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Dedicated to the Participants of ic-cmtp4

The 4th International Conference on Competitive Materials and Technology Processes
Preface

Thanking to the mathematicians, phisicists, chemists, biologists, medics, geologists and engineers materials science is one of the most gynamic growing disciplines in our days.. In my early engineering practice between 1973-1985 the understanding of mechanical, physical, thermal and chemical properties of metals, ceramics, minerals and composite materials helped me in development and design new construction of machines and equipment for ceramic and building industries, waste water treatment plants and plastic industry.

From 1986 as managing director of the Hollohaza Porcelain Manufactury Co. understanding the materials properties and their behavior in technology processes helped me in development of productivity our company technology lines, machines and equipment and improve the quantity and quality of production and final products. Thanking to this me and my company were awarded in USA with the World Selection Trophy for Quality and Export Merit in 1989.

Connecting the theoretical and applied materials science with technological processes contributed us at IGREX Ltd. to develop a new family of ceramic reinforced or ceramic based light weight hetero-modulus, hetero-viscous and hetero-plastic complex composite materials with excellent physical and mechanical properties including hardness, thermal schock resistance and extreme dynamic strength.

The experiences in rheology I have started in Moscow (Russia) at Mendeleev Universiy as a student under the supervision of professors Vlasov, Balkievich and Sarkisov in he end of 1970th. As a student and later as a young engineer and ‘scientist’ I have learned a lot especially from professors Sarkisov and Balkievich who were inventors of the new materials as for nuclear power plants as aerospace. Since then I am author of three doctoral thesys (PhD., Dr.Eng.Sc. and Dr.Habil.), author or co-author two patents and more than 250 scientific papers.

My research and publication activity can be devided on the following three periods.

- From 1970 to 1985 I have strong collaboration with my Russian professors and young scientific colleagues and I published my results together with them or alone in Hungarian or in Russian languages.
- From 1986 I could organize my Hungarian group and until 2005 I published our results mainly in Hungarian.
- Since 2008 I am trying to publish my results only in English except the education guides for the MSc and PhD students at the University of Miskolc in Hungary and Tomsk State University in Russia.

In 1999 the Department of Ceramics and Silicate Engineering was established by me at University of Miskolc. In this book are collected some of papers in chronological sequence to give an overview about my research in materials science. In these papers sometimes my co-
authors are my PhD students, sometimes industrial experts or my university colleagues in Hungary, Russia, France, Israel and United Kingdom.

The Hungarian origin papers were translated into English by myself, so I would like to apologize for the grammatical mistakes and for my poor English.

Prof. Dr. GÖMZE, A. László
Some actual questions of crushing theories – comminution of plastic-viscoelastic materials on pan mill

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Translated from Hungarian Az aprítási elmélet néhány aktuális kérdése – képlékeny viszkoelasztikus anyagok aprítása görgőjáraton


Abstract. Crushing is one of the most energy consumption in material processing. Especially large volume of energy requires in preparing raw materials for ceramic and building industry. The classical grinding and comminution theories are not able to give realistic estimation the energy requirements of crushing complex material structures which have plastic-visco-elastic rheological properties. Analizing and comparing the most popular crushing theories the author has found that both rheo-mechanical properties of crushed materials and geometrical and technical parameters and characteristics of the equipment have to be taken into consideration to determine the required energy consumption. Using this conception the author gives a new mathematical and mechanical model to determine energy requirements of pan mills for grinding and comminution so complex visco-elastic-plastic materials like convectional brick clays.

1. Introduction

The crushing and comminution are one of the most important processes at the technology line of solid materials. In the food, pharmaceutical, chemical, mining and metallurgical industry the required grain size distribution and geometrical shapes of raw materials and additives are achieved by crushing and milling machines. Crushing and comminution are very important also to achieve the required specific surface of the used materials in the technological processes. Thanking to the large production volume crushing and comminution are especially important in the processing of silicate-based materials including processes and technologies of building materials also. It is obvious that the speed and activity of chemical processes managed by diffusion in solid phases very strong depends on the numbers and sizes of particles contacts [1, 2, 3, 4, 5 and 6]. Thanking to this circumstance in our days it is not enough only the determination of energy requirements of crushing and comminution technology but it is
necessary to manage the produced grain sizes and their geometrical shapes including their macro- and microstructures and distributions in space.

In this paper the author tries to find answers on these open questions of grinding and comminution on the basis of crushing materials on pan mill.

2. Overview of the phylogeny of the crushing theories

2.1. The classical crushing theories based on classical mechanical approach

Between the development of crushing theory and infrastructures investment – road and railway line building – can be fined an interesting parallelity. The first crushing theory developed by Rittinger in Prussia in 1867 [7] as product of the dynamic growth of railway line and roads. This theory based on the energy requirements of crushing the essence of which is that the energy need is proportional with the volume of the generated new surfaces.

It is easier to understand the Rittinger’s theory using Fig. 1, where the cubic with \(d_1\) edge length is crushed by parallel planes to cubic with \(d_2\) edge length. The created by this way number of new small cubic can be determined as:

\[
N_{k} = n^3
\]  
(1)

While the volume of generated new crushed surface is:

\[
A = 2 \cdot 3(n-1) \cdot d_1^2, \text{[m}^2\text{]}
\]  
(2)

![Fig. 1. Interpretation of the Rittinger's crushing theory](image)

On the basis of Fig. 1 it is obvious that the number of fracture surfaces can be determined as:

\[
N = 3(n-1)
\]  
(3)

where \(n\) is the degree of comminution because:

\[
n = \frac{d_1}{d_2}
\]  
(4)

Suppose that the energy requirement of crushing of unit edge length cubic by one fracture plane is \(W_1\). In this case the energy requirement of crushing of cubic with \(d_1\) edge length to the
small cubic of \( d_2 \) edge length can be determined as:

\[
W = d_1^2 \cdot N \cdot W_1 \text{ [Nm]} \quad (5)
\]

Substitute (3) and (4) to (5) we will get the Rittinger’s equation of the energy requirement of crushing the cubic with \( d_1 \) edge length to the small cubic of \( d_2 \) edge length as:

\[
W = 3d_1^2W_1 \left( \frac{d_1}{d_2} - 1 \right) \text{ [Nm]}, \quad (6)
\]

This equation – the ‘surface theory’ of crushing – assumes the followings:
- the crushing force is proportion with the energy requirements of comminution,
- the mechanical stress is homogeneously distributed on the fracture surface,
- the volumes of required energy for crushing are independent on the mechanical and rheological properties of crushed materials but they are proportional with the generated new fracture surfaces.

At the end of the 1800 years in Europe railway lines and road buildings construction boom were obvious. Thanking to this Kirpitsev [8] in Russia and Kick [9] in the UK almost in the same time published their new developed theories in 1885. It was the second theory of energy requirement of crushing and nowadays this theory so-called ‘volume theory’. During the crushing rocks for the railway embankment Kirpitsev and Kick had observed that the created new fracture surfaces were not parallels and had a wide variety of geometrical shapes, thanking to which it was impossible to determine the largeness of the new surfaces.

Based on their experiments and theoretical approaches on comminution and crushing of solids the required energy is proportional with the volume of crushed grains and multiplication of mechanical stresses and elastic deformation developed in the grains. This means that to crush solid cubic with edge length of \( d \) the required energy of crushing can be described as:

\[
W = d^3 \int_0^E \sigma \, d\varepsilon \quad (7)
\]

If we take into consideration that the volume of the strain of elastic deformation can be determined as:

\[
d\varepsilon = \frac{1}{E} \, d\sigma \quad (8)
\]

then the (7) can be rewrite as:

\[
W = d^3 \cdot \frac{1}{E} \int_0^\sigma \sigma \, d\sigma = d^3 \frac{\sigma^2}{2E} \text{ [Nm]} \quad (9)
\]

where:
- \( \sigma \) – the fracture strength of the crushed material, N/m²
- \( E \) – the elastic module of the crushed material, N/m²
The third theory of crushing was developed only in the middle of the 20th century by F.C. Bond [10] in USA in 1952. It is not accidental that the third theory was developed by an American scientist as from 1940 in this country was a very dynamic construction industry thanking to the building of new railway lines and highways.

The essence of Bond’s theory is that the requirement energy of crushing of a grain with a certain geometrical volume and shape must be determined as a geometric mean of the values get by the surface and volume crushing theories. This means that using the Bond’ theory the energy requirement of crushing of the grain with $d_1$ edge length is proportional with the reciprocal values of square root the grain sizes before and after comminution and can be described as:

$$W = C_B \left( \frac{1}{\sqrt{d_2}} - \frac{1}{\sqrt{d_1}} \right), \text{[Nm]}$$  \hspace{1cm} (10)

where $C_B$ - constant of Bond.

All these three “classical” crushing theories were further developed by R.J. Charles [11] in 1957 and described them in uniform equation as:

$$dW = -C \frac{d(d)}{d^a}$$  \hspace{1cm} (11)

From this equation (11) the required crushing energy for a solid with $d_2$ edge length can be determined by Charles as:

$$W = -C \int_{d_1}^{d_2} \frac{1}{d^a} d(d), \text{[Nm]}$$  \hspace{1cm} (12)

In our days the eq. (12) is accepted as “fundamental equation of crushing” as depending on the values of exponent $a$ we can get the equations of Kirpitsev-Kick ($a=1$), Bond ($a=1.5$) and Rittinger ($a=2$).

These classical theories of crushing by mechanical point of view can be successfully used for the determination of acting forces and working energy requirement of crushing machines and comminution equipment. A lot of scientists and mechanical engineers [12, 13, 14, 15] developed their theories basing on the conception that the energy requirement of the crushing machines divided by the followings:

- the utilized energy for crushing or comminution is proportional with the generated new fracture surfaces,
- the unutilized energy for crushing generally is turned for heating and elastic deformation of the crushed grains (it must be reminded that the above authors never determined the real value of this unutilized “harmful” energy)
- the energy which has turned to beat the outside and inside friction ratio of crushing machines and equipment.
2.2. Formation and development of the mechano-chemical approach of crushing theory

The classical mechanical theories of Rittinger, Kirpitsev, Kick, Bond and Charles were not able to notice and describe the mechano-chemical phenomena and processes like aggregation and agglomeration [16] taking place during fine comminution of solids. The revision of classical crushing theories from the mechano-chemical point of view first time was mentioned by soviet scientists [17, 18 and 19] in the 1960s. In the development of basic principles of mechano-chemical approach of crushing theory and the acceptance of it internationally a Hungarian scientist from University of Veszprem, prof. Zoltan A. Juhasz [20, 21, 22] had a very important role.

By the mechano-chemical approach of crushing theory in the solids there are reversible and irreversible processes under mechanical loads. The values of stresses and deformation of grains in the moment of fracture very strong depends on nature of crushing and the rheo-mechanical properties of grains.

In the same time there are material structural changes occur in the grains meanwhile release free energy thanking to which the surfaces of the grains become chemically active. These material structure changes generally are dislocation, vacancy and interstitial, from which in the vacancy there are forming local mechanical stress peaks.

The mechano-chemical approach of crushing theory can answer the reasons of the aggregation and agglomeration under fine milling, point out the activation of the generated “new” fracture surfaces and on these active surfaces new chemical bonds and crystal structures occur during the agglomeration processes (Fig. 2).

![Fig. 2. The efficiency of fine milling](From Zoltan A. Juhasz: Mechano-chemie and agglomeration lecture [22]. Spoken in MTA Reading Room, Budapest, April 16, 2003)

In our days the examination of mechano-chemical approach of crushing theory is accepted and used for the efficiency of fine comminution in all industrial developed countries. In development and dissemination of this theory together with prof. Juhasz had very important
role of prof. Ludmilla Opoczky [23, 24, 25] also. Her researches contribute to verify the role in fine comminution of the so-called surface active additives and their application in the cement industry.

2.2. Formation and development of technological approach of crushing theory
At the beginning of 1970s in the Soviet Union there was huge investment in the infrastructural structure of country including buildings of houses and cities, as well as building of roads, highways and railway lines between the regions and countries of the Union. One of the largest infrastructure investments of that time was the starting of the building program of Baikal-Amur railway network (in Russian BAM). These gigantic constructions have required unbelievable large volume of crushed rocks and raw materials as well as building materials with different mineralogical combinations and physical, chemical and mechanical properties. This huge volume of crushed materials required energy efficient and reliable machines and equipment for crushing and comminution. So it is obvious that new crushing theory which have based on the physico-mechanical property of cloth materials and geometrical and engineering technological parameters of crushing machines was developed in the Soviet Union in the 1970s [26, 27, 28 and 29].

The Author of present work could participate in this material specific and equipment oriented new crushing theory as a scholarship student in Moscow [26, 27] and later in Hungary as young MSc mechanical engineer. So, on the basis of rheological properties of elasto-viscoplastic convectional brick clays with mined moisture and we were the first who successfully described mathematically [29] the flow and deformation of the clay minerals during their crushing on the high speed smooth roller machines. Thanking to this new developed theory was enabled mathematically determine the intensity of mixing and homogenization during the comminution process. Thanking to this new developed mathematical equations the values of shear and compressing stresses generated inside of crushed materials can be determined depending on its position in roller gap [30, 31 and 32].

In 1980 was developed the mathematical model of rolling of molted viscous glasses [33] and in 1982 together with soviet scientists [34] was successfully described mathematical equations for crushing on high speed smooth rollers of visco-elastic materials like limestone and coals.

The advantages of the developed in this time technological approach of crushing theory is that both rheo-mechanical properties of crushed materials and their changes during their comminution as well as geometrical and engineering technological parameters of equipment are taking into consideration. So the consumption of energy on comminution, mixing and homogenization of grains during the crushing taking into consideration as technologically useful energy.
2.3. Mechano-chemical phenomena on pan mills

The Department of Ceramic and Silicate Engineering of University of Miskolc has a pan mill which is perfect for crushing, fine comminution, mixing and homogenization of materials having different chemical and mineralogical completion as well as physical, mechanical and rheological properties. Thanking to its multifunctional opportunities this laboratory equipment (Fig. 3) is wide range used by the department’s colleagues for laboratory practices almost at each lectures to demonstrate mechano-chemical phenomena during production of material mixtures with the required grain sizes and distributions. The mechano-chemical phenomena taking place during fine comminution of materials can be observed on this laboratory equipment during crushing ceramic raw materials. Using the laboratory equipment the times (Fig. 2) of beginning of aggregation ($t_{ar}$) and the beginning of agglomeration ($t_{al}$) as well as efficiency of crushing can be determined as function of the followings:

$$t_{ar} = f(Q, m, D, n, t_0), \text{[min]},$$

$$t_{al} = F(Q, m, D, n, t_0), \text{[min]},$$

where:

- $Q$ – the mineral completion and chemical composition of crushed materials which can be homogenous or mixed materials
- $m$ – the quantity of crushed materials on the laboratory pan mill in the same time [kg];
- $D$ – the grain size of the largest particles before crushing [mm];
- $n$ – the king shaft speed of pan mill, [1/min];
- $t_0$ – the rated gap which is determined at the beginning of crushing process, [mm].

Fig. 3. The laboratory pan mill

Fig. 4. The grain structure of STRONG&MIBET lime powder after 20 and 40 minutes grinding on laboratory pan mill
These independent factors can be determined and changed depending on the experimental plan. To study the mechano-chemical phenomena it is necessary taking specimens by 5 minutes of crushing and examine the structure by Scanning Electron Microscopy. Using SEM is it to determine the type of mechano-chemical processes during crushing and the nature and rate of aggregation and agglomeration (Fig. 4).

3. Design method of pan mills based on technological approach – mathematical definition of material mixing and homogenization during grinding

3.1. Selection of examination method

The essence of the technological approach of crushing theories is based on the physico-mechanical properties of comminuted materials including their rheological models and equations, inside and outside friction ratio, as well as geometrical, technical and technological parameters of the equipment. In the present case the comminuted material is convectional brick clays with mined moisture, having rheological model of Bingham which can be described with rheological equation as:

\[ \tau = \tau_0 + \eta \frac{du}{dx} \text{ [MPa]} \]  

(15)

The crushing of materials on pan mills with roller \( R_1 \) radius occurs in the gap between the roller and grinder plate. This equipment can be modeled as pair of cylinders or rollers from which the second roller is the grinder plate with endless radius \( R_2 \)

\[ R_2 = \infty \]  

(16)

For the mathematical analysis of the physical, mechanical and technological processes taking place during crushing on pan mill it is expedient to choose a coordinate system the origo of which is fixed in accordance to the pan mill machine. This means that this coordinate system will be rotated together with the crankshaft/king shaft. From this coordinate system the roller will rotate only around of its own axis meanwhile the grinder plate is as a cylinder with endless radius and its “peripheral speed” will equal with the peripheral speed of pan mill roller (Fig. 5.). This occurs because of the coordinate system is moving above the grinder plate with peripheral speed of roller.

