in the initial state consisted of Al, O, Si, Ca, Mg, Fe. Synthetic zeolites contain a high Al content and low Si content. Zeolite SCT-323 containing titanium and relatively high content phosphorus is different from SAPO-34.

On Figure 1, figure 2 it is shown SEM-pictures and X-ray patterns of SAPO-34 and natural zeolite.

The SEM data showed that particles of natural zeolite powders has irregular shapes with an average particle size of 27 µm. Compared with natural zeolite particles of synthetic zeolite powders are closely matched and have shapes close to cubic with an average particle size 1.7 µm for SAPO-34, 1.5 µm for SCT-323.

Calculations of the X-ray pattern of natural zeolites showed that the structure of zeolite consists of seven different phases: smectite 15A 20%, quartz 8%, low-cristobalite 15%, clinoptilolite 14%, illite 2M1 15%, orthoclase 9%, calcite 6%, amorphous phase 13%.

Structure of synthetic zeolites consisting Aluminum Silicate Phosphate (PDF-2 00-047-0630). Amorphous phase in zeolites, in an amount 83% for SAPO-34, 85% for SCT-323.
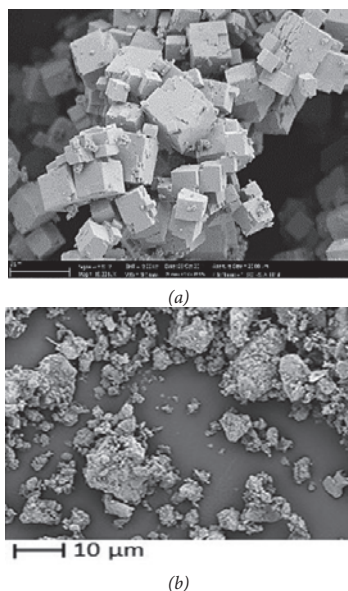

(a)

(b)

Fig. 1. SEM-picture, for (a) SAPO-34, (b) for natural zeolites
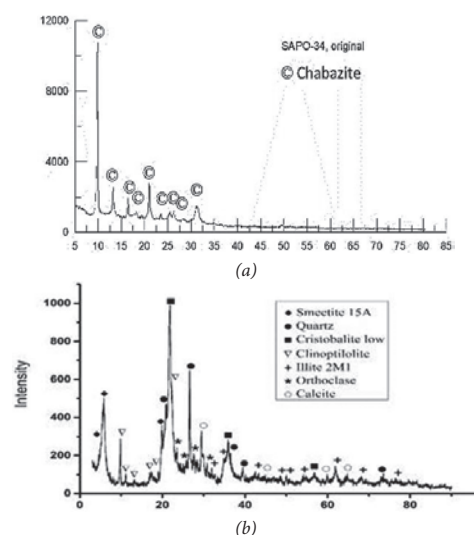1. ábra A (a) SAPO-34 és a (b) természetes zeolitok SEM felvétele

(a)

(b)

Fig. 2. X-ray pattern, for (a) SAPO-34, (b) for natural zeolites
2. ábra A (a) SAPO-34 és a (b) természetes zeolitok röntgendiffraktogram felvétele

3.2. Mechanical activation

Synthetic zeolites have initial high specific surface area (561 m^2/g for SAPO-34, 573 m^2/g for SCT-323) compared with natural zeolite (19 m^2/g).

Experimental results regarding the change in BET specific surface area of zeolite samples with mechanical activation time in a planetary ball mill are shown in figure 3.
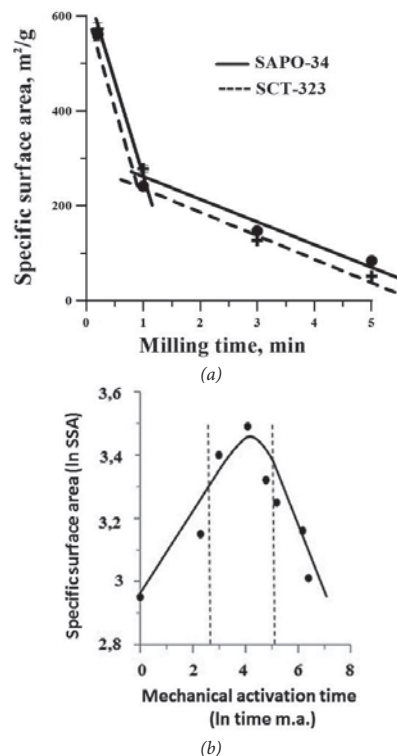

(a)

(b)

Fig. 3. The dependence of specific surface area values of zeolites from milling times (a) for synthetic zeolites, (b) for natural zeolite
3. ábra A zeolitok fajlagos felületének függése az őrlési időtől (a) szintetikus és (b) természetes zeolit esetén

During the first 60 minutes, the specific surface area of natural zeolite powder increases, reaching 33 m^2/g. After 120 minutes, the specific surface slightly decreases and after 600 minutes of activation, there is a significant reduction to 20 m^2/g.