The forces developing in the grains during the crushing of materials in the gap between the roller and grinder plate have to be in equilibrium. Using this equilibrium of mechanical forces and coordinate system described above a system of mathematical equation can be formulated the decision of which will be:

\[ \frac{dp}{dy} = \frac{d\tau}{dx} \]  

(17)
3.2. Speed conditions forming in the materials during their crushing in the gap between the roller and the grinder plate

To solve the speed condition forming in the material during their crushing in the gap between the roller and the grinder plate expedient substitute the shear stress equation (15) into the equilibrium equation (17) and create equation:

$$\frac{dp}{dy} = \frac{dt}{dx} \left( \tau_0 + \eta \frac{du}{dx} \right) \text{[Pa/m]}$$

(18)

After integration of eq. (18) the flow and deformation speed distribution of materials in the pan mill gap can be described as:

$$u = \frac{1}{\eta} \left( -\tau_0 \chi + C_1 \chi + \frac{dp}{dy} x \right) + C_2, \text{[m/s]}$$

(19)

Where the constants of integration $C_1$ and $C_2$ can be determined from the technical parameters of grinding machine and coordinate system (Fig. 5) using the following boundary conditions:

$$u = v, \text{if } x = 0 \text{ and } u = v, \text{if } x = t$$

(20)

Substitute (20) into (19) after some mathematical step the constants of integration can be determined as:

$$C_1 = \tau_0 - \frac{t}{2} \frac{dp}{dy}$$

(21)

$$C_2 = \eta \cdot v = \eta (\omega_1 R_1)$$

(22)
Substitute (21) and (22) into (19) after some operation, the flow and deformation speed conditions of crushed materials can be described as:

\[ u = \frac{1}{2\eta} \left( \frac{dp}{dy} x^2 - \frac{dp}{dy} \chi t + 2\eta \omega_1 R_1 \right), [\text{m/s}] \]  

(23)

The differential \(\frac{dp}{dy}\) can be determined from the volumetric performance of grinding machine by the following:

\[ V_1 = \int_0^t u \cdot L \cdot dx, [\text{m}^3/\text{s}] \]  

(24)

where:

- \(V_1\) – the volume of crushed material through unit time at the randomly chose \(t\) gap between the roller and grinder plate, \([\text{m}^3/\text{s}]\);
- \(L\) – the width of the roller mantle, \([\text{m}]\);
- \(U\) – the flow speed of crushed material at the \(t\) gap section, \([\text{m/s}]\).

After putting (23) into (24) and integration the volumetric performance of pan mill grinding machine through unit time is:

\[ V_1 = \omega_1 LR_1 t - \frac{L}{12\eta} \frac{dp}{dy} t^3, [\text{m}^3/\text{s}] \]  

(25)

At the same time the volumetric performance of the pan mill through unit time at the nominal gap \(t_0\) (Fig.5) can be described as:

\[ V_2 = L \cdot t_0 \cdot R_2 \cdot \omega_1 [\text{m}^3/\text{s}] \]  

(26)

As the volumetric performance of the pan mill at any of its gap section has to be the same value, equations (25) and (26) must be equal, so:

\[ \omega_1 LR_1 t - \frac{L}{12\eta} \frac{dp}{dy} t^3 = \omega_1 LR_1 t_0, [\text{m}^3/\text{s}] \]  

(27)

from where:

\[ \frac{dp}{dy} = \frac{12\eta \omega_1 R_1}{t^3} (t - t_0)(x^2 - tx) + \omega_1 R_1, [\text{m/s}] \]  

(29)

The value of section \(t\) can be variable from the width of nominal gap \(t_0\) up to \(T\) value of which depends on outside friction ratio \((\mu_0)\) between the surfaces of material and roller. This means:

\[ t_0 \leq t \leq T, [\text{m}] \]  

(30)

The equation (29) very well illustrates that the deformation and flow speeds developing in the materials during their crushing in the gap between the roller and grinder plate of pan mill are independent on the physical and mechanical properties of the crushed materials like crystal structures, viscosity, bending strength etc. At the same time the values of these deformation and flow speeds fundamentally depends on the geometrical \((R_1)\) and technological \((\omega_1\) and \(t_0)\)
parameters of grinding machine, as well as quantity of the loaded materials (T) and their positions (t) in the gap.

The Fig. 6 very well illustrates the flow characteristics and mixing of the crushed material particles in the gap between the roller and the grinder plate depending on their geometrical position. The illustrated speed vectors have shown an effective mixing efficiency of materials under the pan mill roller during grinding and comminution. This “direction” of material speeds can give a good answer why the pan mills are used as “mixing” machines in several cases in different technologies. In the practice the efficiency of mixing and homogenization are much more effective as the equation (29) describes the material speed distribution in the gap only in the middle of the roller of width \( L_1 \). From the Fig. 7 it is obvious that the roller meets with the materials at different speeds by its width creating different deformation speeds depending on distance from the crankshaft/king shaft.

Exactly, thanking to the rotation of rollers with width \( L_1 \) around the crankshaft the peripheral speed at the inner edge of roller will be:

\[

v_{1b} = \frac{\pi n r_{1b}}{30}, \ [m/s]
\]

in the middle:

\[

v_1 = \frac{\pi n r_1}{30} = \omega_1 \cdot R_1, \ [m/s]
\]

and at the outer edge:

\[

v_{1k} = \frac{\pi n r_{1k}}{30}, \ [m/s]
\]
The peripheral speed of roller with width of $L_1$ can be determined as:

$$v_1 = \omega_1 \cdot R_1, \text{[m/s]} \quad (34)$$

Thanking to this the peripheral speed of the roller mantle ($v_1$) will be faster than the inner edge peripheral speed ($v_{1b}$) generated on the roller surface by the crankshaft:

$$\Delta v_{1b} = v_1 - v_{1b} = \frac{\pi L_1 n}{60}, \text{[m/s]} \quad (35)$$

Meanwhile the peripheral speed of the roller mantle ($v_1$) will be delayed than the outer edge peripheral speed ($v_{1k}$) generated on the roller surface by the crankshaft:

$$\Delta v_{1k} = v_1 - v_{1k} = \frac{\pi L_1 n}{60}, \text{[m/s]} \quad (36)$$

This means that the mantle of the roller will be slide (Fig. 7) and create not only efficiency mixing but increasing shear stresses inside of the crushed materials in the pan mill gap.

The average value of this slide at the $i^{th}$ roller can be determined as:

$$v_{iac} = \frac{\pi L_in}{120}, \text{[m/s]} \quad (37)$$

Where:

$L_i$ – the width of the $i^{th}$ roller of the pan mill

$n$ – the rotation of the crankshaft, [min$^{-1}$].

4. **Energy requirement of the crushing through pan mills**

Technologically exploit energy can be determined as:

$$W_{tech} = W_R + W_t, \text{[Nm]} \quad (38)$$

where:

$W_R$ – the required energy to crush materials with certain mechanical compression strength, module elasticity and viscosity [Nm]

$W_t$ – the required energy to crush the materials in pan mill gap through shear stress created by the roller [Nm]

It is obvious from the equation (15) that the materials having Bingham rheo-mechanical models that energy ($W$) is turned not only on crushing but on intensive mixing and homogenization.

Except of the technologically exploit for crushing energy there are some other energy requirements for moving some technical parts and elements of crusher equipment which can be described as:

$$W_{KH} = W_{gm} + W_{ge} + W_{ka} + W_{kt}, \text{[Nm]} \quad (39)$$
where:

\( W_{gm} \) - the energy requirement turns on the moving of construction elements and on rolling resistance of the pan mill rollers, [Nm];

\( W_{gc} \) – the energy requirement turns on the outside friction ratio between the surfaces of crushed materials and roller mantle as well as grinder plate during its slide with average speed of \( v_{iac} \) (37), [Nm]

\( W_{ka} \) – the energy requirement turns on friction ratio between the surfaces of crushed materials and deflector knife [Nm]

\( W_{kt} \) – the energy requirement turns on friction ratio between the surfaces of grinder plate and deflector knife [Nm]

The crushing machine as pan mill is applicable for the comminution of materials with certain physical, mechanical and rheological properties only if:

\[
W_{KH} \geq W_{tech}
\]  

(40)

If the conditions of (40) will not realize it is necessary to increase the mass of rollers or the rotation of crankshaft – or both in the same time.

Both the technologically required energy \( W_{tech} \) and the construction required energy \( W_{KH} \) can be mathematically deducted and determined. The deductions and mathematical determination of these energy requirements are quite complicated so it is expedient to deduct and determine them in an individual scientific work.

5. Conclusions

Summarizing the above it is obvious that the crushing theories starting with the classical mechanical approach through the mechano-chemical and technological approach are still developing in our days. Thanking them the more efficient crushing machines and equipment can be developed. The new equipment must be specialized and take into the consideration the physical, mechanical and chemical processes taking place in the crushed and grinded materials during their comminution. It is also very important to understand the technological opportunities of the selected mechanical equipment or crusher as well as the changes in the morphological structure and rheological properties of the solids.

Using the laboratory pan mill in the University of Miskolc at the Department of Ceramic- and Silicate Engineering limestone granules were successfully comminuted and observed the mechano-chemical phenomena during their crushing. So we were the first who could experimentally determine so mechano-chemical phenomena as aggregation and agglomeration including the technologically required times of grinding in spite that the pan mills generally are used for the crude crushing. Moreover using pan mills can be realized so complex examinations and optimization of crushing time as they are described in (13) and (14)

On the basis of rheological model and equation of Bingham and geometrical and
technological parameters of pan mill new mathematical model was developed and successfully determined and described for the deformation and speed distribution of materials during their crushing in the gap between roller and grinder plate of pan mills (29). This equation (29) attractively illustrates the intensity of mixing and homogenization of particles during their comminution.

The technologically exploit required energy for crushing on laboratory pan mill also was determined in equation (38). At the same time the mathematical descriptions of the energy requirement turn on material crushing through compressing stress ($W_R$) and shear stress ($W_\tau$) are quite complicated so it would be necessary to develop and describe them in one or two independent publication.

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Miskolc, NME, 1980. 1-49. old.


Investigation of rheological properties of asphalt mixtures

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Abstract. Asphalt mixtures are one of the most popular building materials in Hungary because of the highway program of the government. In spite of this large popularity some of the mechanical properties of asphalts are not disclosed enough till today. Particularly there is no mechanical model usable to understand and explain the rheological behaviors of asphalt mixtures with different composition of bitumen and mineral raw materials. The present used in industry rheological model of Burgers is not reliable enough to understand mechanical properties of asphalt mixtures because of the included Maxwell element. This means under any kind of mechanical forces the asphalt surfaces of roads must be continuously deformed in spite of these forces are as small as possible. The rheological model of Burgers suggests the lifetime cycle of asphalt roads and highway must be very very short which is inconsistent with the real lifetime cycle of asphalt roads.

On the basis of rheo-tribometer instrument developed and patented by Gömze, A.L. and others the authors have investigated and tested standard Marshall-specimens of asphalt mixtures with different composition of bitumen and mineral raw materials. In their experiments the authors used different temperatures, loading pressures, shear ratios and deformation speeds. As a result of these laboratory tests the authors could find out a new rheological model and mathematical terms to describe the real rheological properties of asphalt mixtures.

Keywords: asphalt mixtures, elasticity, measurement, plasticity, rheology, rheological model, viscosity

1. Introduction

The investigation of rheological properties of the complicated viscous-elastic-plastic materials has 25-30 years tradition at the University of Miskolc thanking to the collaboration with the scientists [1, 2, 3 and 4] of the famous University of Civil Engineering in Moscow. Further these investigations were also made independently [5, 6, 7 and 8] by the members of research group in ceramics and silicate materials. The rheological research has got a new boost [9, 10, 11, 12 and 13] after establishment of
Department of Non-Metallic Materials Technology as well as Department of Ceramics and Silicate Engineering in July 1st, 1999. From that time was developed a new combined rheo-tribometer which gave an opportunity for examination and investigation rheological, mechanical and tribology properties of so complicated material structure like asphalt mixtures, asphalt pavements and asphalt concretes. The principle and construction of the developed instrument has got patent in Hungary [14]. The schematic draw of the new instrument is shown in Fig.1.

Fig.1. Schematic draw of combined rheo-tribometer

1-instrument table, 2-small drive, 3-electric motor, 4-cable drum, 5-cableway, 6-batching car (with the shearing plate), 7-inductive displacement detector, 8-force-meter (spider), 9-heatable specimen holder, 10-pneumatic power cylinder, 11-magnetic valve, 12-pressure gauge, 13-compressor, 14-thermostat, 15-control unit, 16-data recorder (spider 8), 17-computer (capturing and processing data)

2. History

The pavements of modern roads for automobile transports are made from high quality, frost proof and wear resistant asphalt. These asphalt pavements are produced through compression of special mixtures of bitumen, stone flours, rock dusts, sands and minerals of different fractures. By Skovranko [15] the asphalt pavements are mixture of binders and granulated minerals and can be divided as closed, tight and after compacting sorts. One of the investigations of relationship between the mechanical properties and material structures of asphalt pavements was made by Gezencvej [16]. He was also one of the first scientists who emphasized and underpinned the importance of the relationship between temperature, granular structures and rheological properties of fresh mixed asphalts and their behavior during compacting under the road roller. After the rheological experiments he made on Marshall-probes he has characterized the asphalt pavement as an elastic-viscous-plastic material. In spite of these characteristics Gezencvej has recommended the rheological model of Burgers (Fig.2) which is rheological model of viscoelastic material models and it has no plastic elements.
It is obvious from the Burgers-model that this kind of material will have a residual (and further permanent) deformation in each case when an outside loading force will develop in it a mechanical stress larger than 0. This means that asphalt pavement with Burgers-model will be irreversible deformed in each case when the generated in it mechanical stress will:

$$\sigma > 0$$

(1)

The deformation response function of this kind of materials can be characterized as:

$$\varepsilon_0(t) = \varepsilon_1(t)\varepsilon_m(t) + \varepsilon_{k0}(t)$$

(2)

where:

$\varepsilon_1(t) = \sigma/E_1$ – the deformation response function of Hooke-element

$\varepsilon_1(t)$ - deformation response function of Newton-element

$\varepsilon_1(t)$ - deformation response function of Voigt-Kelvin-element

On the basis of Burgers-model the irreversible deformation of asphalt pavement is:

$$\varepsilon_m(t) = \sigma/\eta_1$$

(3)

and the value of which will permanently grow and never will reversible in time thanking to the new loading forces of car wheels on the road.

3. Experiments

The examinations of rheological properties of Marshall-probes made from asphalt mixtures with different mineralogical, granular and bitumen compositions were examined on the new developed and patented instrument has shown in Fig.1. During the shear tests the specimen were put into the specimen holder (9), pressed with pneumatic cylinder (10) up to surface pressure (p) and heated up to temperature (T).
through thermostat (7) and these pressure and temperature were held during the test. The variable speed (v) of shear plate (6) was also constant in the certain experiment. So the “cutting” shear stress could be measured as function of compaction pressure, material containment (Q), temperature and shearing speed as:

\[ \tau = f(p, Q, T, v) \text{[MPa]} \]  

(4)

The measured data was saved and stored by computer. Some of typical shear stress – displacement diagrams are shown in Fig.3 where all independent parameters (factors) were fixed except the temperature. These diagrams very well illustrate the complexity of rheological – shearing – properties of asphalt mixtures, pavements and asphalt concretes. Fixing the values of measured shear stress (\(\tau\)) and the distance (H) between the lower edge of the specimen holder (9) and the shearing plate (6) as well as the adjusted shear speed (v) the effective viscosity can be determined and fix and count by the attached computer (17) as:

\[ \eta = \tau(H/v) \text{[MPas]} \]  

(5)

4. Results and discussions

For the examination of rheological properties of asphalt pavements and asphalt concretes the same method were used which were developed by Gömze [8, 17, 18] to determine the rheological parameters of elastic fiber reinforced viscous-plastic materials and plasticized asbestos cement pastes. For the creep tests of asphalt pavements the combined rheo-tribometer instrument (Fig.1) was converted as it is shown in Fig.4.

Fig. 4. Schematic draw of creep tests for determine the deformation-time curves
\(F_1=\text{var - the loading force to create shear stress (N), } P_{\text{ny}}=F_2/A=\text{var – the pressure stress (MPa) in the tested material created by normal force } F_2 \text{ (N), } A=\text{const. – cross section (sheared surface) of Marshall-probe (mm}^2\text{), } Q=\text{var – the material and/or granular composition of Marshall-probes} \)

Depending on the values of the loading force \(F_1\) the typical deformation-time curves are shown in Fig.5. In case when \(F_1\) generate in the Marshall-probe shear stress less than the yield strength of the asphalt mixtures, concretes and pavements we can get the upper form of the deformation-time diagram, and in case when \(F_1\) generate shear stress larger
than static yield point and stress the lower drawing is got.

From the deformation-time curves the rheological model (Fig.6) and rheological parameters can be determined by method which is detail described in [8]. Main advantages of this new instrument are that from the generated deformation-time curves can be determined the most important rheological parameters of the tested materials as function of shear stress, pressure stress, material composition and temperature. These parameters are:

- instantaneous elasticity module (6):

\[ E_1 = f(\tau, p, Q, T) \] [MPa] (6)

- delayed elastic modulus (7):

\[ E_2 = f(\tau, p, Q, T) \] [MPa] (7)

- viscosity of the damaged material structure (8):

\[ \eta_1 = f(\tau, p, Q, T) \] [MPas] (8)

- viscosity of the undamaged material structure (9):

\[ \eta_2 = f(\tau, p, Q, T) \] [MPas] (9)

- static yield point (yield stress) of the tested materials (10):

\[ \tau_0 = f(\tau, p, Q, T) \] [MPa] (10)

On the basis of the realized experiments successfully were determined the most important mechanical and rheological parameters of asphalt pavements and asphalt concretes at different temperatures and mechanical stresses. The influence of the loading forces on these rheological parameters is shown in Table 1 at temperature of 100°C.

Table 1. The measured rheological parameters of asphalt pavements at different loading forces

<table>
<thead>
<tr>
<th></th>
<th>100 N</th>
<th>150 N</th>
<th>200 N</th>
<th>250 N</th>
<th>300 N</th>
<th>350 N</th>
<th>400 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau) [MPa]</td>
<td>0,0122238</td>
<td>0,018357</td>
<td>2,024476</td>
<td>0,030595</td>
<td>0,036714</td>
<td>0,042833</td>
<td>0,048952</td>
</tr>
<tr>
<td>(E_1) [MPa]</td>
<td>6,3636</td>
<td>3,818</td>
<td>3,182</td>
<td>4,545</td>
<td>4,773</td>
<td>5,568</td>
<td>5,415</td>
</tr>
<tr>
<td>(E_2) [MPa]</td>
<td>4,2425</td>
<td>3,818</td>
<td>8,483</td>
<td>5,303</td>
<td>4,772</td>
<td>4,949</td>
<td>2,828</td>
</tr>
<tr>
<td>(\eta_1) [MPas]</td>
<td>6,874</td>
<td>28,128</td>
<td>48,3</td>
<td>81,91</td>
<td>139,58</td>
<td>114,676</td>
<td>210,54</td>
</tr>
<tr>
<td>(\eta_2) [MPas]</td>
<td>0,572</td>
<td>2,4818</td>
<td>0,1186</td>
<td>12,6</td>
<td>5,473</td>
<td>6,745</td>
<td>11,6</td>
</tr>
<tr>
<td>(\gamma_n) [s^{-1}]</td>
<td>0,0032051</td>
<td>0,0032051</td>
<td>0,0032051</td>
<td>0,0016025</td>
<td>0,0048077</td>
<td>0,0048077</td>
<td>0,0033218</td>
</tr>
<tr>
<td>(\gamma_s) [s^{-1}]</td>
<td>0,135</td>
<td>0,649</td>
<td>0,0139</td>
<td>2,376</td>
<td>1,146</td>
<td>1,362</td>
<td>4,101</td>
</tr>
<tr>
<td>(t_1) [s]</td>
<td>1,0802</td>
<td>7,367</td>
<td>15,17</td>
<td>18,022</td>
<td>29,24</td>
<td>20,595</td>
<td>38,88</td>
</tr>
<tr>
<td>(t_2) [s]</td>
<td>0,031876</td>
<td>0,0201311</td>
<td>0,018608</td>
<td>0,043722</td>
<td>0,030067</td>
<td>0,0383164</td>
<td>0,076223</td>
</tr>
</tbody>
</table>

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Fig. 5. Typical deformation-time curves of asphalt mixtures and pavements depending on loading forces.

Fig. 6. Rheological model of asphalt pavements and asphalt concretes based on bitumen binders and mineral crushed stones and gravels.

The realized creep tests of asphalt materials on the developed speed instrument have shown the character of mechanical stress relaxation – therefore the reversibility a certain part of deformation which was created in the materials by the loading forces. Analyzing the measured parameters and their values as well as their characteristics the authors have found a new rheological model for asphalt pavements and cooled asphalt mixtures which are shown in Fig. 6. This new rheological model shows the complexity of materials like mineral gravels reinforced bitumen bound asphalts.

These complicated material structures like described above asphalt mixtures with damaged and undamaged particles under mechanical forces like automobile wheels can be characterized with “rheo-mechanical” equation as:

\[
\tau(t) = \tau_0 + \eta_1 \dot{\varepsilon} + \eta_1 \tau_1 \ddot{\varepsilon} - \dot{\tau} \left[ t_{fr} - t_r \left( 1 - \frac{\eta_1}{\eta_2} \right) \right] - t_{e} t_{fr} \ddot{\varepsilon} \quad [\text{MPa}] \quad (11)
\]

where:
- \( \dot{\varepsilon} \) – the first derivative of the deformation developing in material or shear rate (s\(^{-1}\))
- \( \ddot{\varepsilon} \) – the second derivative of the deformation developing in material or first derivative of shear rate (s\(^{-2}\))
- \( \tau_0 \) – static yield point (MPa)
- \( t_r \) – the delay time of the elastic deformation in the material (s)
$t_{fr}$ – the time of relaxation of mechanical stresses in material(s)

The equation (11) looks very complicated and probably it is better to transform into the shape like was used in equation (5). In this case the effective viscosity measured by instrument can be described as:

$$\eta_e = \frac{\tau_0 + \eta_1 \varepsilon + \eta_1 t_r \varepsilon}{\varepsilon + t_{fr} + t_r \varepsilon + \varepsilon \left(t_{fr} - t_r (1 - \frac{\eta_1}{\eta_2})\right)}$$

(12)

The equation (12) shows the complexity of the viscosity of asphalt pavements and asphalt concretes measured and fixed on combined rheo-tribometer during the rheological test of Marshall-probes.

5. Conclusions

On the basis of investigation and examination of rheological properties complex material structures like ceramic raw materials, concretes and elastic fiber reinforced viscous-plastic materials at the Department of Ceramics and Silicate Engineering in University of Miskolc the authors examined the rheological properties of asphalt pavements and asphalt concretes and successfully created a rheological model (Fig.6) which can give adequate answer on phenomena of troughs taking place under the automobile wheels on asphalt pavements and asphalt concretes of roads.

As results of the realized investigation and experiments the authors gave a mathematical equation (11) which capable describe and explain the complexity of mechanical properties and behavior of asphalt pavements during their usage in different climate zones and conditions.

The realized investigation and examination at wide range of mechanical stresses and temperature of asphalt pavements and asphalt concretes made from different mineral and bitumen compositions have shown the complexity of the rheological properties and their mechanical behavior under different mechanical stresses and temperatures during their exploitation.

References


Relations between the material structures and drying properties of ceramic bricks and roof tiles

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Abstract. In our days when energy costs can be solved the competitiveness not only of a certain company but the ceramic brick and roof tiles industry also it is very important to understand the thermodynamic processes and changes in the material structures during drying of plastically formed semi-products. In their work the authors underline that the plastically formed ceramic bricks and roof tiles have large number of micro-pores and micro-capillars with “diameters” less than 1 or 2 µm. Remove the water drops from these micro and submicro pores and capillars it is necessary to load mechanical or thermomechanical pressure with hundreds of MPa or more to overcome the surface tension of these water drops. Finally the authors have found that increasing the temperature and speed of drying the drying shrinkage has decreased considerably decreasing the tensile stress inside the ceramic bricks and roof tiles specimen.

Keywords: drying, microstructure, pore-structure, porosity, heat transfer, shrinkage

1. Introduction

Engineers and experts working at brick and ceramic roof tile manufacturing plants have been engaged in making the drying of produced green bodies more efficient already since the end of the 19th century [1, 2]. However, the first theoretic study - significant in respect of material science as well - was hallmarked with the name of Pukall W. [3] at the end of the twentieth years of the last century. This apparent delay of the applied theoretic researches is obvious, since the demand aiming at the theoretic and experimental analysis of material flowing, transformation and thermal processes occurring during the drying of such complicated material structures like extruded green bricks or pressed ceramic green roof-tiles, presented itself for the first time only at the middle of the 20th century, when artificial dryers came into general use [4, 5, 6, 7].

From this era it is worth mentioning the name and work of Csiszkij A.F. [8] determining not only the shrinkage, the bending- and compressive strength of the dried profiles on the basis of regression equations, but establishing at the given temperature
also the "critical drying time" pertaining to the knee presenting itself at the end of the linear drying, shrinking section, based on the Bigot curves. For the analyses - for setting the regression equations - Csizskij altered the raw material composition, the mineral- and moisture content, the drying temperature as well as the relative moisture content of the drying air. His work is all the more significant because in the field of ceramics he was the first scientific researcher to process the obtained test results by means of mathematical-statistic methods. Later Csizskij’s results were developed further on by Schmidt H. [9] and Ratzenberger H. [10 and 11] applying the quadratic polynominal regression model.

From among the European researchers analysing the drying sensitivity and drying properties of the raw materials for brick and ceramic roof-tile production, Bálint Pál and Tóth Kálmán [12] were among the first to succeed in stating the relation between mineral composition of the mining materials used for green production and the parameters of the applied manufacturing and drying technology using the regression equation with 0,9 correlation coefficient. Their work was focused among others on plasticity, the drying sensitivity and the porosity of the dried product (profiles) as a function of the montmorillo- nite and chlorite content of the different mining materials used for the production and the mass ratio of grains less than 10 μm resp. 2 μm fractions. More publications were issued on the statistic method applied by them and the results of their research work [13, 14].

Several reports were published in the journal „Építőanyag” (Building material) on the results attained in the analysis of the drying properties of mining materials for the brick and tile industry. Surely, the most important works of them are those elaborated by Bálint P. [14], Sopronyi G. [15], as well as Vér- tesffy K. and Verdes S. [16], testing by up-to-date mathematical and statistic methods the drying properties of the newly formed green products of the brick and tile industry as a function of the mineral content of the mining materials - the quantity of materials belonging to the caolonite, illite and smectite group. The obtained regression equations enabled the conclusion that it was the quantity - the proportion - of the mineral materials belonging to the smectite group that exercised the greatest influence on both the drying process and the physical and mechanical properties of the dry semiproducts.

2. Materials, theoretical and experimental procedures

Nowadays, apart from the quality, it is the specific energy costs that essentially determine the market competitiveness of a product or technology. As far as the reduction of the specific energy costs is concerned, it is of vital importance to understand and correctly interpret the thermomechanical processes occurring during drying and dehydration of brick and tile basic materials and formed green bodies [17]. The discovery and comprehension of physical-chemical connections and relations between the microstructure as well as the drying and dehydration properties of brick and tile basic materials resp. green bodies can significantly contribute to the improvement of
the efficiency of the applied drying technologies and the reduction of the specific energy costs of the drying procedures [18]. At the same time the ever increasing transmission capacity of the raw material preparation and extrusion machines of the production lines applied in the brick and tile industry [19] also requires that the pressed green products be dried during a considerably shorter period. During our research work aiming at the discovery and comprehension of the relations between the material structure of the brick and ceramic roof-tile green products as well as their drying and dehydration properties, 18 basic materials - mining materials - from Hungary, 6 ones from Romania and 4 ones from Austria were analyzed. Our tests were aimed at replying the following questions:

- What does the extent of drying shrinkage and drying sensitivity depend on?
- Mechanical stresses of what character and what size do occur during the drying of green bricks and roof-tiles?
- How is the drying procedure influenced by the temperature, the relative moisture content of the drying air as well as the mineral composition, the moisture content and the microstructure of the green brick?
- What can cause dehydration cracks following perfect drying?

When examining the drying properties of the green brick and pressed ceramic roof-tile, we determined first of all the mineral composition of the obtained mining materials using a Bruker D8 ADVANCE type X-ray apparatus, then established the BET and Langmuire specific surface area of the uncrushed samples taken from them by means of a Tristar-3000 apparatus. Thereafter we measured the moisture content of the obtained basic - mining - materials; and carried out the usual thermo-analytical tests by plotting the DTA, TG and DTG curves in the temperature range of

\[ 20^\circ\text{C} \leq T \leq 1000^\circ\text{C} \] (1)

using a derivatograph. Having completed the above basic tests we prepared mixtures according to the formulas specified in the experimental plan then adjusted the moisture content values as required for forming. We used a laboratory muller to produce the grain size and grain structure required for forming, then prior to the extrusion we determined again the BET and Langmuire specific surface areas. The green profiles required for the tests were produced by means of a KEMA–PVP5 type vacuum extrusion machine, while a „HOKER” type climatic chamber was used for drying. This type of climatic chamber has an advantage whereby the temperature and the quantity of the drying air can be regulated together with its relative moisture content and flow rate. For plotting the Bourry-Morozov drying diagrams shown in Fig. 1., we measured the length, the cross section and the mass of the tested profiles per given time units.

Our tests showed that the basic materials–materials, the Bourry-Morozow diagrams of which had a greater – more inclined – negative angular coefficient at the initial section, were more sensitive. The green bricks prepared therefrom shrank significantly
quicker – more intensively – in the initial phase of the drying procedure compared to those having a less inclined negative angular coefficient in the same phase.

For the mathematical determination – calculation – of the energy required for the convective drying of the green bricks and green ceramic roof tiles in an in-line chamber type quick-drier, a so-called agitator vessel model was used under adiabatic thermal- and energy-transfer conditions. Later, having learned the work of Junge K., Tretau A. and Specht E. [20], we used for our tests the mathematical relations developed by them. For the simulation of the kinetics of quick drying, the above authors have developed well applicable software as well, enabling the simple and quick modeling – testing – of the relation among the supply air mass flow, the green product water load, the energy requirement of drying, the evaporation rate and the planned drying curve.

![Typical Bourry-Morozow diagrams of the drying procedure of the green bricks](image)

**Fig. 1.** Typical Bourry-Morozow diagrams of the drying procedure of the green bricks

To our regret, the Junge-Tretau-Specht software was not available for us; thus we tested the mathematical relations given in their work [20] by means of the MathCAD program well-known for us. Mainly the curves shown in Fig. 2, taken over from the author’s work, raised our interest, whereby the increase of the temperature of the drying air involves considerable decrease of the energy requirement of drying.
In their above mentioned work [20] the authors also describe that as a result of quicker drying at higher temperature the drying shrinkage of the green brick products will decrease. We often experience the phenomenon of reduced drying shrinkage as well; Fig. 3 shows an example demonstrating the drying shrinkage of green bricks composed of 4 mixtures of different composition.

<table>
<thead>
<tr>
<th>Components [dkg]</th>
<th>Mixture 1</th>
<th>Mixture 2</th>
<th>Mixture 3</th>
<th>Mixture 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>100</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>D</td>
<td>50</td>
<td>0</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>Sawdust</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>23.4</td>
</tr>
<tr>
<td>Total</td>
<td>390</td>
<td>340</td>
<td>400</td>
<td>413.4</td>
</tr>
</tbody>
</table>

Fig. 3. Drying shrinkage of green bricks composed of four different compositions

3. Results and discussion

Fig. 3 is showing the drying shrinkage of the green bricks as a function of the mineral composition and the drying temperature, clearly demonstrates that the composition has at least the same influence on the drying shrinkage as the temperature. From
among the mining materials illustrated in the figure „A” contained more of montmorillonite and illite, „B” of illite and smectite, „C” of illite and chlorite and „D” of chlorite and mainly silica flour (exceeding 50%). At the same time materials „A” and „D” contained also muscovite and kaolinite in appr. 5 to 10 mass%. The saw-dust added in 3 mass% as a pore-forming additive has a remarkable drying shrinkage reduction effect!

The differences in the drying shrinkage and drying sensitivity of the green bricks made of different basic materials, mixtures, revealed the importance of the mineral composition, the moisture content, the microstructure, grain- and pore-sizes of the applied basic materials. While testing the material structures to discover the effect of the microstructure on the drying shrinkage, it was interesting to observe how the tetartoid [18] crystal structure of the quartz (Fig. 4) reminded of the water molecule structure [17]; respectively how the dipolar H-O-H chain [21] formed by the water molecules resembled the –Si-O-Si-O-crystal chain of the silicate soda glass [22].

Fig. 4. Structure of the quartz crystal and the water molecule

It is due partly to its above mentioned material structure, partly to its dipolar property, that water can be so properly used for wetting the basic materials of bricks and ceramic tiles, the mineral mixtures rich in quartz. At the same time it is well-known that the tensile stress produced by the surface stress in the water drop can be determined on the basis of the following relation:

\[ p = \frac{2\sigma \cdot \cos \alpha}{r}, \text{[Pa]} \]  

(2)

where:
- \( \alpha \) - wetting angle,
- \( \sigma \) - surface stress of the water drop, [N/m],
- \( r \) - radius of the water drop, [m].

Consequently it is essentially important to learn the microstructure (Fig. 5) of the raw materials to be applied even before forming (extrusion).
In Fig. 5 the size, the shape and the open porosity of the different grains of the mining material used for brick production can be observed well, and the form and size of the gaps (cavities) among the grains can also be seen well. By means of the figure the total volume of the pores and „gaps” in the clay used for green production can be determined as follows:

\[ V_{p\delta,a} = \sum_{i=1}^{A} V_{npi} + \sum_{j=1}^{F} V_{zpj} + \sum_{k=1}^{C} V_{kp} + \sum_{l=1}^{D} V_{htl}, [m^3] \]  

(3)

After the extrusion the free gaps among the grains will cease; part of them will be converted into closed or open pores and capillaries, while the other part of them will definitively cease; the total pore volume can be determined as follows:

\[ V_{p\delta,e} = \sum_{i=1}^{E} V_{npi} + \sum_{j=1}^{F} V_{zpj} + \sum_{k=1}^{G} V_{kp}, [m^3] \]  

(4)

The symbols used in relations (3) and (4) are as follows:
- A, B, C, E, F and G - number of the open and closed pores as well as capillaries in the clay used for green production respectively in the extruded green brick.
- D - number of the gaps among the grains of the clay prior to extrusion.
- \( V_{npi} \) - i-th open pore volume, \([m^3]\),
- \( V_{zpj} \) - j-th closed pore volume, \([m^3]\),
- \( V_{kp} \) - k-th capillary volume, \([m^3]\),
- \( V_{htl} \) - l-th gap volume among the grains, \([m^3]\)
The specific pore volume of the clay used for green production can be determined by means of the following relation:

$$V_{af} = \frac{V_{a,5}}{V_{p5,a}} \cdot 100\% \text{[\%]}$$  \hspace{1cm} (5)

while for the determination of the specific pore volume of the extruded green brick the following relation can be applied:

$$V_{tf} = \frac{V_{nt5}}{V_{p5,e}} \cdot 100\% \text{[\%]}$$  \hspace{1cm} (6)

where:

- $V_{a,5}$ - total volume of the clay used for green production, before extrusion; [m$^3$]
- $V_{nt5}$ - total volume of the extruded green „compact“ brick, before drying; [m$^3$]

While the green products for brick production are extruded, respectively the green ceramic tiles are pressed, the water used for the forming processes „gets jammed“ into these open and closed pores, the capillaries and gaps among the grains, which is to be removed during drying. The smaller the pores filled with water are - in case of identical total volume - the more energy will be required for their removal (evaporation). Thus for example in case of a 200 μm diameter pore the heat transferred to the water drop shall ensure that the pressure produced by evaporation surpass the 1,5 MPa tensile stress produced by the surface stress of the water drop. In case of a water drop jammed in a 2 μm diameter pore this value is already 150 MPa! Driers and drying technologies applied at present are not capable of producing evaporation „steam-pressure“ of such an extent. Among others it is due to the high pressure required to remove the water from the micropores that at least 1 to 3% water still remains in each case in the green brick and ceramic roof-tile products when drying is over.