For synthetic zeolites are observed fast and sharp decrease specific surface area of the zeolites decreases during the milling.

During the 1 minute, the specific surface area of synthetic zeolite powder rapidly decreases, reaching 241 m²/g for SAPO-34 and 278 m²/g.

After this period decreases with prolonging the milling time, so it can be assumed that the minimum values of the specific surface area are achieved after 5 minutes of milling. The values of specific surface area of zeolite samples activated for 5 min were 83 m²/g for SAPO-34 and 51 m²/g for SCT-323.
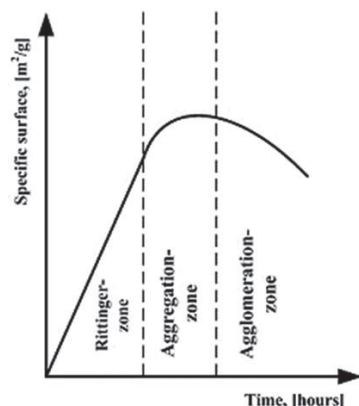

Fig. 4.   Theoretical curve of specific surface as function of grinding time
4. ábra   A fajlagos felület és az őrlési idő kapcsolata

The theoretical curve of developed specific surface as function of grinding time is shown in Figure 4 [10]. Three well-shaped curves can be observed representing this theoretical curve. They are: Rittinger-zone: the increase of the specific surface is proportional to the grinding time; Aggregation-zone: the intensity with which the increase of the specific surface decreases with the grinding time; Agglomeration-zone: the specific surface decreases with the comminution time [11]. The changes of the specific surface area of the natural zeolites corresponding to the theoretical curve.

Because of the small particle size of synthetic zeolite SAPO-34 and SCT-323 with the increase in milling time takes place to agglomeration of particles only. Specific surface area of synthetic zeolites correspond to the agglomeration-zone on theoretical curve.

With the increase in the mechanical activation time there is also a change in the particles size of zeolite powders, as shown in figure 5.

The initial of natural zeolite-average was 27 μm. After activation of 20 minutes, particle size was 5.5 μm and after 600 minutes of milling time, the particle size became 28 μm. Most particles have lost their initial shape and converted into a spherical shape during the mechanical activation [12,13].

With the increase in milling time, the particles size of synthetic zeolites decreased. Moreover most particles have lost their initial cubic shape and converted into spherical and also irregular shapes during the milling process on different milling times. The zeolite-average was 1.7 μm for SAPO-34, 1.5 μm for SCT-323. Then, after milling treatment at 1 minute the zeolite-average was 1.5 μm for SAPO-34 and 1.2 μm for SCT-323, after milling treatment at 5 minute the zeolite-average was 0.9 μm for SAPO-34 and 0.7 μm for SCT-323.
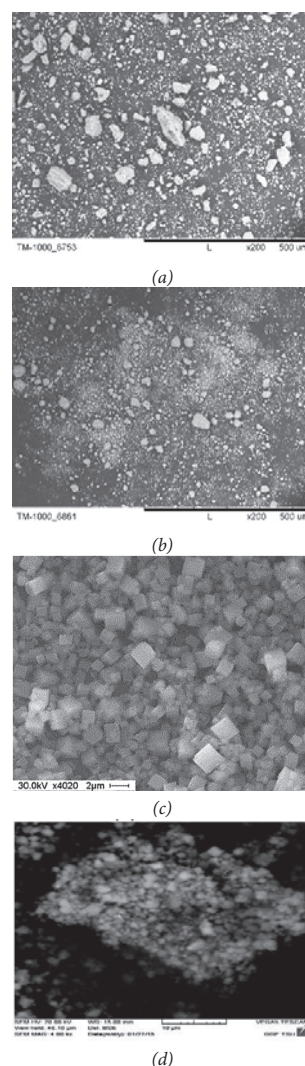

(a)

(b)

(c)

(d)

Fig. 5.   SEM-pictures, initial of natural zeolite (a), after 600 minutes (b), initial of SAPO-34 (c), after 5 minutes (d) of milling time in a planetary ball mill
5. ábra   A bolygó golyósmalomban történő őrléskor a természetes zeolit (a) kezdeti és (b) 600 perces őrlés utáni illetve a SAPO-34 (c) kezdeti és (d) 5 perces őrlés követően kapott minták SEM felvételei

Selected XRD patterns of mechanically activated of synthetic zeolite powders and change mineralogical composition of natural zeolite during mechanical activation are shown in Figure 6.

All of the diffraction peaks of synthetic zeolites decreased and/or disappeared with the increase of mechanical activation time.

In addition, amorphisation occurred and an increase in amorphisation was observed, from 83 to 90% for SAPO-34 and from 85% to 93% for SCT-323. The tendency of the peaks that belong to the zeolite phase Aluminum Silicate Phosphate to disappear and this tendency increased with the milling time.

The quantitative analysis of XRD patterns showed radical changes in mineralogical compositions, as shown in figure 5 (c). The proportions of all mineralogical components of natural zeolite changed in dependence on the activation time. The most intensive changes can be observed in mineral components of smectite 15 A, clinoptilolite, illite 2M1 and calcite. After 60 minutes of milling time the content of smectite 15 A – decreased from 20% to 10%, clinoptilolite from 14% to

9%, meanwhile the amount of orthoclase – grew from 9% to 12% . In mineralogical composition, the considerable changes continued up to 600 minutes of mechanical activation. At 600 minutes of activation time the zeolite content of smectite 15 A, clinoptilolite, illite 2M1, and calcite reached its minimum value of 0.5%, 1%, 3%, 1% respectively, meanwhile the amount of quartz increased up to 17%. Under mechanical activation the amount of quartz, low-cristobalite, orthoclase mineral components were also not stable, but their content have varied not so strong. In addition, during the mechanical activation it occurred amorphisation, which increase from 13% to 52%.
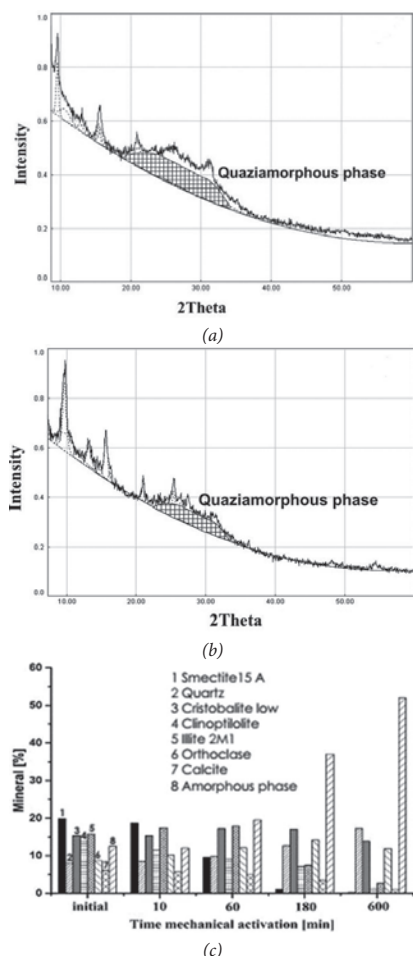

Fig. 6. X-ray diffraction patterns of zeolites during 5 minutes milling time, for (a) SAPO-34, (b) for SCT-323, mineralogical composition of natural zeolite during mechanical activation (c)

6. ábra 5 perces mechanikai aktiváláson átesett minták röntgendiffrakciós görbéi (a) SAPO-34, (b) SCT-323 és (c) a természetes zeolit ásványi összetételének változása az őrlési idő függvényében

4. Conclusion

The mechanical activation of the natural zeolite corresponds to the curve of the developed specific surface as function of the milling time. It has been shown that during the first 60 minutes, the specific surface area increases, reaching a maximum, after which a sharp decrease occurs. Mechanical activation of synthetic zeolite powders corresponds to the agglomeration zone due to the small particle size of SAPO-34 and SCT-323. For synthetic zeolites are observed fast and sharp decrease specific surface area of the zeolites decreases during the milling.

During the mechanical activation it was observed an increase of system amorphisation by 8-10% for synthetic zeolites, by 40-45% for natural zeolite.