Quick drying at high temperature of porous materials like green bricks or ceramic roof-tiles raises several questions. For example: What will happen when the water in steam form passes across the „wall“ of the product at high pressure, through a nanometre diameter, needle-like capillary and arrives in one or more macrometer size pores [23]? or: How can the phenomenon of the so-called „heat pipe effect“ observable in such cases be explained [17]? The reply to these questions can be found only in the changes occurred in the material structure - the micro- and nano-structure - of the formed green brick and ceramic roof-tile during the drying procedure (Fig. 6 and 7).

Fig. 6 illustrating the material structure at thousand times magnification demonstrates how the surface of the grains building up the green brick, the form and size of the gaps among the grains change during the drying procedure as a result of temperature increase. When the drying temperature is increased from 150°C to 300°C, the size of the gaps among the grains considerably increases, while the grains themselves will become smaller due to the thermal shrinkage. The gaps among the grains will continue to exist in the form of closed pores or capillaries even after burning,
thus the applied drying temperature and technology are of decisive importance in respect of the material structure, the thermal physical properties and the mechanical strength of the burnt brick and tile products.

Fig. 6. Change in the material structure of the green brick in case of drying at 150°C and 300°C.

Fig. 7 demonstrates the material structural changes over the surface of a single grain of the green brick as a function of the drying temperature, at ten thousand times magnification.

Fig. 7. Change of the material structure of a single grain.

According to Fig. 7, as the temperature is increased from 150°C to 300°C, the tested independent grain - of some 10^m size only - became essentially more compact; while the number of the open pores over its surface considerably decreased and their size became smaller. Simultaneously, as the drying temperature increased the surface of the tested grain became less articulated, while the number of the submicronous and nano-size crystals - grains - considerably increased.

6. Conclusions

The results of the performed thermodynamical analyses, drying experiments and material structural tests can be summarised as follows:
Prior to drying, the material structure of the formed green brick and ceramic roof-tile is rather articulated, it is full of some micrometer or smaller pores and capillaries, thus internal pressure of more MPa shall be produced to surpass the surface stress. The production of such an internal “steam-pressure” requires considerably higher drying temperature compared to the value being generally in use at present!

As the drying temperature was increased - the drying process was accelerated - the drying shrinkage of the formed green bricks and ceramic roof-tiles decreased in each case, reducing thereby the tensile stress in the drying product produced by the shrinkage.

The material structural tests performed on the produced profiles before and after drying revealed that as the drying temperature increased, the gap among the micrograins increased as well, while the grains themselves shrunk. At the same time due to the great number of gaps - pores and capillaries - among the micrograins, and their increased size resulted from more intensive drying, the shrinkage of the produced profiles decreased as far as the macro-size was concerned.

The drying temperature and the drying dynamics can essentially influence the material structure of the brick and ceramic roof-tile, whereby also their mechanical and physical properties, most important in respect of their application, will be influenced. The discovery and comprehension of these relations require further tests and researches.

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Impact of nitrogen atmosphere on sintering of alumina ceramics

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Abstract. In this paper the influence of nitrogen atmosphere during sintering on alumina ceramics is examined. The authors have found that thanking to the nitrogen atmosphere a new material phase can be formed increasing the mechanical properties of the traditional Al₂O₃ ceramics. The investigation of microstructures and material compositions of sintered in nitrogen atmosphere alumina ceramics scanning electronmicroscopy, EDAX and X-ray diffracture methods were used.

1. Introduction

Several industries, like electronics have been using products made of very high purity (>99.9%) Al₂O₃ powder because of their excellent mechanical and electrical properties. These products are mainly produced by dry pressing, sintering. In order to achieve the special mechanical features the use of the right technology is as important as the selection of the raw material.

Many studies are investigating the sintering behavior of alumina, its microstructure [1, 2, 3]. Our work until now has focused on obtaining deeper knowledge about these properties and on the description of mechanical characteristics of alumina, heat treated in nitrogen atmosphere [4].

Heat treatment in nitrogen gas is a well-known technology for steels, resulting the increase of surface hardness of steels, their wear resistance, resistance to repeated use and corrosion. In this procedure alloy elements - carbon, nitrogen, silicon, and aluminum - are entered into the surface layer of the steel by diffusion - modifying, improving its mechanical and chemical properties [5, 6, 7].

The purpose of the present study is to present the results of heat treatment in nitrogen inert gas of alumina ceramics, and to discover the changes in the microstructure of the surface layer.

According to the literature several authors are dealing with the use of nitrogen atmosphere by adding other additives (AlN) [8, 9, 10, 11]. During the sintering the nitrogen - entered in the form of gas or solid substance (AlN) - and its reaction with the rigid, solid material produces a new substance, a very tough material, keeping its mechanical properties. The result of heat treatment in nitrogen inert gas is the
production of AlN and AlON, besides Al₂O₃. AlN has several excellent properties, its thermal conductivity, specific resistance is high, and dielectric constant is moderately low. AlN cannot be found in the nature. It can be produced by nitridation of metal aluminum powder, or by the carbothermic reaction of alumina powder [12]. AlON is a kind of polycrystalline material, the structure of which is just the inverse of spinel. It is a glass-like, poreless material of great hardness, but with low heat conductivity. Among the methods to be used for the production of alumina nitride phase the most popular are simultaneous reduction and nitridation of Al₂O₃, oxynitridation of metal aluminum during firing, its gas phase reaction with AlCl₃, direct reaction between Al₂O₃ and AlN [9].

According to the literature the reaction of Al₂O₃ and AlN produces AlON phase above 1650°C, which can be made by plasma spraying, adding AlN, sintered in nitrogen gas.

In the plasma spraying technology first the Al₂O₃/AlN composite powder is sintered in Ar/N₂ plasma (-10000K), which is direct nitridation of alumina. With this method cubic lattice AlN can be produced, containing N- and O-ions. The AlN and γ-Al₂O₃ content of the thus produced material is growing compared to the AlN and Al₂O₃ content of the original (starting) material. Thus further heat treatment is required in nitrogen gas at 800-1200°C for 2 hours with temperature holding. As a result of later heat treatment the AlN will be of hexagonal lattice, the AlN quantity will increase, but the γ-Al₂O₃ content will decrease [13].

The quantity of AlN added to Al₂O₃ and the sintering temperature influence significantly the material microstructure.

![Fig. 1. Phase diagram of AlN- Al₂O₃](Taken from: Alien M. Aiper: Phase Diagrams in Advanced Ceramics 29 [14])
During sintering in nitrogen gas homogenous microstructure is achieved with lower
(<10 mol%) AlN content, AlION appears on the contact surface of alumina. At higher AlN
content the produced AlION is around the grain boundary of alumina.

McCaulley and Corbin sintered in situ the AlN and Al₂O₃ powders, grinded together.
Several combinations of production parameters were discovered. As shown by Figure 1
the liquid phase can be found in a very narrow stripe of the solid phase at high
temperature. The results of sintering at 1975°C are grain porosities, but the higher
temperature (2025°C) produces much less porosity and ALON.

The method was improved later; the starting powder is 0.5 μm and smaller grain size
distribution ALON powder, formed by preliminary reactions [15]. Reaction of the
starting powder:

\[
\text{Al}_2\text{O}_3(s) + C(s) + N_2(g) \geq \text{ALON}_n(s) + \text{CO}_2(g)
\]  

Tabary, Servant and Alary observed that carbon is present in two forms. On the one
hand, in the form of graphite not entering into reaction during melting, and on the
other side in a form embedded into separations, becoming an Al-O-N-C quaternary
system.

Fig. 2 shows the phase structure of „ALONC“ in Mol quantity along the line connecting
points a P₁ (25% Al₂O₃ - 75% AlN) and P₂ (60% Al₂O₃-20% AlN - 20% Al₄C₃). The
intersection point of Al₂O₃-Al₄C₃ section can be 26.5mol% Al₄C₃, not following the
literature value. Thus Al O C can be found at 20 mol% Al C and Al₂OC, and also at 50
mol% Al₄C₃. Three dominant AlN based compositions can be distinguished. The general
form is AlN- Al₂O₃ in pseudo-binary system it is AlₙO₃Nₙ₋₂. In the Al₂O₃- Al₄C₃ pseudo-
binary phase this formula becomes Al₁₄₋₄O₁₅ₓC₃ where \( x = 8; 6; 5; 4,4 \) and 4; and the
\( M/X = n/n+1 \) ratio is equal to 4/5, 5/6, 6/7, 7/8, and 8/9, where \( M = (n_{Al}) \) and \( X =
(n_{O}+n_{C}) \). [16]
2. Test conditions

During the experiment the sintering abilities of alumina powders of different purity were investigated with the use of nitrogen gas. Table 1 shows the compound of the powders applied by us, according to the datasheet of the manufacturer partly 3% polyvinyl-ester, polyvinyl-ethanol, polyvinyl-glycol, partly 6% magnesium-silicate and 5% alkali-earth metal carbonate are needed to the preparation of pressing powders. Of the Kreutz SPG 95 and Alcoa CT 3000 SDP alumina powder is shown in Table 1. annular specimen were made with bilateral pressing by the mechanical press of Mikeron Kft, where the diameter of the pressing tool dowel was 34,6 mm, the diameter of the housing was 47,7 mm.

Table 1. Content of applied pressing powder

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kreutz SPG 95</th>
<th>Alcoa CT 3000 SDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>= 95%</td>
<td>99,7%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2,2%</td>
<td>0,02%</td>
</tr>
<tr>
<td>MgO</td>
<td>1,40%</td>
<td>0,1%</td>
</tr>
<tr>
<td>CaO</td>
<td>1,10%</td>
<td>0,03%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt; 0,2%</td>
<td>0,08%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>&lt; 0,3%</td>
<td>0,02%</td>
</tr>
</tbody>
</table>

Part of the raw specimen was pre-sintered in normal way, at 1250°C, the remaining part in nitrogen gas at 1420°C in composition-type resistor furnace. The pre-sintered semifinished product was sintered at 1640°C in Nabel HT128 type furnace of Mikeron Kft.

The additive content of pressing powders was tested by DSC- equipment. Microstructure of the burnt specimen was tested by SEM, EDAX and X-ray diffraction meter.

3. Results

The DSC diagram of Al₂O₃ powders was taken into account to the establishment of test conditions (Figure 3). The investigation confirmed that in the presence of oxygen the organic materials begin to evaporate at 240-250°C out of the 95 and 99,7% content pressing powder. The evaporation process lasts nearly until the attainment of 800°C. Thus in our test during the pre-sintering process the N₂ gas had been continuously flown from 500°C. It is known that with the reduction of oxygen the dissociation of organic materials cannot be completed, thus some percentage carbon is left in the biscuit baked, sintered ceramics [17].

Fracture surface of samples pre-sintered in nitrogen gas and burnt in normal atmosphere (Figure 4) was tested, analyzed.

It can be seen on Fig. 4, that in the external layer of the specimen a new,
characteristically different - form the traditionally sintered Al$_2$O$_3$ ceramic - structure had developed.

Fig. 3. DSC analysis of 95% Al$_2$O$_3$

Fig. 4. Fracture surface of N$_2$ heat treated, sintered Al$_2$O$_3$ by SEM (95% Al$_2$O$_3$; pressure: 177,1 MPa; max time of pressure: 15 s)

Fig. 5 shows the spectrum of the average composition of the fracture surface. The picture shows that besides aluminum and oxygen, carbon has also appeared.

Figure 6 shows outer layer of the fracture surface of 95% Al$_2$O$_3$ ceramic with
M=10000X enlargement. Square granules typical of alumina, as well as the great number of tiny granules left out of consideration until now were observed! The tiny granules are only of 0.1-1 μm size. Here the traces of a new phase in the middle of the specimen could be seen.

Fig. 5. Fracture surface of N₂ heat treated, sintered Al₂O₃ by EDX

Fig. 6a. Fracture surface of N₂ heat treated, sintered 95% Al₂O₃

Fig. 6b. Innert part at fracure surface of N₂ heat treated, sintered 95% Al₂O₃

The structure of ceramics heat treated in nitrogen gas was determined on the basis of X-ray diffraction test. The results are shown on Figure 7. It can be seen that next to the tips of Al₂O₃ carbon in crystal form, and also Al₄N₃CO (ALONC) had appeared. Most of the ALON tips fit to the diffractogram, its presence is still not completely proved. The results of our experiments are significant, since we have proved, that already at relatively low temperature ALONC is produced in alumina ceramics of traditional „contamination“ pre-sintered in nitrogen gas.

Observations of Tabary, Servant and Alary support our findings, that carbon is present in two forms. Once in the form of graphite, which does not enter into reaction during melting, and in the form of Al-O-N-C quaternary system.
4. Conclusion

1. Our tests clearly confirm that during sintering of Al$_2$O$_3$ nitrogen gas exercises similarly positive impact on the material structure and mechanical behaviour of the ceramics, as is the case with nitridating, or carbo-nitridating of steel alloys. It was proved by SEM photos that close to the surface of the sintered body 0,1 μm granules develop and distribute in large volume in the material structure, owing to the presence of which the water and gas compactness and mechanical stability of the material system is significantly increasing.

2. On the basis of the tests it can be stated, that with the use of the right production technology (pressing, sintering atmosphere, sintering temperature) excellent quality products can be produced of the 92 - 99,7% Al$_2$O$_3$-content basic materials of traditional „contamination“, which had only be produced until now of the 4th and 5th generation high purity Al$_2$O$_3$.

References


Remnants of organic pore-forming additives in conventional clay brick materials: Optical Microscopy and Scanning Electron Microscopy study

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Abstract. The transformation in the convectional brick clays of the organic pore forming additives during their firing was examined. These organic pore forming additives were rice husks, sunflower seed husks and sawdusts. The firing of convectional brick clays with these bio-origin pore forming additives was made in normal atmosphere (oxidation) at 900°C. The mineral composition of the used convectional brick clay and pore forming additives before and after firing were examined by X-ray powder diffraction (XRPD), the thermal physical properties by derivatograph (DTA), by optical (OM) and scanning electron microscope (SEM). The authors have found that these bio-origin pore forming additives preserved their morphological structures meanwhile part of them became mineralogical structure.

1. Introduction

Conventional clay bricks are the most frequently used building materials in the past few centuries of human history. Production of clay bricks does not desire special raw material processing, preparation process or firing techniques, the bricks can be prepared from the raw clay, in producing facilities set up in the nearby of raw material source, decreasing the costs of production. The clays used in brick production are a mixture of plastic, hydrated minerals - the clay mineral fraction, and nonplastic minerals. The plastic minerals are clay minerals such as montmorillonite, vermiculite, chlorites, illite and kaolinite. The non-plastic part of clays is made up by micas, most frequently muscovite and biotite, feldspars and quartz. Carbonates like calcite and dolomite, or siderite also are present in variable amounts. As impurities, iron oxy-hydroxides and detrital organic matter are present.

During time, clay brick production techniques were adapted to fit the requirements of new product types. Where buildings were exposed to high humidity media, the resistance of brick was increased by rising the firing temperatures. Excessive plasticity of raw clays was treated by the addition of vegetal materials, usually straw. The same
technique was applied when an increase in the dry mechanical resistance was desired. Possibilities of improving the mechanical properties of fired products by the addition of organic materials of vegetal origin, like rice husks [1] or derived products of these, like sawdust ash [2] or rice husks ash [3] were also investigated.

By the increasing energy demand of heating of the buildings for human living, the attention of brick producers was directed towards the thermal isolation capacity of building materials. In the case of traditional clay brick, the solution for increasing the thermal isolation capacity (thus decreasing heating costs) is the artificial increase of porosity. Beyond the primary porosity of fired clay material, caused by the decomposition of carbonates, contraction of clay minerals and organic matter combustion, the introduction of pore-forming additives contributes to the increase of porosity of bricks. Different inorganic (calcite, dolomite [4]) and organic (wastes from different industrial activities [5], [6], [7]) types of additives were tested for suitability in brick production. In published papers, the attention of brick producers is directed towards the ceramic properties of materials with additives, such as compressive and bending strengths, capillary water up-take and capacity of heat conductivity, which are the main properties that characterize building materials [8], [9]. However, the transformation reactions of the additives and their interactions with the transformations suffered by the clay during firing are also important to know, from the point of view of microstructure stability and mineral phase equilibrium in the fired products [10], [11].

In this study we discuss results of observations made on the transformation of sawdust, sunflower seeds hull and ungrounded rice husks in fired laboratory samples.

2. Materials and Methods

The samples considered in the present study were obtained from clay used in brick production, mixed with the three organic pore-forming additives: sawdust, sunflower seeds hull and rice husks. Sample preparation and firing was done in the micro-pilot laboratory of the Department of Ceramic Materials and Silicate Engineering, at the University of Miskolc. The admixtures were homogenized in a Koller homogenizer and cylindrical samples of 3 cm in diameter were extruded by vacuum extruder. Extruded samples were oven-dried and fired at 900°C in oxidative atmosphere, with linear heating up and a soaking time of 2 hours.