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A Si-Al-O zeolitok mechanikai tulajdonságai
A szerzők ismertetik a mechanikai aktiválás hatását a Tokaj környéki természetes zeolitok és a SAPO-34, SCT-323 szintetikus zeolitok morfológiájára, fajlagos felületére és fázisösszetételére. A szintetikus zeolitoknak bolygó golyósmalomban történő mechanikai aktiválása során csökken a fajlagos felülete; míg a természetes zeolitok fajlagos felületének változása függ az őrlési időtől (Rittinger-, aggregációs- és agglomerációs szakasz). A mechanikai aktiválást követően a rendszerben található amorf fázis aránya a szintetikus zeolitok esetén 8-10%, a természetes zeolitoknál pedig eléri a 40-45% nagyságot. A kapott eredmények nagy gyakorlati jelentőséggel bírnak, egyben a zeolitok további vizsgálatainak az alapját képezik.
Kulcsszavak: kristályszerkezet, mechanikai aktiválás, morfológia, röntgendiffrakció, zeolit

Formation of Pore Structure in Zirconia-Alumina Ceramics

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Abstract

In this research work different pore forming methods and sintering temperatures were applied to create micropores in zirconia (ZrO_2), alumina (Al_2O_3) and ZrO_2-MgO composite ceramics in range from 4% up to 68%. The authors have found that the used different pore forming additives and sintering temperatures are influenced very strong not only the pore sizes and their distributions but on final compression strengths also. Using aluminum hydroxide for pore forming at sintering temperature of 1450-1650 °C 62% porosity can be obtained at more than 200MPa compressive strength.

Keywords: alumina, aluminum hydroxide, ceramics, composites, microstructure, pore forming, porosity, sintering, zirconia

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1. Introduction

Porous ceramic materials have found wide application in various fields and it is can be used as filter elements, catalyst carriers and heat-shielding elements. As compare to metals and polymers, ceramics have some advantages: high hardness, chemical inertness, wear resistance and thermal shock resistance, etc.

Operational properties of porous ceramic materials are largely determined by the parameters of the internal structure, such as pore volume, average pore size, shape and their contiguity. For example, a material with closed porosity and low thermal conductivity can be used as a thermal barrier, while open and connected polymodal porosity, combined with chemical inertness, is applicable to the filtration of liquids and gases.

Modern methods of pore structure formation make it possible to obtain porous ceramics with the necessary properties and characteristics by introducing various pore-forming additives into the initial powder compositions and sintering parameters changing. At present time there are several technologies for the production of porous ceramic materials: sintering of disperse systems at low temperatures, introduction of a pore-former or gas bubbles into a curable ceramic slurry. In [1] is described a method for obtaining a highly porous, up to 95%, ceramic, based on the rapid freezing and freeze-drying of a ceramic suspension. This makes it possible to obtain dendritic pore structures that can be good gas-filtering elements. The creation of macroporous structure described in [2] allows obtaining pores morphology similar to inorganic bone matrix. The choice of the method for creating the material pore structure is determined by the necessary morphology, functional properties and the corresponding application of the future product. Nevertheless, many of the technologies like additive technologies [3-5] for obtaining the necessary pore structure can be difficult or expensive, that prevents their wide use [6, 7].

One of the most common technologies for creating pore structure in ceramic materials is introduction of pore-forming particles into the initial powder composition followed by pressing and sintering. The selection of pore-former depends on the pores required average size and shape. The pore-forming material should be thermally removed particles, for example paraffin, rosin, ammonium carbonate and some types of polymers.

Another common method of porosity formation is the decomposition of hydroxides, for example, aluminum, zirconium, magnesium, etc. to their oxides with H_2O evaporation. This method of pore formation avoids the presence of impurities on the internal surfaces of the porous ceramic matrix [8].

Despite the fact that such studies devoted a considerable amount of work, comprehensive studies on the porosity formation laws in ceramics based on oxides using various methods of pore formation is not enough.

The purpose of this work is to study a pore structures formation in ceramics based on alumina and zirconia using organic pore-forming particles, hydroxides and variation in the sintering parameters.

2. Materials and methods

It have been studied ceramic composites ZrO_2-MgO with 0-100 wt. % MgO, ZrO_2-Al_2O_3 with 0-75 wt.% of $Al(OH)_3$ and Al_2O_3 with 0-100 wt.% of $Al(OH)_3$ in the initial powder compositions.

The mean size of particles of ZrO_2 powder stabilized with 3 mol. % MgO were 0.5-6 μm, magnesia were 7 μm. Alumina powder was obtained by annealing $Al(OH)_3$ at 1100 °C, the particle size was 50-100 μm. The particle size of the alumina powder was 50-100 μm.

Powder mixtures were obtained by mechanical mixing of powder components and cold uniaxial pressing at 190 MPa using steel mould, followed by sintering in an air atmosphere with holding time one hour.

Materials with bimodal porosity were obtained by adding and burning out ultra-high molecular weight polyethylene (UHMWPE) particles with an average size of 50 μm, adding to the initial powder mixtures, followed by annealing at 300 °C for removing polyethylene particles and sintering at 1600 °C similar [9]. Two other methods of pore formation were used in ZrO_2-MgO composite as changing of sintering temperature from 1200 °C to 1600 °C and decomposition of $Al(OH)_3$ with evaporation of H_2O sintering at temperatures 1450 - 1650 °C [10, 11].

The microstructure was studied by scanning electron microscope; pore volume was measured by the Archimedes method. The compressive strength was determined by using a universal testing machine with a constant strain rate $7*10^{-4}s^{-1}$.

3. Results and discussion

On figure 1 are shown that ZrO_2-MgO compacts with highest sintering temperature had a minimum porosity – 4%. Decreasing of sintering temperature was accompanied by a nonlinear increasing of pore volume up to 60%. The average pore size of ceramics sintered at 1600 °C were 8 μm, with standard deviation, σ, is 6 μm, these data are illustrated by microphotography on figure 2. Decreasing of sintering temperature leads to increasing of the pore sizes from 14 μm and σ = 11 μm for 1500 °C and 17 μm and σ = 10 μm for 1400 °C.

Figures 3 shows a scanning electron microscopy image of the ZrO_2-Al_2O_3-$Al(OH)_3$ fracture surface, and figure 4 shows a polished surface of Al_2O_3-$Al(OH)_3$ ceramic material after sintering at 1600 °C. During the sintering alumina one can observed a decomposition of hydroxide and formation of irregular shape pores. Estimation of pore size distribution are shown that the average pore size is 2.1 μm in ZrO_2-Al_2O_3 ceramic and 4 μm in Al_2O_3.
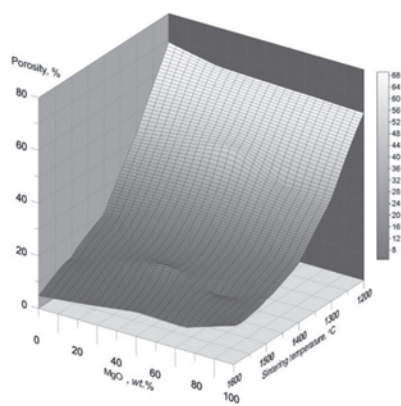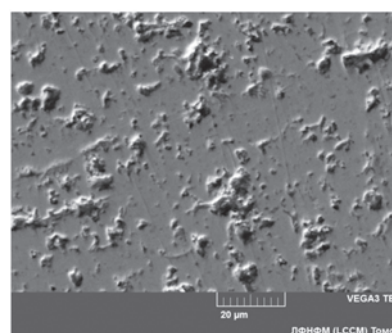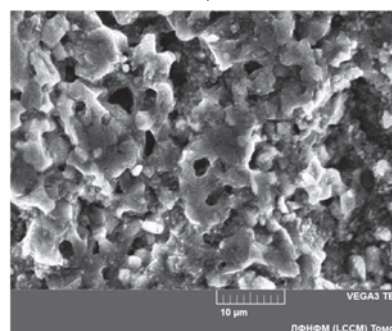

Fig. 1. *Porosity of ZrO₂-MgO vs. composition and sintering temperature*
1. ábra *A porózus ZrO₂-MgO összetétele és szinterelési hőmérséklete*

a)

b)

Fig. 2. *The microstructure of the polished surface (a) and the fracture surface (b) of the ZrO₂-50wt. %MgO ceramic sintered at 1400 °C.*
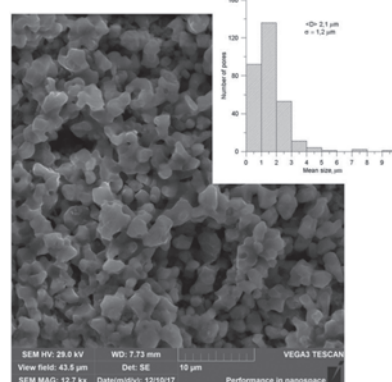2. ábra *Az 1400°C-on szinterelt ZrO₂- 50m% MgO kerámia csiszolat (a) és töretfelületének (b) mikrostruktúrája*

Fig. 3. *a) Microstructure of the ceramic fracture surface, based on ZrO₂ with the 75% addition of aluminum hydroxide. Sintering temperature 1600 °C and pore size distribution*
3. ábra *Az 1600°C-on szinterelt 75% alumínium-hidroxid adalékkal készült ZrO₂ kerámia töretfelületének a szerkezete és a pórusméret eloszlása*
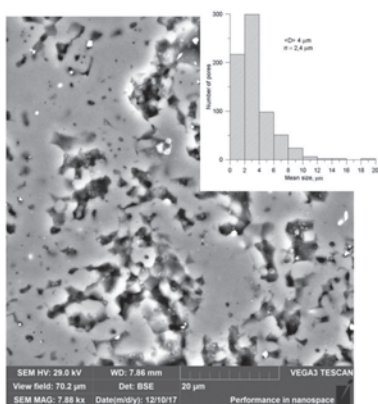
Fig. 4. a) Microstructure of the polished surface of ceramics alumina-75% aluminum hydroxide; Sintering temperature 1600 °C and pore size distribution