The determination of mineralogical compositions and observations on the microstructure of raw and fired samples were performed at the Department of Mineralogy and Petrology, University of Miskolc. The compositions of raw materials pore forming additives and fired samples were determined by X-ray Powder Diffraction (XRPD) on a Bruker D8 Advance diffractometer in Bragg-Brentano geometry equipped with Cu-Ka radiation source. Clay and fired samples were prepared by grounding in agate mortar, while samples of additives were ground via liquid N₂ freezing. Thermal behavior of clay and additive samples was tested by Derivative Thermal Analysis (DTA)
Characterization of raw additives and fired samples was performed by Scanning Electron Microscopy (SEM) and Optical Microscopy by plane- polarized light (OMPL). OMPL observations were carried out on a Leitz -Wetzlar microscope, on thin sections prepared from fired samples, in order to distinguish between amorphous and crystalline phases associated with grains of additives. Samples for OMPL were embedded in acrylic resin and polished with diamond paste. Parallel with SEM observations, the chemical composition of different phases was checked by Energy Dispersive Spectrometry (EDS) on a Jeol JXA 8600 Superprobe at 15 kV and 15 and 20 nA. Back-scattered Electron (BSE) imaging technique was applied to enhance chemical contrasts in the microstructure. SEM analyses were carried out, with graphite coating, both on fracture and polished surfaces. For the later, samples prepared for OMPL were used.

The mineralogical composition of clay, by XRPD, is given by illite, kaolinite, vermiculite and chlorite, among with important amounts of quartz, calcite and dolomite. Presence of muscovite and feldspars is significant also. Pyrite and goethite are present as accessory minerals.

**Characterization of raw additive samples**

Based on XRPD analysis the organic pore-forming additives are composed mainly of cellulose (Fig. 1).

![Fig. 1. XRPD pattern of additives. Cellulose is the main component](image)

The DTA analyses revealed the main thermal domains in which the organic matter of additive samples suffers transformation reactions (Table 1). The first domain is characterized by a strong endothermic reaction between 50 and 190 °C, associated with a weight loss of ~ 7% due to the loss of adsorbed water and volatile compounds. The second domain is determined by the strong exothermic reaction between 190 and 390°C, associated with weight losses in different percents for the different samples. This reaction is due to the oxidation of hard organic compounds from the composition of...
vegetal matter, like lignin and cellulose. After this reaction, the cellulose framework of organic matter decays. Following the second domain a series of smaller endothermic reactions can be observed, with a continuous weight loss up to 15%. These reactions can be associated to polymorphic transformations of phases of residual carbon and inorganic compounds from the vegetal matter [12].

Table 1. The main thermal reactions of vegetal additive material

<table>
<thead>
<tr>
<th>Thermal domain</th>
<th>Parameters</th>
<th>Sawdust</th>
<th>Sunflower seeds hull</th>
<th>Rice husks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ΔTG wt%</td>
<td>7,66</td>
<td>6,91</td>
<td>7,4</td>
</tr>
<tr>
<td></td>
<td>DTA T₀</td>
<td>52</td>
<td>49</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>DTA T_max</td>
<td>116</td>
<td>113</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>DTA T₁</td>
<td>184</td>
<td>186</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>ΔDTA</td>
<td>-5,421</td>
<td>-6,959</td>
<td>-9,925</td>
</tr>
<tr>
<td>2</td>
<td>ΔTG wt%</td>
<td>51,25</td>
<td>53,2</td>
<td>41,95</td>
</tr>
<tr>
<td></td>
<td>DTA T₀</td>
<td>170</td>
<td>191</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td>DTA T_max</td>
<td>295</td>
<td>276</td>
<td>285</td>
</tr>
<tr>
<td></td>
<td>DTA T₁</td>
<td>385</td>
<td>376</td>
<td>379</td>
</tr>
<tr>
<td></td>
<td>ΔDTA</td>
<td>11,921</td>
<td>14,055</td>
<td>14,736</td>
</tr>
</tbody>
</table>

Observations by SEM on the raw additive material helped to understand the structure of vegetal materials used and to link the observed remnants to the original materials (Fig. 6 and 7). The composition of vegetal samples was checked for cations and mineral matter content by EDS measurements. The grains from sawdust have a fibrous structure, with fibers empty on the inside. The material building up fibers has a massive structure; contents of Ca, Mg and locally Si were detected. The structure of material building up the hull of sunflower seed has a more porous structure, longitudinal channels can be observed. Porosity of material is increasing towards the interior of the hull. The outermost sheet has a compact structure and is enriched in K (the lighter sheet of the structure showed in Fig 6, image from the center). The structure of rice husks is compact, and towards the inner side a gradual enrichment in Si is observed. The innermost sheet is very rich in Si and has an uneven surface.

**Characterization of fired samples**

After firing, all the samples presented the characteristic homogenous “brick” colour, indicating the uniformity of firing. The semi-quantitative mineralogical composition of the fired samples determined by XRPD is listed in Table 2. The composition is that characteristic for clay bricks made from clay with carbonates [13], characterized by the presence of newly formed minerals such as diopside and gehlenite. The gehlenite is present as an intermediate member of the gehlenite -ackermanite series. Muscovite
and quartz are preserved from the clay material, and a neo-formation of feldspars is observed. The mineral phases present do not defer between samples with different additives, only variation in their relative percentage can be observed.

Table 2. Semi-quantitative mineralogical composition of the fired samples based on XRPD

<table>
<thead>
<tr>
<th>Phases</th>
<th>F(%)</th>
<th>R(%)</th>
<th>N(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite calcian (NaCa)AlSi₃O₈</td>
<td>27</td>
<td>23</td>
<td>29</td>
</tr>
<tr>
<td>Gehlenite Ca₂(MgAl)(Si₂AlO₇)</td>
<td>11</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Quartz SiO₂</td>
<td>32</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>Augite MgCaFeSi₂O₆</td>
<td>8</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Hematite, syn Fe₂O₃</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Muscovite K(AlSi₃)O₈</td>
<td>5</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Microcline maximum K(AlSi₃)O₈</td>
<td>10</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>Anhydrite CaSO₄</td>
<td>3</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Pseudowollastonite Ca₃(Si₃O₉)</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Akermanite Ca₃Mg(Si₂O₇)</td>
<td>1</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

A. OMPL study. Observations by optical microscope with plane-polarized light in thin sections were performed to study the relations of the remnants of pore forming additives to the matrix of the samples.

Based on the optical properties, the material building up the remnants PA is of inorganic nature, with amorphous structure and colored by hematite identically to the matrix of the samples. The different PA generates remnants in different relations to the matrix. Contraction of the mineralized remnant relative to the original size of additive grain can be determined as the distance between the remnant and the pore enclosing it. In the case of sawdust, the material of remnants is mostly jointed with the matrix, without large separation surfaces surrounding it (Fig. 2). The fibers from wood materials inner structure are preserved, replaced by the inorganic, mineral matter, filled or empty in the inside (Fig 2, left image).

The external walls of fibers are totally preserved and not deformed. The remnant is made up by amorphous material. The circular section of fibers suggests an elastic behavior during the shaping process, the extruding do not cause irreversible deformation of flexible vegetal structures. The absence of separation surfaces indicates the good adherence of sawdust grains to the clay particles, and a low rate of contraction during combustion of organic compounds.
The samples with sunflower seeds hull show less developed remnants, a more pronounced contraction of organic matter before mineralization is observed, materialized under the form of inner rings, with identical geometry to the pores created by the combustion of organic matter (Fig 3). The higher rate of contraction is due to the lower cellulose contain of sunflower seeds hull than of sawdust grains. The morphology of pores enclosing remnants is similar to that of raw additive grains, thus we have to deal again with elastic behavior during extruding process. The sameness between pores and remnant grains geometry suggests a low rate decomposition process, which allows contraction without skewness. The remnants observed in samples with rice husks are a glass like, slightly colored matter, forming a network structure that preserves the walls of cells from the rice husks. From point of view of contraction and amount of remnant phase formed, these samples could be placed between the former two (Fig. 4). The shape of pores from the honeycomb-like structure is similar to the structures observed in the raw samples (Fig. 5). This suggests the elastic behavior of grains again and a high content in mineral components of raw organic structure. Small quartz-like crystals can be observed in the glass like phase.
A symmetrically arranged network of amorphous phase is formed (left image at II N, right image at xN).

Besides the parallel orientation of elongated grains in the matrix to the PA, due to pressed-processing of samples, no mineralogical, chemical or grain-size zoning is observed around grains of PA.

B. SEM study. SEM observations were carried out on both raw samples of additives, and the remnants of additive grains in fired samples. In order to prepare polished surfaces the samples were embedded in synthetic resin, both the raw and the fired samples. This way the preservation of structures for the remnants was assured. In Fig. 6 the representative structures are shown for the three additives. The question of the origin of remnants was solved by matching the SEM observations made on the raw samples with that from fired samples.
In Fig. 7 remnants of additives from fired samples are shown in order to emphasize the perfect preservation of structures. Due to the application of BSE imaging, we were able to characterize the chemical homogeneity of samples, too. On the raw samples one can easily distinguish the enrichment of K in the case of sunflower seeds hull and the Si for the rice husks. This chemical zoning is not visible on the remnants, most likely because these parts richer in mineral matter survived the firing mainly. In the case of samples
with sunflower seeds hull we can observe an oriented distribution of mica flakes, parallel to the wall of pores (as seen in central image from Fig. 7, white elongated grains represents the transformed mica lamellae). This means that sunflower seeds hulls are stronger in raw state than the forces applied when samples were extruded and created oriented structures in the microstructure.

Fig. 7. BSE images of the fired samples, on polished surfaces. On the 1., samples with sawdust, in the 2. sample with sunflower seeds hull, on the 3. sample with rice husks.

On fractured surface, observations have revealed the 3D shapes of remnants of PA and confirmed the replacement of the organic matter by an inorganic one, during the process of firing. The shapes are preserving the morphology of hard parts of the different organic additives, practically replacing the organic components. Samples with sawdust are characterized by the presence of remnants built up by parallel fibers of ~30 μm in diameter (Fig. 8), partially filled with inorganic substance.

In samples with sunflower seeds hull, remnants are characterized by the presence of polygonal plates of 10 μm wide and 5 μm long (Fig. 9, left image), arranged in multiple rows, in elongated shapes, filled with inorganic substance, separated by a narrow line at joints (Fig. 9, right image). The remnants represent the K-rich parts from the original material of the hull.
Sample R is characterized by the presence of a cellular structure, with rhomboidal cells of 10 μm wide and 25 μm long (Fig. 10), inside the remnants of the husks. These structures are the remnants of Si-rich components inside the husk, mostly the cellular membrane.

From SEM observation on polished surface no presence of reaction rims around the remnants of organic additives was observed, indicating the homogeneity of the material. The chemical composition of remnants was tested by Energy Dispersive Spectrometry measurements. In the case of F sample the composition is dominated by Mg, Ca with Si and Al and small amounts of Fe. The N sample is similar to the F sample, with variable Mg-Ca ratio, while in the case of R sample the composition is SiO₂ with minor Fe present.
Fig. 10. Secondary electron image on remnants of rice husk grain. On the left image, totally preserved network structure from the interior of husks. On the right, detailed image of cells.

3. Conclusions

The main mineralogical composition of fired samples is not affected by presence of the remnants from organic additives. The degree of fidelity at which the structures from vegetal materials are preserved is unique. This is showing a slow and linear decomposition of organic compounds that allowed the non-organic fraction of material to rearrange and replicate the structure.

The remnants of organic additives can be characterized by OM, SEM and EDS. The presence of the remnants of organic additives in the microstructure of brick materials may have several effects on the properties of bricks produced from the test material. Since the grains of pore-forming additives are replaced by a solid substance in different percentage, the effect of additives over the heat conductivity capacity should not be the one expected. To understand the manner in which the addition of vegetal materials to brick materials influences the production process, and properties of fired products, further research is made.

Although the question of applying organic additives in the brick production have been investigated from the points of view of ceramic properties (raw plasticity, hardness, apparent porosity, bulk density, compressive strength), the matter of replacement of the original organic compound by a secondary inorganic compound, with the preservation of the initial morphology, wasn’t discussed. The importance of this process in the thermal isolation and mechanical properties of bricks, as well as the impact on mineralogical composition of samples, is subject for further investigation.

The phenomenon of replacing organic, vegetal with inorganic, mineral matter could have importance in archeological studies.
References


Examination and determination of the fly ash ratio for optimization mechanical properties of cements

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¹ University of Miskolc, Faculty of Materials Science, Department of Ceramic and Silicate Engineering
²Holcim Hungaria Zrt.

Translated from Hungarian A pernye bekeverési arányának vizsgálata, meghatározása a gyártott cement mechanikai tulajdonságainak optimalizálása céljából

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Abstract. Investigation and determination of the admixture ratio of fly ash aiming at the optimization of mechanical properties of the cement produced. Nowadays cement is an important building material which can be produced from natural raw and fuel materials as well as from waste materials like tires, pet coke and fly ash. The aim was to analyze the influence of the granular structure and quantity of the fly ash and limestone powder admixture together and separately on the mechanical properties of the cement. The authors tried to find a mixture which has the same or even better quality as the original cements or composite cements.

1. Introduction
The cement is one of the most important bonding materials for building industry with increasing inquiries since 1990s and has wide range of composition. For its production not only natural raw materials like limestone and clay minerals can be used but different waste and recycled materials e.g. tires, pet coke, paper sludge, slag, fly ash [1]. From this it is obvious the importance of cement industry in accordance to recycling and consumption of different dangerous and non-dangerous waste materials. The consumption of these alternative (additional) materials gives us not only a certain economic advantages but we can save the volume of fossil energy sources and clinker minerals keeping or increasing the qualities like pressure and bending stress, workability, frost.

The aims of the present work are to find out the influence of grain size distribution and quantity of fly ash and limestone on the technological and mechanical properties of cement powders. For this material compositions with fly ash and limestone powder were chosen similar to the standard cements and composite cements.
2. **Experiments and processes**

The laboratory experiments were realized in the “Labatlan plant” of HOLCIM Hungary Co. Ltd. The specimen were prepared on the base of cement CEM I 42,5 R produced in Rohoznik (Slovakia). To this cement were add and mixed fly ash from power station “Gyongyosvisonta” in the following two versions:

a) crude fly ash in 25% and 30%

b) ground fly ash in 5%, 10%, 15%, 20%, 25% and 30%.

2.1. **The fly ash as ingredient of cement**

It is obvious from the several years’ experiments that a certain group of minerals influence very positively on the properties of cements. From the industrial waste or secondary raw materials the slags and fly ashes are the most used recycled components in the cement industry. Thanking to their fine grain structure and mineralogical composition these materials have pozzolan-like characteristics and the ability to chemically bind the calcium-hydroxide \([\text{Ca(OH)}_2]\). The intensity of pozzolan properties very strong depends on the so called glass phases of fly ash. These glass phases have increased portion of reactive or very reactive SiO\(_2\) and Al\(_2\)O\(_3\), in the Hungarian fly ashes the portion of these reactive SiO\(_2\) and Al\(_2\)O\(_3\) can reach the values of 70-80%. In spite of these high portions their “pozzolan reactivity” is smaller than the natural pozzolan like trass or silica fume. The weakness of “pozzolan reactivity” is expressed not only with the small quantity of bonded calcium-hydroxide \([\text{Ca(OH)}_2]\) but with the slow hydration reaction between the \(\text{Ca(OH)}_2\) of cement and active components of fly ash [3]. In spite of the relatively slow reactivity of cements with fly ash they have higher subsequent strengthening and good resistance to the aggressive environment [1].

The properties of composite cements based on Portland cement and fly ash strong depend not only on the quantity of added fly ash but from its grain sizes and grain distributions. The finer grain sizes give a better quality of these composite cements both for work and for finer mechanical strength after hydration.

The quality of used fly ash satisfied to MSZ EN 1197-1:2000 standard as its loss on ignition is smaller than 5% and its free calcium-oxide (CaO) less than 1% by weight. To prepare specimen or examination of composite Portland cements with fly ash in “Labatlan” (Hungary) mined limestone powders were used in the following proportions: 5%, 10%, 15% and 20%. Later our experiments have shown that increasing the limestone ratio higher than 10% by weight (15-20%) the mechanical strength will decrease considerably after the hydration.
Table 1. Mineral position of fly ash used

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45,92%</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>13,11%</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15,90%</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>11,84%</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>3,02%</td>
<td></td>
</tr>
<tr>
<td>S₃</td>
<td>4,30%</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>1,44%</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>1,71%</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0,0163%</td>
<td></td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0,170%</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0,530%</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0,223%</td>
<td></td>
</tr>
<tr>
<td>SrO</td>
<td>0,00485%</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Granulometry of the crude and ground fly ash used

<table>
<thead>
<tr>
<th></th>
<th>Crude fly ash</th>
<th>Ground fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,200 mm</td>
<td>8,84</td>
<td>1,6</td>
</tr>
<tr>
<td>0,090 mm</td>
<td>26,64</td>
<td>4,6</td>
</tr>
<tr>
<td>0,063 mm</td>
<td>38,00</td>
<td>9,8</td>
</tr>
<tr>
<td>0,045 mm</td>
<td>47,20</td>
<td>22,1</td>
</tr>
</tbody>
</table>

Table 3. Analytical properties of the fly ash used

<table>
<thead>
<tr>
<th></th>
<th>Crude fly ash</th>
<th>Ground fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss on ignition (%)</td>
<td>1,90</td>
<td>3,00</td>
</tr>
<tr>
<td>HCl insoluble (%)</td>
<td>57,72</td>
<td>50,51</td>
</tr>
<tr>
<td>SO₃ (%)</td>
<td>4,03</td>
<td>3,98</td>
</tr>
<tr>
<td>CaO free (%)</td>
<td>0,48</td>
<td>0,75</td>
</tr>
</tbody>
</table>

2.2. The expected behavior of limestone fillers as component of cement

In the cement industry the limestone fillers were used only as extender (3m%) before entry into force the standard EN197-1 in 2001. The limestone as inert material doesn’t contribute remarkably to the mechanical strength of hydrated cement. If there are more than 5 m% it can be influence on the starting mechanical strength because decrease the required water quantity of forming and hydration. Thanking to the spacer effect of limestone fillers the mechanical strength of the hydrated cement will increase with decrease of their grain sizes in the first two days. Meanwhile this strengthen cannot be observed in 28 days products because of the hydration level of clinker minerals. As limestone has diluent effect the decrease of clinker components can be compensated through their grain size and specific surfaces.