4. ábra Az 1600°C-on szinterelt 75% alumínium-hidroxid adalékkal készült Al_2O_3 kerámia csiszolat felületének szerkezete és a pórusméret eloszlása

On figures 5 are shown the dependences of pore volume in ZrO_2-Al_2O_3 and Al_2O_3 ceramics after sintering vs. aluminum hydroxide content and sintering temperature. It can be seen that in ZrO_2-Al_2O_3 ceramics the pore volume increases with increasing of hydroxide concentration and almost does not changes with sintering temperature. Alumina ceramic, obtained with an aluminum hydroxide addition showed an increasing of porosity with increasing of $Al(OH)_3$ concentration, but decreasing with increasing of sintering temperature, figure 6.
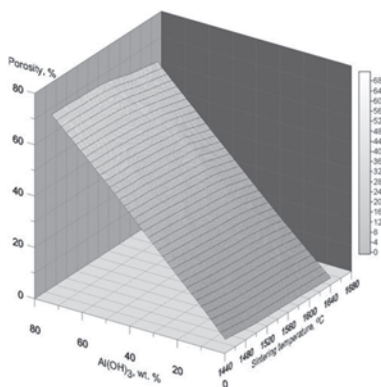

Fig. 5. Dependence of pore volume in ceramics based on ZrO_2 vs. aluminum hydroxide content and sintering temperature

5. ábra A ZrO_2 alapú kerámia pórustérfogatának változása az alumínium-hidroxid tartalom és a szinterelési hőmérséklet szerint
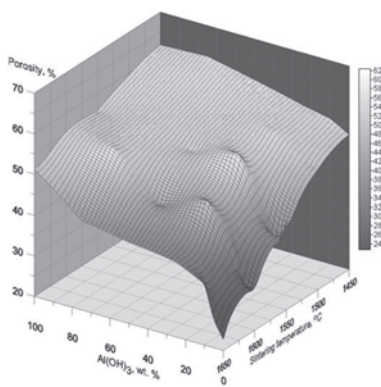

Fig. 6. Dependence of pore volume in ceramics based on Al_2O_3 from the concentration of aluminum hydroxide and the sintering temperature

6. ábra Az Al_2O_3 alapú kerámia pórustérfogatának változása az alumínium-hidroxid tartalom és a szinterelési hőmérséklet szerint

Addition of UHMWPE to the ZrO_2-MgO composite leads to creation a bimodal pore structure and increases the average micropores size up to 30 µm without a dependence on the MgO concentration. As one can see from figure 7 that in sintered ZrO_2-MgO ceramic there are two pore types - with average size about 100 and 10 µm. The large pores have the morphology of the pore-forming particles - spherical-shape which can be both isolated and connected. Pores of smaller sizes are formed by the compacting of powder particles parameters and its mean size is 29 µm. The pore size distributions are shown on Figure 8 and as one can conclude from Table 1 its does not depends on MgO content.
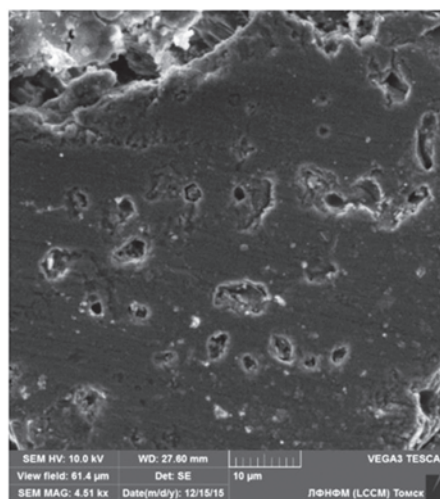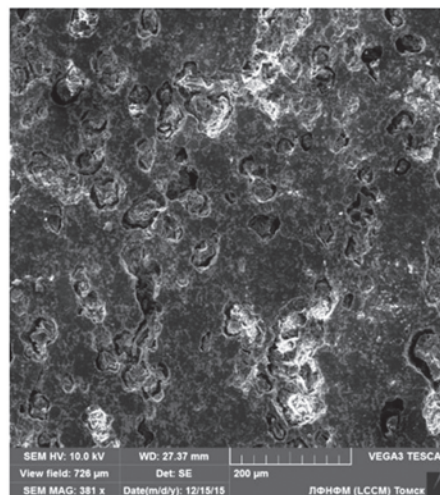

Fig. 7. Microstructure of ZrO_2-MgO porous ceramics

7. ábra A porózus ZrO2-MgO kerámia mirkoszerkezete

MgO, mass %	The average size of micropores, µm; Standard deviation, µm	The average size of macropores, µm; Standard deviation, µm	Porosity, vol. %
0	29; σ=19	98; σ=31	45
25	30; σ=23	104; σ=21	43
50	27; σ=17	94; σ=27	45
75	26; σ=17	101; σ=30	49
100	28; σ=20	105; σ=27	47

Table 1. The average pore size of ZrO_2-MgO ceramics

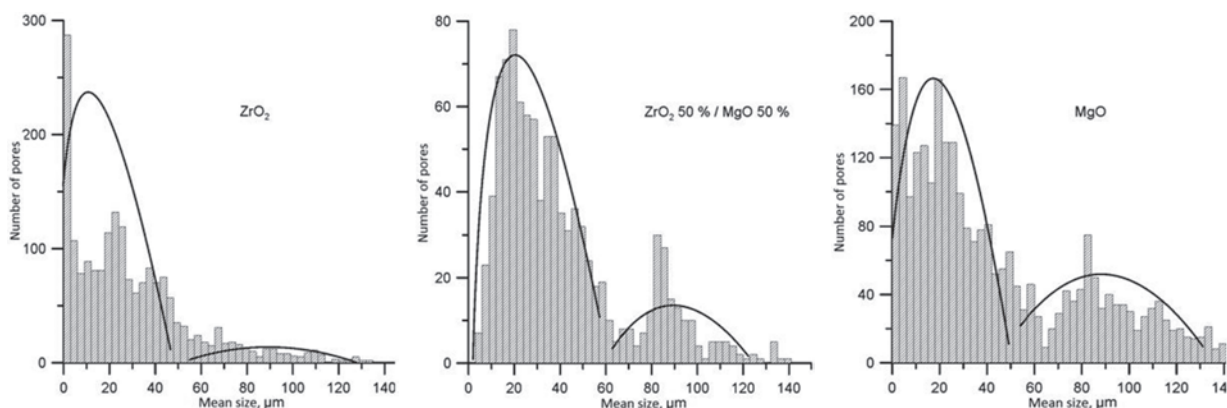1. táblázat A ZrO2-MgO kerámiák átlagos pórusmérete

Fig. 8.   Pore size distribution according to composition
8. ábra   A pórusméret-eloszlás az összetétel szerint

Pore-forming technologies, based on the changes of sintering temperature and Al(OH)$_3$ and UHMWPE addition, makes it possible to obtain micropores with an average size up to 17 μm. Average pore size of ceramic obtained with Al(OH)$_3$ addition in initial powders were 2.1 μm in ZrO$_2$-Al$_2$O$_3$ ceramic and 4 μm for Al$_2$O$_3$ ceramic.

Increasing of ZrO$_2$-MgO composite sintering temperature from 1200 to 1600 ºC leads to a decrease in porosity from 68 to 4%. The average size of micropores decreases from 17 to 8 μm without significant dependence of components in the initial powder composition.

Determination of compression strength of a ZrO$_2$-MgO composite, sintered without adding pore-forming particles are shown, that strength increases with sintering temperature increasing, the maximum strength is 230 MPa can be achieved after sintering at highest temperature 1600 ºC, figure 9.

Figures 10 and 11 are shown the compression strength of ZrO$_2$-Al$_2$O$_3$ and Al$_2$O$_3$ ceramics. Both ceramics showed the increasing of strength with increasing of sintering temperature and decreasing of aluminum hydroxide concentration in initial

powder composition. Ceramics based on ZrO$_2$ has maximum compressive strength 64 MPa after sintering at 1650 °C without the aluminum hydroxide addition. The minimum compressive strength was 8 MPa after sintering at 1450 °C and with aluminum hydroxide addition 75%. At the maximum sintering temperature and the minimum content of aluminum hydroxide the Al$_2$O$_3$-based ceramic had compressive strength 165 MPa. The minimum compressive strength was 10 MPa for ceramic sintered as aluminum hydroxide content with a sintering temperature 1450 °C. The compression strength of the ZrO$_2$-MgO composite with bimodal porosity increases with an increasing of MgO content in the composition from 18 to 33 MPa.

4. Conclusion

Thus, the methods of pore volume formation in ceramics allow to obtain the pore volume in ZrO$_2$ and Al$_2$O$_3$ ceramics in the range from 4% to 68% and sintering temperature increasing leads to decreasing of the average pore size and pore volume.