From literature of [4] and [5] it is well known that the maximum volume of limestone powders and fillers in composite cements cannot be more than 20 m% as the strength of hydrated cement will be destroyed.
### Table 4. Mineral content of the limestone used

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<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>1,55%</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>0,660%</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃</td>
<td>0,240%</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>53,80%</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>0,800%</td>
</tr>
<tr>
<td></td>
<td>SO₃</td>
<td>0,0300%</td>
</tr>
<tr>
<td></td>
<td>K₂O</td>
<td>0,120%</td>
</tr>
<tr>
<td></td>
<td>Na₂O</td>
<td>0,0700%</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>0,0100%</td>
</tr>
<tr>
<td></td>
<td>P₂O₅</td>
<td>0,00100%</td>
</tr>
<tr>
<td></td>
<td>Mn₂O₃</td>
<td>0,00100%</td>
</tr>
<tr>
<td></td>
<td>SrO</td>
<td>0,00100%</td>
</tr>
</tbody>
</table>

### Table 5. Granulometric structure of the limestone used

<table>
<thead>
<tr>
<th>Sleeve residual</th>
<th>Ground limestone, standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,200 mm</td>
<td>5,46</td>
</tr>
<tr>
<td>0,090 mm</td>
<td>20,84</td>
</tr>
<tr>
<td>0,063 mm</td>
<td>32,92</td>
</tr>
<tr>
<td>0,045 mm</td>
<td>42,45</td>
</tr>
</tbody>
</table>

### Table 6. Analytical characteristics of the limestone used

<table>
<thead>
<tr>
<th></th>
<th>Ground limestone, standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>izz.veszt. (%)</td>
<td>42,87</td>
</tr>
<tr>
<td>HCl oldhatatlan (%)</td>
<td>1,38</td>
</tr>
<tr>
<td>SO₃ (%)</td>
<td>0,10</td>
</tr>
<tr>
<td>CaO free (%)</td>
<td>0,00</td>
</tr>
</tbody>
</table>

For the laboratory investigation there were prepared four different composite “Portland” cement mixes with the following composition (Table 7):

### Table 7. Composition of the prepared composite portlandcement mixtures

<table>
<thead>
<tr>
<th></th>
<th>CEM I 42,5 R (%)</th>
<th>Ground fly ash (%)</th>
<th>Ground limestone (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>
Fig. 1. Influence of the admixtures on the compressive strength after 2 days

Fig. 2. Influence of the admixtures on the compressive strength after 7 days

Fig. 3. Influence of the admixtures on the compressive strength after 28 days
After preparing and homogenization of the composite cement mixtures the grain size distributions were determined with automatic screen equipment. Parallel to these there were measured and determined the values of water requirement, setting time, dimensional stability and optimal vibration frequency and amplitude of forming. The compression strength and bending strength of specimen were examined in 2, 7 and 28 days.

3. Results and discussion
The physical and mechanical properties of prepared specimen were determined by the standard of MSZ EN 196.

From the diagrams of Figure 1 it is obvious that there are not big differences between the compression strengths of 2 days old specimen prepared with different additional materials. Increasing the volumes and proportions of these additional materials the mechanical strengths are decreased. After 7 days (Fig. 2) there are differences in mechanical strength depending of the used volume of fly ash and other additives. These differences are much higher after 28 days (Fig. 3).
Summary and conclusions
In this work were examined the influences of
- the ratio and grain structures of used fly ash
- the ratio of limestone powders or fillers
- and their combined effect on mechanical properties especially the mechanical strength of hydrated composite cements.

The laboratory experiments were realized in the “Labatlan plant” of HOLCIM Hungary Co. Ltd. The specimen were prepared on the base of cement CEM I 42,5 R produced in Rohoznik (Slovakia).

Using the “Gyongyosvisonta” fly ash up to 20 m% as main additive of composite “Portland” cement the mechanical strengths of the hydrated specimen have increased considerably (13%) with increasing the volume of fly ash up to 20%. Meanwhile the added limestone fillers don’t influence noticeably on the mechanical strength. Thanking to the additives of fly ashes and limestone fillers the total requirement of cement clinkers can be decreased up to 20-25% in the concretes, so the CO load on the environment can be decreased considerably.

On the basis of the realized experiments the following composition of the composite “Portland” cement can be recommended: clinker minerals 75m%, fly ash 15m% and limestone fillers 10m%. This composition gives on 2-5% better mechanical strength after hydration as the standard “Portland” cement.

References
Alumina-based hetero-modulus ceramic composites with extreme dynamic strength - phase transformation of Si\textsubscript{3}N\textsubscript{4} during high speed collisions with metallic bodies

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Abstract. Till today several kinds of ceramics and ceramic matrix composites are developed for extreme environmental conditions. Most of these ceramics have microstructures with relatively „big” crystals, having high rigidness and strong inclination to nick, pitting and rigid fractures, so they are not usable for collision with metallic or other bodies under high speeds like 800 m/sec or more. On the basis of several years experiments in development and testing of ceramic materials and corundum matrix composites the authors successfully developed new alumina-matrix composite materials reinforced with Si\textsubscript{2}ON\textsubscript{2}, SiAlON, AlN and Si\textsubscript{3}N\textsubscript{4}. These new alumina based ceramic matrix composites were tested under collisions with different metallic bodies having high densities and speeds higher than 800 m/sec. During the collisions the kinetic energy of flying metallic objects distributing to fracture energies, heatings and recrystallizations both of ceramic and metallic bodies. In the centres of collisions, where oxygen was absent, the authors have found new, high density “diamond-like Si\textsubscript{3}N\textsubscript{4}” materials with cubic crystals, where nitrogen atoms distributed in the centres of the cubes. These new crystal structures of Si\textsubscript{3}N\textsubscript{4} in the alumina matrix have extreme dynamic strength and hardness, like diamond. Having surplus of oxygen in the centres of collisions this new “diamond-like Si\textsubscript{3}N\textsubscript{4}” was not observed, when a very strong oxydation of metallic bodies was taken place.

Using the energy conception of collision, the authors mathematically described the energy engorgements of destruction of ceramic materials and heating of participating bodies as well as energy engorgement used for the phase transformations of ceramic and metallic particles during their collision.

Keywords: hetero-modulus, Young’s modulus, ceramics, Si\textsubscript{3}N\textsubscript{4} diamond, CMC, alumina, collision, dynamic strength, energy engorgement, nano-particles, hardness.
1. Introduction

In the last 15-20 years the engineers and experts working in ceramic manufacturing plants and scientists working in laboratories of universities and research institutions have been engaged into development of more efficiency ceramic materials and items for different industrial purposes [1, 2, 3, 4]. Till today several kinds of ceramic materials and ceramic matrix composites are developed with high values of mechanical strength and hardness [5, 6, 7, 8]. Most of these ceramics or ceramic matrix composites have material structures with relatively "big" crystals, having high rigidity and strong inclination to nick, pitting and rigid fractures, so they do not have the required dynamic strength, and they are not suitable for collision with other materials and bodies under high speeds. Because of these, most of ceramics and CMC-s cannot be used for collision with metallic bodies having high densities and speeds higher than 800 m/sec.

The mechanical properties including the dynamic strength of high performance technical ceramics and CMC-s very strong depend not only on chemical structures and components, but from the technological parameters and processes as well [9, 10, 11, 12]. These technological parameters, which are influencing very strong on mechanical behaviour and dynamic strength of alumina matrix ceramic composites, are the followings:

- the grain size and shapes of the used raw material powders and their distribution in the forming instruments before, during and after compacting;
- the values and distributions of mechanical forming pressures in the ceramic powders during their compacting [13];
- the level of relaxation of the inside pressure in the compacted ceramic items after forming and sintering;
- the firing temperatures, firing curves and atmospheres of their syntering [14].

2. Materials and theoretical procedures

Applying the well-known and relatively not expensive raw materials of alumina powders and using uni-axial pressing and creating a special forming pressure distribution during the compacting and applying a special sintering atmosphere and technology, a new sort of hetero-modulus corundum matrix composite materials with extreme mechanical properties was developed. This new sort of corundum matrix composite materials, reinforced with Si$_3$N$_4$, Si$_2$ON$_2$, SiAlON and AlN particles of sub-microne and nanosizes has not only excellent compressive and bending strength and high surface hardness, but excellent dynamic strength as well, during collisions with metallic bodies of high density. They have especially good dynamic strength during collisions, when the speeds are higher than 800 m/sec. The typical forms of microstructures of these new hetero-modulus alumina matrix ceramic composites are shown in Fig. 1. On these microstructure pictures the submicrone and nano-size grains and whiskers of Si$_2$ON$_2$, SiAlON, Si,N. and AlN can be seen, which are distributed roughly uniform between the
polycrystals of alumina.

In Fig. 2 the typical destructions of high purity alumina ceramic items are shown after collisions with high density metallic bodies, flying with speeds higher than 800 m/sec. These kinds of destructions and cracks show that during the collisions the kinetic energy of flying objects is engorged by fractures through pressure stress and shear stress, as well as heating and phase transformation with recrystallization of material particles in the place and surrounding of the collisions.

This phenomena can be described by Eq. 1.

\[ W_K = W_F + W_S + W_H \] [Nm] (1)

where:

- \( W_K \) - kinetic energy of flying object, [Nm];
- \( W_F \) - fracture energy engorgement through pressure stress, [Nm];
- \( W_S \) - fracture energy engorgement through shear stress, [Nm];
- \( W_H \) - energy engorgement through heating and recrystallization of flying object particles and alumina-based ceramic materials in place and surrounding of the collision, [Nm].

The kinetic energy of flying objects very strong depends on their density and its homogenity. The energy conception of collision was presented on XI\textsuperscript{th} Khariton’s Reading [15] and described in detailes in proceedings of this International Conference [16].

When flying (metallic) object has homogeneous density during high speed collision the energy engorgement by destruction of ceramic bodies having only one Young’s modulus
can be described by Eq. 2.

\[ \frac{u^2}{2} \rho \cdot V = \frac{R_p^2}{2E} \cdot A_1 \cdot l_1 + \frac{R_s^2(v+1)}{E\nu} \cdot A_2 \cdot l_2 + W_h, [Nm] \]  

(2)

where:

- \( \nu_1 \) - the Poisson ratio;
- \( p \) - density of the flying object, [kg/m\(^3\)];
- \( A_1 \) and \( A_2 \) - surfaces of fractures, [m\(^2\)];
- \( E \) - Young’s modulus of ceramic material, [N/m\(^2\)]; \( l_1 \) and \( l_2 \) - deep and length of fractures, [m];
- \( R_p \) and \( R_s \) - the pressure and shear strength of ceramic plates or tiles, [N/m\(^2\)];
- \( u \) - speed of flying object at the moment of collision, [m/s];
- \( V \) - volume of the flying object, [m\(^3\)].

In virtue of Fig. 1 it is easy to understand the submicrone grains, whiskers and nano-particles containing nitrogens have different values of Young’s modulus comparing with the alumina matrix and them. These kinds of material structures have a composition of several Young’s modulus, multiple mechanical properties and named hetero-modulus materials [15, 16, 17, 18, 19]. The dynamic strengths of these developed new heteromodulus ceramics were examined under collisions with high density metallic bodies flying with speeds higher than 800 m/ sec. As it is shown in Fig. 1, alumina-based ceramic composites developed by us have submicrone and nano-size grains and whiskers of Si\(_2\)ON\(_2\), SiAlON, AlN and Si\(_3\)N\(_4\), which have different Young’s modulus. The energy engorgement of these hetero-modulus ceramic bodies during high speed collisions strong depend both on values of Young’s moduluses of hetero-modulus ceramics and on inhomogenity of densities of flying objects. When the flying objects are built-up from materials of inhomogeneous densities and ceramics have several Young’s modulus, the energy engorgement of these hetero-modulus ceramics can be described by the followings:

\[ \frac{u^2}{2} \sum_{i=1}^{n} \rho_i \cdot V_i = \sum_{j=1}^{N} \frac{R_p^2}{2E_j} \cdot A_{ij} \cdot l_{ij} + \sum_{j=1}^{N} \frac{R_s^2(v_j+1)}{E_j\nu_j} \cdot A_{2j} \cdot l_{2j} + W_h, [Nm] \]  

(3)

where:

- \( \rho_i \) - density of the „i-th” component of flying object, [kg/ m\(^3\)];
- \( \nu_j \) - the Poisson ratio of „j-th” Young’s modulus component of ceramic body;
- \( A_{ij} \) and \( A_{2j} \) - surface of fractures of „j-th” Young’s modulus component of ceramic body, [m\(^2\)];
- \( E_j \) - the Young’s modulus of the „j-th” component of ceramic body, [N/m\(^2\)];
- \( i=1,2,...,n \) - the numbers of different density components of flying object;
- \( j=1,2,...N \) - the number of different Young’s modulus components of ceramic body;
- \( l_{ij} \) and \( l_{2j} \) - deep and length of fractures of „j-th” Young’s modulus component of ceramic body, [m];
- \( R_{pj} \) and \( R_s \) - the pressure and shear strength of „j-th” Young’s modulus component of
ceramic body, \[N/m^2\];
- \(u\) - speed of flying object at the place and moment of collision, \[m/s\];
- \(V_i\) - volume of „\(i\)th” density component of flying object, \[m^3\].

The “thermic part” of collision energy, which means the energy engorgement through heating, phase transformation and recrystallization of flying object particles and alumina-based CMC materials in place and surrounding of the collision can be described by Eq. 4.

\[ W_H = W_{HS} + W_{RC} + W_{RM} ; [Nm] \]  

where:

- \(W_H\) - energy engorgement through heating, \([Nm]\);
- \(W_{HS}\) - energy engorgement through heat transfer and heating of materials in and surrounding of the collision and fall, \([Nm]\);
- \(W_{RC}\) - energy engorgement through recrystallization of ceramic particles in and surrounding of the collision and fall, \([Nm]\);
- \(W_{RM}\) - energy engorgement through melting, spraying and recrystallization of the falling metallic body, \([Nm]\).

Measuring the temperatures, the deeps and lengths of destructions and cracks of ceramic items in the places and surroundings of collisions, from Eq. 3. and Eq. 4. the part of kinetic energy, turned into phase transformation and recrystallization of ceramic particles can be mathematically solved and described by Eq. 5.

\[ W_{RC} = \frac{u^2}{2} \sum_{i=1}^{n} \rho_i \cdot V_i \left( \sum_{j=1}^{n} \frac{\rho_j}{\omega_j} \cdot A_{ij} \cdot t_{ij} + \sum_{j=1}^{n} \frac{\rho_j}{\omega_j} \cdot \left( \frac{v_{ij}+1}{v_{ij}} \right) \cdot A_{ij} \cdot t_{ij} \right) (w_{HS} + W_{RM}) ; [Nm] \]  

If the flying metallic objects have high densities and speeds higher than 800 m/sec, a huge volume of energy is turning to phase transformation, which is in hand with temperature over 1000 °C and pressure stress higher than 150-200 GPa. Because of these, phase transformations and recrystallizations can be observed both in alumina polycrystals and in the Si\(_2\)ON\(_2\), SiAlON, AlN and Si\(_3\)N\(_4\) submicrone and nano-sized particles and whiskers.

### 3. Results and discussion

These new corundum matrix composite materials, reinforced with Si\(_2\)ON\(_2\), SiAlON, Si\(_3\)N\(_4\) and AlN particles and whiskers of sub-microne and nano-sizes have not only excellent compressive and bending strengths, but extreme dynamic strength, as well. Typical destructions of materialstructures of these new alumina matrix hetero-modulus ceramic composite materials are shown in Fig. 3.

As it can be seen in these SEM pictures during collision with high density metallic bodies flying with speeds about 850-950 m/sec, the directions of destructions of the
ceramic microstructure follow the directions of the hits of flying metallic objects. Fig. 3a. shows how some “large” particles destroyed and moved a certain distance together with hit metallic objects. Fig. 3b. shows how the surface of the hetero-modulus ceramic body can be melted and transformed into amorf substance at the place and just near of the hits and collisions.

Having surplus of oxygen in places of collisions a very strong oxidation of the falling metallic bodies can be observed, as it is shown in Fig. 4. The energy turned into phase transformation and recrystallization of alumina-based hetero-modulus ceramics is described by Eq. 5. Measuring the deeps and lengths of destructions and cracks of ceramic items as well as their temperatures in the places and surroundings of collisions, and substitute them into Eq. 5, it is easy to find the energy, turned into phase transformation and recrystallization of hetero-modulus ceramic materials themselves.

During the high speed collisions with high density metallic bodies a strong recrystallization process in the material structures can be observed. The typical recrystallized material structures of the new developed corundum matrix composites, reinforced with submicrone and nano-size grains and whiskers of Si₂ON₂, SiAlON, Si₃N₄ and AlN are shown in Fig. 5., after high speed collisions. When there is no oxygen in the
places of collisions and the falling metallic bodies with high density have speeds higher than 800 m/sec, the particles of $\text{Si}_3\text{N}_4$ can turn into cubic crystallic structure with nitrogen atoms in the centres of each cubics. These $\text{Si}_3\text{N}_4$ particles with new cubic crystallic structures have high density and extreme high hardness and mechanical strength equivalent to diamond. When there was no oxygen at the places of collisions these new “diamond-like $\text{Si}_3\text{N}_4$” particles were obtained because of the huge volume of collision energy, and followed it very strong recrystallization process. When we had surplus of oxygen in the place of collision, these new “diamond-like $\text{Si}_3\text{N}_4$” particles were not observed. In these cases strong crystal growth phenomenas were taken place as it is shown in Fig. 5b.

Fig. 5. The recrystallized microstructures of alumina-based ceramic items after collision

After the high speed collisions with metallic bodies these new crystals of alumina-based hetero-modulus ceramics, both with recrystallized “diamond-like $\text{Si}_3\text{N}_4$” (Fig. 5a.) and large alumina crystals (Fig. 5b.) were polluted by sprayed liquid metal drops on their surfaces. These $\text{Si}_3\text{N}_4$ ceramic particles with cubic crystallic structures with nitrogen atoms in centres of each cubic, arised in places and surroundings of collisions without oxygen, have excellent mechanical properties and hardness like diamond.
4. Conclusions

Understanding the phenomena in the collisions under high speeds and advantageous of hetero-modulus ceramic materials having several Young’s modulus, some new, alumina-based ceramic matrix composites were developed, reinforced with submicron and nanoparticles of $Si_2ON_2$, SiAlON, $Si_3N_4$ and AlN. These developed new hetero-modulus alumina-based ceramic matrix composites are well-resistant to collisions against metallic objects, flying with speeds between 850-950 m/sec. During the collisions the kinetic energy of flying metallic objects are distributing to energies of fractures, heatings and recrystallizations both of ceramic and metallic bodies participated in the collisions process.

During the high speed collisions with high density flying metallic bodies, in the alumina-based ceramics and CMC-s a strong in-situ crystal growth process can be obtained when we have surplus of oxigen in the places of collisions. This phenomena can be the reason of a rigid fracture of the ceramic items and CMC-s during the next collision with any kind of flying objects.

When there is no oxygene in the places and moments of collisions in the alumina-based ceramic composites reinforced with $Si_2ON_2$, SiAlON, $Si_3N_4$ and AlN, a new, "diamond-like $Si_3N_4$" can be developed, having cubic crystals with nitrogen atoms in centres of cubes. These new, "diamond-like $Si_3N_4$" ceramic particles have excellent mechanical strength and hardness like diamond.

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Mechanical stress relaxation in hetero-modulus, hetero-viscous complex ceramic materials

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Abstract. Hetero-modulus, hetero-viscous complex materials have several advantages in accordance to mechanical and thermal properties comparing with the traditional ceramics and ceramic matrix composites. In this paper the authors examined in details the high speed collision processes between flying metallic objects and ceramics, such as a-Si₃N₄, |3-Si₃N₄, Si₂ON₂, SiAlON, AlN and 3Al₂O₃2SiO₂ reinforced alumina matrix hybrid materials, as well as their rheo-mechanical structures and properties. Understanding the high speed collision process, material structures, rheological properties of such a complex hybrid material, the authors in this paper mathematically describe the mechanical shear stress and its relaxation during and after high speed collisions in a-Si₃N₄, P-Si₃N₄, Si₂ON₂, SiAlON, AlN and 3Al₂O₃2SiO₂ reinforced alumina matrix composites. The dynamic strength of the developed and examined corundum matrix complex materials was tested through collision with high density metallic flying bodies, with speed higher than 900 m/sec and described in works [27, 29, 42]. Analytical methods applied in this research were scanning electron microscopy, X-ray diffraction and energy dispersive spectrometry. Digital image analysis was applied to microscopy results, to enhance the results of transformation.

Keywords: ceramics, CMC, elasticity, hybrid materials, plasticity, stress relaxation, viscosity

1. Introduction

In the last 15-20 years scientists, engineers and experts working in laboratories of universities and research institutes or in ceramic manufactory plants have been engaged in development of more efficient ceramic materials and items for different industrial purposes [1-4]. The sophisticated industry and technology [5-7] require higher and higher assumption against to mechanical properties, such as hardness [8-13], strength [14-20], wear resistance [21-24], toughness [25, 26] and dynamic strength [27-29]. Till today several types of ceramic materials and ceramic matrix composites (CMC) are develop with excellent mechanical properties, with high values of mechanical strength and hardness, but most of these materials have microstructures with relatively large
crystals, having high rigidness and strong inclination to nick, pitting and rigid fractures. Generally materials with these kinds of crystal structures do not have required dynamic strength, and they are not suitable for collisions with other materials and bodies under high speeds. Because of this substantial research has been done in ceramic industry to reduce grain size [30-34] aiming to increase the above favorable mechanical properties. However to increase mechanical properties the authors often use a simultaneous pressure during sintering applying hot isostatic pressing sintering [20, 33, 35] or spark plasma sintering [36, 37], as presence of pore in the ceramic structure results a significant decrease in its mechanical strength. To obtain high density alumina-zirconia ceramics Wang, Huang and Wu [38] used two-step sintering process, and by Hernández, Torre and R. Rangel [39] Al$_2$O$_3$ matrix cermet were produced from mechanically mixed powders containing Al, Fe and Ti metals as reinforcements.

Examining the material structure and excellent mechanical properties of SiAlON ceramic composites the advantages of hetero-modulus materials first was described by German scientist Dr. Hasselman and his co-authors [40] in early of 1980‘s. The values of Young’s modulus and melting temperatures of advance materials, metal alloys and ceramics (Fig. 1.) was introduced by Igor Shabalin [41] as CE6 Session chair in Symposium ceramics and Engineering of XIV$^{th}$ International Clay Conference (14 ICC).

Fig.1. Melting points and elastic modulus of advanced technical materials (Taken from Igor Shabalin, 14-icc, Session CE6)

From Fig. 1 it is obvious that most of ceramics, borides, nitrides and carbides have both high values of Young’s elastic modulus and melting points. Constructing a new material structure from particles - components - having different Young’s modulus and melting temperatures a new hybrid material could be create with the following valuable advantages:

- high damage tolerance,
- ability to absorb and dissipate the elastic energy during crack propagation,
- good thermal shock resistance.
Understanding the advantages of hetero-modulus materials new corundum matrix ceramic composites reinforced with Si$_3$N$_4$, SiAlON, AlN and 3Al$_2$O$_3$2SiO$_2$ particles were successfully developed by the authors [27, 29, 42]. In this work our aims are the following:

- understand the mechanical behavior and properties of hetero-modulus, hetero-viscous complex materials and create their rheo-mechanical model,
- describe mathematically the mechanical stress development and relaxation during and after high speed collision in this kind of complex materials.

2. Materials and experimental procedures

The high speed collision process and energy engorgement through fractures of traditional and hetero-modulus ceramics were already described in details by authors in works [27, 32, 42]. The thermic part of collision energy also was described in the above works and in [29], but there is no works in accordance to high speed collision behavior of hetero-modulus and hetero-viscous complex and hybrid materials in spite of their following advantages are obvious:

- high damage tolerance,
- higher deformation tolerance,
- ability to absorb and dissipate the collision energy,
- relax by time mechanical stress developed in body during high speed collisions.

The mechanical model of complex material structures completed from particles having different values of elastic modulus and viscosity could be modelled by Fig. 2.

To achieve this kind of mechanical model with several Young’s modulus, plasticity and viscosity, our high purity Al$_2$O$_3$ powder was polluted and mixed with submicron particles of SiO$_2$, Si$_3$N$_4$, SiAlON, AlN, Ti$_2$O$_3$ and other oxides and elements. This new material composition was milled in planetary-ball mill through several hours, and finally a powder mix containing 92 m% of Al$_2$O$_3$ was got. This powder mix were compacted uni-axially, using high speed flying punches with high kinetic energy by principle as shown in Fig. 3.

There are several methods are used to develop SiAlON particles and transform a-Si$_3$N$_4$ into P-Si$_3$N$_4$, but all of them used sintering temperatures much about 1700 °C or hot pressing at 1800 °C under pressure of 23 MPa or more [43-47]. In our case we used multi-steps sintering technology processes in which the compacted specimens first were pre-sintered in nitrogen (N$_2$) atmosphere under special firing curves. Due to phase transformation and recrystallization occurred during the following steps of sintering a new hetero-modulus and hetero-viscous corundum matrix composite (CMC) was developed reinforced with micron and submicron whiskers, nano-particles and viscous glass-like phases as it is shown in Fig. 4.
Fig. 2. Mechanical model of hetero-modulus, hetero-viscous materials

\[ \Delta l_i = a_{i1} + a_{i2} + a_{i3} \]

\[ \Delta l_2 = a_{i1} + a_{i2} + a_{i3} \]

\[ \Delta l = \Delta l_1 + \Delta l_2 = \ldots = \Delta l_n \]

\[ \Delta l = a_1 + a_2 + \ldots + a_n \]

\[ F = \sum_{i=1}^{n} F_i \]

- \( a_{11} \) - \( a_{n1} \) - deformations of elastic particles
- \( a_{12} \) - \( a_{n2} \) - deformation of viscous-plastic particles
- \( a_{13} \) - \( a_{n3} \) - deformation of viscous-elastic particles
- \( E_{11} \) - \( E_{n1} \) - Young modulus of Hooke particles
- \( E_{12} \) - \( E_{n2} \) - Young modulus of viscous-elastic particles
- \( F_1 \) - \( F_n \) - forces on material particles
- \( \eta_{11} \) - \( \eta_{2} \) - viscosity of viscous-elastic particles
- \( \tau_{01} \) - \( \tau_{0n} \) - static yield stress in viscous-plastic particles
- \( \Delta l \) - total deformation of particles

Fig. 3. Principle of compacting specimens under high speed flying punches with high kinetic energy

Fig. 4. Achieved microstructures after sintering
### 3. Results and discussion

The shear stresses developing during high speed collisions in the above introduced (Fig. 4.) hetero-modulus and hetero-viscous hybrid materials could be described by (1)

\[
\tau_0 - \tau \left[ \frac{\eta_1}{\eta_e} + 1 + n_\tau - n_\gamma \left( 1 + \frac{\eta_1}{\eta_2} \right) \right] + \frac{\eta_1 n_\gamma}{\eta_e} \ddot{\tau} - n_\tau n_\gamma \dddot{\tau} = 0
\]

(1)

where:
- \( \eta_1, \eta_2 \) and \( \eta_e \): viscosities of elastic-viscous-plastic, elastic-viscous parts and effective viscosity of the hybrid hetero-modulus and hetero-viscous body,
- \( \tau_0 \) and \( \tau \): static yield point of body and shear stress developed during deformation and destruction in the material,
- \( n_\tau \) and \( n_\gamma \): stress relaxation time and delay time of elastic deformation,
- \( \dot{\tau} \) and \( \dddot{\tau} \): first and second derivatives of shear stresses developed in hetero-modulus and hetero-viscous ceramic and CMC bodies during high speed collision with flying objects.

The effective viscosity of the hetero-modulus and hetero-viscous complex materials could be determined by (2) as the following:

\[
\eta_e = \frac{\tau_0 + \eta_1 \dot{\gamma} + \eta_1 n_\gamma \ddot{\gamma}}{\gamma + n_\tau + n_\gamma \gamma + \gamma [n_\tau - n_\gamma (1 + \frac{\eta_1}{\eta_2})]}
\]

(2)

where:
- \( \dot{\gamma}, \ddot{\gamma} \) and \( \dddot{\gamma} \) the first, second and third derivate of deformation-speed gradients

Involving the following new symbols:

\[
A = -n_\tau n_\gamma
\]

(3.1.)

\[
B = \frac{\eta_1 n_\gamma}{\eta_e}
\]

(3.2.)

\[
C = -\left[ \frac{\eta_1}{\eta_2} + 1 + n_\tau - n_\gamma \left( 1 + \frac{\eta_1}{\eta_2} \right) \right]
\]

(3.3.)

\[
D = \tau_0
\]

(3.4.)

\[
x = \tau
\]

(3.5.)

the (1) could be rewrite to the following well-known form:

\[
A \ddot{x} + B \dot{x} + C x + D = 0
\]

(4)

During the high speed collision \((u \geq 1000 \text{ m/s})\) there is no plastic deformation in materials, so \(D=0\) and (4) could be rewrite as:

\[
A \ddot{x} + B \dot{x} + C x = 0
\]

(5)
The (5) is well-known as the mathematical equation of damped harmonic oscillation, the solutions of which are the followings:

\[ \ddot{x} = C_1 e^{\lambda_1 t} + C_2 e^{\lambda_2 t} \]  
\[ \lambda_{1,2} = -\frac{B}{2A} \pm \frac{B^2 - 4AC}{2A} \]  
\[ X^* = -\frac{D}{C} \]

where:

\[ C_1 \text{ and } C_2 \text{ are the constants of integration.} \]

Substitute the above expressions the general equation of shear stress relaxation in hybrid hetero-modulus and hetero-viscous ceramics and CMC after high speed collision could be described as:

\[ \tau = C_1 e^{\left(\frac{B}{2A} + \frac{B^2 - 4AC}{4A^2} \lambda \right) t} + C_2 e^{\left(\frac{B}{2A} + \frac{B^2 - 4AC}{4A^2} \lambda \right) t} - \frac{D}{C} \]

Substitute the A, B, C and D with the original material constants the value of the mechanical shear stress developed in hetero-viscous and hetero-modulus particles reinforced corundum matrix matrix composite material during high speed collision and its relaxation mathematically could be described as the following:

\[ \tau = C_1 e^{\left(\frac{\eta_1}{2\eta_2} + \frac{\eta_3^2}{4\eta_2^2} + \frac{\eta_1}{\eta_2} + 1 + \eta_1 - \eta_2 \left(1 + \frac{\eta_1}{\eta_2}\right) \right) t} + C_2 e^{\left(\frac{\eta_1}{2\eta_2} + \frac{\eta_3^2}{4\eta_2^2} + \frac{\eta_1}{\eta_2} + 1 + \eta_1 - \eta_2 \left(1 + \frac{\eta_1}{\eta_2}\right) \right) t} + \frac{\tau_0}{\eta_1 + 1 - \eta_1 \left(1 + \frac{\eta_1}{\eta_2}\right)} \]

4. Conclusions

Understanding the high damage and deformation tolerance and ability to observe and dissipate the collision energy of hetero-modulus and hetero-viscous submicron and nanoparticle reinforced corundum matrix hybrid ceramics and CMCs, the authors successfully created a rheo-mechanical model (Fig. 2.) and mathematical equation (Eq. 8.) to mechanically characterize such a complex material structures of ceramics and composites.

This kind of mechanical model and mathematical equation can help in development high damage and deformation tolerance complex materials like α-Si₃N₄, β-Si₃N₄, SiO₂N₂, SiAlON, AlN, 3Al₂O₃2SiO₂ submicron and nano-particle and liquid phase particle (glass) reinforced alumina matrix hybrid materials.
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References

Effect of ceramic additives on mechanical properties of alumina matrix composites

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Abstract: Alumina ceramics have excellent mechanical properties for technical application. The lower purity alumina compacting powders are used in wide range of engineering ceramic industry. These powders contain low amounts of additional materials (SiO₂, CaO, MgO).

In this article, the authors present the achievement of some mechanical experiments using variable ceramic additives for preparing test specimens. The aim of this work to enhance the mechanical performance of the lower purity alumina (94%) develops a ceramic composite system. Further aim of this work to attempt to reach the values of mechanical properties of high purity alumina products. Zirconsia was used in variable amounts as restorative material.

Keywords: alumina; zirconia; composite.

1. Introduction

Zirconia as an additive to improve mechanical properties is being big volume appropriation in produce of alumina engineering ceramics. Many methods are available to produce proper ceramic composite material structure. Most of the researches are prefer new technologies and raw material application like the follows: the matrix and intensifier grain size is under micrometer, the composite material systems produced by multifarious technologies, the powder compressing phase is work in the same time with sintering phase (hot pressing), the conventional sintering methods divide several periods. To create a variety of ceramic composite system (grain-reinforced) wide range of modern and common technologies are available. In our work we combined the two production technology to use the advantages of the manufacturing process.

The first phase of a gravity casting, which was preceded by slurry making the second phase is uniaxial pressing technology. Later research demonstrated that the favourable influence of poli-saccharides for the rheology and thixotropy of alumina slurries (Schilling et al., 2002). In other aspects we could use for plasticising dense alumina slurry with addition of poli-saccharides (fructose, glucose) suggested in another research (Kim et al., 2000).

Csanyi (2009) established that the high Al₂O₃-content pressing powders are good for
dynamic, fast pressing. During the nineties research showed a modification of powder compaction equation which describes the behavior of zirconia powders as well (Ramakrishnan et al., 1997). The main problem of uniaxial powder pressing is the anisotropic shrinkage, but later research established that using powder made by spherical particles the phenomena of anisotropic shrinkage can be reduced (Shui et al., 2002). The sintering of samples performed by using the results of our department’s previous research (Csanyi and Gomze, 2008) and international researches (Wang et al., 2009). Generating fine microstructure we applied a modified version of two step sintering method which were investigated by other works (Hesabi et al., 2009). For further refinement of microstructure nitrogen flushing during sintering was applied (Nivot et al., 2006).

The ultimate goal of the work to improve the mechanical properties of a purity of 94%-95% alumina pressing powder and reach the standards of high purity manufactured products.