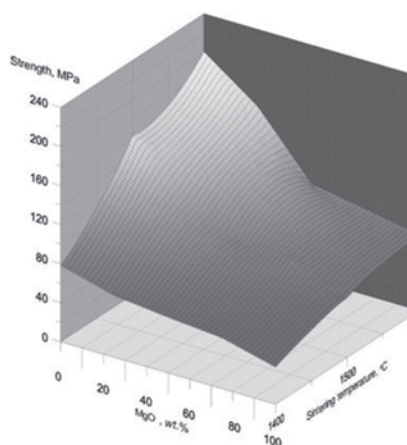It have been found that the introduction of pore-forming

Fig. 9.   Dependence of compressive strength of ZrO$_2$-MgO vs. composition and sintering temperature
9. ábra   A ZrO$_2$-MgO kerámia nyomószilárdságának változása az összetétel és a szinterelési hőmérséklet függvényében
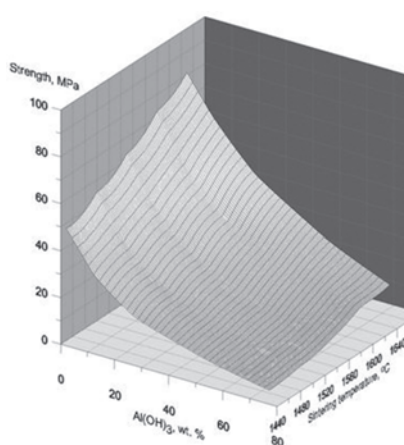
Fig. 10.   Dependence of the compressive strength of ZrO$_2$-based ceramics vs. the sintering temperature and aluminum hydroxide content
10. ábra   A ZrO$_2$ alapú kerámia nyomószilárdságának változása az alumínium-hidroxid tartalom és a szinterelési hőmérséklet szerint
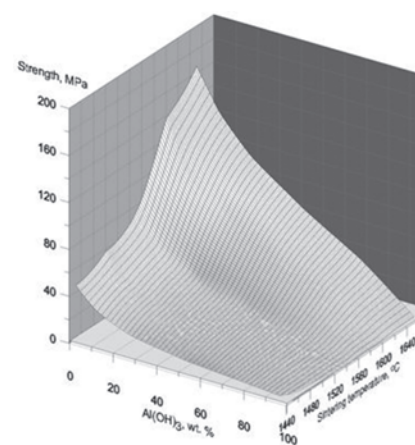
Fig. 11.   Dependence of the compressive strength of Al$_2$O$_3$-based ceramics vs. the sintering temperature and aluminum hydroxide content
11. ábra   Az Al$_2$O$_3$ alapú kerámia nyomószilárdságának változása az alumínium-hidroxid tartalom és a szinterelési hőmérséklet szerint

particles into the ZrO_2-MgO initial powder composition and sintering at 1600 °C makes it possible to obtain a pore structure inheriting the morphology of the pore-forming particles. The maximum compressive strength was 33 MPa. The compression strength of ZrO_2-MgO ceramic obtained without the introduction of pore-forming particles reaches up to 200 MPa.

Addition of aluminum hydroxide to Al_2O_3 with sintering at temperatures 1450–1650 °C allows to achieve a porosity of up to 62%, while the compressive strength is 220 MPa.

Acknowledgement

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Pórusszerkezetek létrehozása cirkónium-oxid – alumínium-oxid kerámiákban

Jelen kutatómunkában különböző pórusképző módszerek és szinterelési hőmérsékletek alkalmazásával cirkónium-oxid, alumínium-oxid és ZrO2-MgO kerámia kompozitokban 4-68%-os mikropórus szerkezetet hoztak létre. A szerzők megállapították, hogy az alkalmazott különböző pórusképző adalékoknak és szinterelési hőmérsékleteknek nem csak a pórusok méretére és elhelyezkedésére van jelentős hatása, hanem a nyomószilárdságra is. Pórusképző adalékként alumínium-hidroxidot és 1450-1650°C-os szinterelési hőmérsékletet alkalmazva 62%-os porozitás érhető el több mint 200MPa-os nyomószilárdsággal.

Kulcsszavak: alumínium-oxid, alumínium-hidroxid, kerámiák, kompozitok, mikroszerkezet, pórusképzés, porozitás, szinterelés, cirkón-dioxid

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[6] Mohamed, K. R. – El-Rashidy, Z. M. – Salama, A. A.: In vitro properties of nano-hydroxyapatite/chitosan biocomposites. *Ceramics International.* 37(8), December 2011, pp. 3265–3271, http://dx.doi.org/10.1016/j.ceramint.2011.05.121
Books:
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- To improve performance and cost benefit for users and general public
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