The zirconia additive is mainly improve the abrasion resistance and heat resistance the aluminum oxide ceramic matrix composites, this property is well known. During the research the standard mechanical tests, the bending strength and the less examined impact test was determined. For the characterization of mechanical properties the two parameters are excellent because the bending strength is the most important of the static loading parameters, while the impact test is used for comparison of the dynamic stress resistance.

2. Experimental procedures

The preparation, of specimens for examinations by a commercially available alumina pressing powder was used (Martoxid KMS-94). The pressing powder average grain size is 150 μm, the pressing powder grains make up basic alumina particles of 10 μm. According to the manufacturer the pressing powder contains ~4% silica and less than 2% any other component (CaO, MgO). The zirconia used as strength phase was stabiliser-free, commercially available ceramic additive with an average grain size of 5 μm (Saint-Gobain Ceramic Materials). A series was prepared with a mixture of the two components, in which increased the amount of ZrO₂ step by step. The reference mixture numbered 1 contained 0% ZrO₂. The previous experiences showed that dry powder mixing is not sufficient to get homogeneous solid components, so distilled water and poly-saccharide plastificater into the slurry was added then a 16 hours of continuous solvent mixing with arm stirrer was performed. Every mixture was 836.5 g. The components of mixtures are shown on Table 1.
Table 1. Mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>KMS-94 Al₂O₃ (g)</th>
<th>ZrO₂ (g)</th>
<th>De-ionised water (g)</th>
<th>Poli-saccharide (g)</th>
<th>Mass of mixture (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>550</td>
<td>0</td>
<td>275</td>
<td>11.5</td>
<td>836.5</td>
</tr>
<tr>
<td>2</td>
<td>536.25</td>
<td>13.75</td>
<td>275</td>
<td>11.5</td>
<td>836.5</td>
</tr>
<tr>
<td>3</td>
<td>522.5</td>
<td>27.5</td>
<td>275</td>
<td>11.5</td>
<td>836.5</td>
</tr>
<tr>
<td>4</td>
<td>495</td>
<td>55</td>
<td>275</td>
<td>11.5</td>
<td>836.5</td>
</tr>
<tr>
<td>5</td>
<td>467.5</td>
<td>82.5</td>
<td>275</td>
<td>11.5</td>
<td>836.5</td>
</tr>
<tr>
<td>6</td>
<td>440</td>
<td>110</td>
<td>275</td>
<td>11.5</td>
<td>836.5</td>
</tr>
</tbody>
</table>

5 mm thick plates were poured to plaster moulds by gravity casting of mixtures, and they dried 24 hours at room temperature on static air. After drying the plates with setted moisture of 2.5%-9% were cut to suitable weight and placed into die box, the semi-dry compression was completed. The uniaxial pressing at 100 MPa was performed using five seconds loading time. The prepared prismatic specimens had nominal crude size of 75 mm x 10 mm x 10 mm. For the removal of residual moisture content drying of 24 hours at 50°C was used.

Sintering was carried out in two separate combustion instead of the conventional one holding time case, in which the role of used shielding gas was investigated. Using of nitrogen atmosphere has beneficial effect of grain grow decreasing and developing homogenous microstructure induced prominent mechanical properties. In the first step low-temperature sintering so-called pre-sintering was used at temperature of 1,320°C and holding time of four hours. Half of the samples were sintered in air, the other half sintered in N₂ atmosphere. The next step was the high temperature sintering in air of each specimen at 1,550°C and application of two hours holding time.

The prepared specimens were investigated by the following mechanical and microstructural testing.

The bending strength and elastic modulus determination of three-point bending test was based on a universal material testing machine (Instron 3360 Series Dual Column Tabletop Universal Testing Systems). The measurement data appeared on the computer connected directly to the device. Schematic illustration of bending test equipment is shown on Figure 1.

The impact strength values were measured with Charpy pendulum test. The specimens for impact test were as the same as for bending test with a 60° V-notch. The average length, width and height of measured specimens ordered 65 mm, 9 mm and 9 mm (after second step of sintering). The mass of used pendulum was 0.05 kg. Impact energy values can be read directly from the scale. A schematic illustration of impact test method was presented on Figure 2.
Figure 1. Block scheme of experiments carried out

Figure 2. Shematic set-up of bending test
3. Results and discussion

a. Flexure strength

For the determination of flexural strength three-point bending test was performed. Tests were conducted at a crosshead speed of 2 mm/min at room temperature (20 ± 1°C) with a relative humidity of 70% ± 5%. The flexural strength and modulus values calculated with a PC automatically by the following equations:

\[ \sigma = \frac{3FL}{2WH^2} \]  

(1)

where
- \( \sigma \) flexural strength (MPa)
- \( L \) specimen length (mm)
- \( F \) total force applied to the specimen by loading pin (N)
- \( W \) specimen width (mm)
- \( H \) specimen thickness/height (mm)

\[ E = \frac{i^3F}{4WH^3d} \]  

(2)

where
- \( E \) modulus (bend) (MPa)
- \( i \) support pin distance (mm)
- \( F \) total force applied to the specimen by loading pin (N)
- \( W \) specimen width (mm)
The results of bending strength grouped by pre-sintering atmosphere are indicated.

Table 2. Comparison of flexure strength

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Flexure strength without using N₂ atmosphere (Mpa)</th>
<th>Flexure strength with using N₂ atmosphere (Mpa)</th>
<th>Difference (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>159.504</td>
<td>114.094</td>
<td>-45.41</td>
</tr>
<tr>
<td>2</td>
<td>145.928</td>
<td>161.58</td>
<td>15.652</td>
</tr>
<tr>
<td>3</td>
<td>176.374</td>
<td>207.92</td>
<td>31.546</td>
</tr>
<tr>
<td>4</td>
<td>205.72</td>
<td>218.972</td>
<td>13.252</td>
</tr>
<tr>
<td>5</td>
<td>230.762</td>
<td>217.466</td>
<td>-13.296</td>
</tr>
<tr>
<td>6</td>
<td>229.56</td>
<td>289.276</td>
<td>59.716</td>
</tr>
</tbody>
</table>

Curves were fitted with quadratic polynomial regression (full line) and confidence level of 95% (dash lines) are shown on each diagram. We tried to get response the change of the atmosphere that application of protective gas is available to realise better mechanical properties of the products than without.

*Without N₂ protective atmosphere:* measured results without the using of protective gas atmosphere are presented in Figures 4 and 5.

![Figure 4. Flexure strength without N₂ atmosphere](image-url)
Figure 5. Modulus without N₂ atmosphere

The zirconium dioxide content of the figures is referred to the percentageous amount of dry substances. The curves clearly show the increasing effect of the ZrO₂ content in flexure strength. The value for our test series is reached the maximum at 15% and 20% ZrO₂ content (230 MPa). The obtained values fitted quadratic polynomial regression curve with 95% confidence level show 0.94 correlations. So in light of the above data stated that the increasing of inclusion of zirconia additive the flexural strength greatly increased by applying an alumina matrix of given parameters. It could be reached that values doubled at 20% of ZrO₂ content.

The elastic moduluses of specimens sintered without using protective atmosphere can be seen on Figure 5.

Growing trend can be observed of the modulus values as like cases of bending strength by increasing the quantity of ZrO₂. In this case the rate of increasing is well approximated by quadratic polynomial regression curve by the statistical data. The data resulted a correlation coefficient of 0.91 on 95% confidence level, so in this case stated that under the effect of zirconia addition to the alumina matrix the elastic modulus values can be improved.

Using N₂ protective atmosphere: measured results using N₂ protective atmosphere were shown on Figures 3 and 4.

The values of bending strength of specimens made with using N₂ protection atmosphere grow almost the same way without using N₂ gas. The maximum value is reached at 20% ZrO₂ content, but due to the nature of the fitted curve further increase is expected.

The statistical results are given proper fit of the regression line, correlation coefficient of 0.92 with 95% confidence level. Flexure strength values can be increased.
with addition of zirconia and using of protective atmosphere. The results of the specimens’ modulus made from the same circumstances is included by Figure 4.

The modulus values of the scale and pace of experienced growth is almost the same as in the case with not using protective gas. The fit of the regression line is appropriate and the size of correlation coefficient is 0.91, so the strengthening effect of zirconia are also established.

![Figure 6. Flexure strength with N\textsubscript{2} atmosphere](image)

![Figure 7. Modulus with N\textsubscript{2} atmosphere](image)
b. Impact strength tests

The determination of impact strength Charpy pendulum test was used. The specific impact strength use in practice. To determine the specific impact strength values from the readable impact energy data the next equation was used:

\[ KC = \frac{K}{S_0} \]

where

- \( K \) impact energy (directly readable) (J)
- \( S_0 \) cross section area (mm\(^2\)).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Impact strength without using N(_2) atmosphere ( \times 10^3 ) (J/mm(^2))</th>
<th>Impact strength with using N(_2) atmosphere ( \times 10^3 ) (J/mm(^2))</th>
<th>Difference (J/mm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.96</td>
<td>3.58</td>
<td>0.62</td>
</tr>
<tr>
<td>2</td>
<td>3.12</td>
<td>2.92</td>
<td>-0.21</td>
</tr>
<tr>
<td>3</td>
<td>2.88</td>
<td>2.92</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>2.94</td>
<td>2.94</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>2.96</td>
<td>3.13</td>
<td>0.17</td>
</tr>
<tr>
<td>6</td>
<td>3.29</td>
<td>3.30</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The impact test results do not give an exact rating metrics, but for comparative studies are excellent. The occurred quick breaks caused by dynamic forces due to rapid crack propagation processes that occur in a small number taking into account of applications of ceramics. Impact test results of the tests are also divided into two groups should be dealt as compared with the two pre-sintering procedures.

**Without N\(_2\) protective atmosphere:** measured results without of using N\(_2\) protective atmosphere were shown on Figure 5. The values of impact strength without protective gas are different nature of bending strength growth. The regression line is matched in this case second-degree polynomial, the test results closely follows. The curve is minimum natured, the minimal rate is reached between 5% and 10% ZrO\(_2\) content. Values are increased above 15% of zirconia content, which it can be concluded that beyond the analysed range further improvements to be expected. The correlation coefficient in this case is only 0.5064 that shows ‘weak’ functional relationship, but it is still an acceptable range.

**Using N\(_2\) protective atmosphere:** measured results of impact strength using N\(_2\) protective atmosphere were shown on Figure 9. The values of specimen series using protective gas has also the minimum effect. The correlation coefficient is 0.0692, which indicates a lack of functional relationship. In this case, it is declared that the ZrO\(_2\) has clear effect on the impact test values. Although the individual values of over 10% ZrO\(_2\) content growth is seen, but it still does not reach the reference mixture values.
Figure 8. Specific impact strength without N₂ atmosphere

Figure 9. Specific impact strength with N₂ atmosphere
c. Microstructural and EDS investigations

The microstructural investigations were made by scanning electron microscope. The equipment is designed with an energy dispersive microprobe (EDS), by which the elemental composition of given area was determined. This method is verified the primary components of microstructural abnormalities, which can be derived from their origin.

The SEM images made about the crack surface of specimens after high temperature sintering (left side - without using protective atmosphere, right side - using protective atmosphere). Significant differences were not observed on the microstructure of the samples inside the body because of the use of different atmospheres. The images shown the imbedded zirconium dioxide particles in a homogeneous distribution therefore, the solvent mixing is quite effective to develop suitable microstructure.

During the fracture of the samples we met only one case, where macroscopic structural failures were discovered on the crack surface. Crack surfaces were appeared after bending test when specimens loaded up to total fracture. These newly created crack surface was analysed with SEM technique. Examined the failure with scanning electron microscope the following images and EDS spectra (Figures 12 and 13) were prepared.

The type of this failure was a zirconia agglomerate, which has one part on Figure 13. The composition of failure was investigated by EDS. Used EDS equipment has a beryllium window on its detector that is foreclosed to detect the elements under sodium therefore oxygen content was not indicated. The horizontal axis indicates the energy of the corresponding element and the vertical axis shows the X-ray counts. It can be observed that zirconium Ka peak showed the highest energy that demonstrated the zirconium aggregation. The developed triangular pyramid can be seen on the figure where the specimen was broken. This pyramid worked like a stress collector peak which facilitated the formation of microcracks and led to fracture. Each formed agglomerates operate like a location for stress collection therefore they are very harmful for the mechanical properties.

Summarise the results of this study concluded that the lower-purity alumina pressing powder can be increased the bending strength with addition of unstabilised ZrO₂. A tendencious growing could be observed from 0 to 20% ZrO₂ which showed by regression curves. The flexural strength values were doubled at 20% of ZrO₂ compared with pure alumina. Other works announce considerably different values of flexural strength. Similar results had been published in mullite and zirconia composite system (Rendtorff et al., 2010), but other studies worked with stabilised zirconia and different processes which induced higher flexural strengths and elastic modules (Gutierrez-Mora et al., 2006). The bending strength can be further increased by using N₂ protection gas at presintering methods (Maneshian and Banerjee, 2009).
Figure 10. SEM images of cracked surface of a specimen contained 97.5% $\text{Al}_2\text{O}_3$, 2.5% $\text{ZrO}_2$

Figure 11. SEM images of cracked surface of a specimen contained 80% $\text{Al}_2\text{O}_3$, 20% $\text{ZrO}_2$

Figure 12. SEM image of a crack surface failure in a specimen contained 90% $\text{Al}_2\text{O}_3$, 10%$\text{ZrO}_2$
This increasing could not be observed in every case, but positive reactions of atmosphere changing were showed in Table 3. Mixing efficiency should be enhanced to avoid the microstructural defects possibly wet milling should be applied. Favourable mechanical data was gained up to 20% zirconia content.

Acknowledgements

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References


Structure and mechanical properties of ZrO$_2$-based systems

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Abstract. The structure and phase composition of zirconia-based nanosystems are studied. It is shown that during mechanical activation this nanosystem is divided into two subsystems with the average size of structural elements differing by two orders of magnitude. The fraction of the quasi-amorphous (X-ray amorphous) phase therewith increases. Through varying the heating rate of such a nanosystem in sintering we may purposefully vary its shrinkage at the stage of isothermal sintering. It is shown that through heating rate variation at sintering of such a nanosystem one can purposefully vary its shrinkage at the isothermal sintering stage. The higher the sintering temperature, the slower the compaction process at the isothermal stage. This allows producing materials with various porosity values but high strength of sintered material. keywords: ceramics, mechano-chemistry, nanostructure, nanocrystalline ZrO$_2$, phase composition, sintering

1. Introduction

The use of nanopowders enables the fabrication of finegrained ceramics which, as a consequence, offer higher strength in comparison with their large-grained analogs [1-4]. At the same time, practical application of fine powders presents a number of difficulties, the most serious of which is their polydispersity, due to their tendency to aggregate. The inhomogeneous packing of agglomerated powder particles in the forming process leads to low density [5] and, hence, low strength of the sintered material and considerably reduces the performance of nanocrystalline powders for the fabrication of high-strength materials.

Nanocrystalline powders produced by plasma-chemical methods show much promise for the production of zirconia- based ceramics [6]. In the course of production they acquire a uniform, as compared to ordinary technologies, component distribution and accumulate a high, in comparison to coarse powders, excess energy. In this case, both the properties of zirconia powders and final properties of products made of them greatly depend on the amount of the stabilizing agent. Of interest in this respect is a zirconia-based system stabilized by various oxides (yttrium, magnesium, etc.). As distinct from other ZrO$_2$-based ceramic materials like [3] and [7, 8], it allows thermal treatment with drastic changes in mechanical properties.
There are several approaches to improve the particle size uniformity of nanopowders. One of them is milling. In this process, disaggregation is accompanied by an activation of the powder: the formation of a highly imperfect structure and new surfaces and the removal of adsorbed gases [9]. It should, however, be kept in mind that mechanical processing of fine powders may cause not only disaggregation but also the reverse process: aggregation. The possibility of using mechanical processing of nanopowders in the fabrication of ceramic articles requires an in-depth study of its effect on the microstructure and properties of ceramics.

The purpose of this work was to study the effect of grinding of ultrafine ZrO$_2$-3wt.%MgO powder after ball-milling processes on the microstructure and properties of the ceramics produced from the powder.

2. Experimental

ZrO$_2$ powder was prepared by decomposing an aqueous solution of zirconium and magnesium nitrates in a high-frequency plasma. Plasma pyrolysis of liquid precursors is among the most effective processes for the preparation of fine zirconia powders. One important advantage of this method is that the reactions involved take place under nonequilibrium conditions, which ensure rapid nucleation and slow growth of new phases. At the same time, this method has a number of drawbacks, the main of which is its low selectivity. The broad size distribution of particles produced by the plasma pyrolysis of liquid precursors is due not only to aggregation but also to the large difference in geometry between individual particles [10, 11]. Ultrafine ZrO$_2$-3wt.%MgO powder was used in the present studies. It was dry-ground in a tumbling mill with high-density alumina ceramic media for up to 50 h. Ceramic samples were produced by hot pressing at 50 MPa and 1400°C for 10 min and were tested in three-point bending. The morphology of the particles and the micro-structure of the ceramics were examined by scanning electron microscopy on a Philips SEM 515. Phase composition and lattice parameters were determined by X-ray diffraction on diffractometer with CuKα, radiation.

3. Results and discussion

The data of transmission electron microscopy have shown that powders consisted of spherical particles and a large number of irregular shaped particles among which fragments of hollow spheres and films are present [12]. According to the obtained estimates, the amount of the spherical particles was about 20 % of the total amount of particles in the studied powders. Some particles both spherical and irregular shaped were transparent for the electron beam and it may thus be inferred that their thickness did not exceed 50 nm. The irregular shaped particles formed numerous agglomerates in the powder, while the spherical particles were mostly isolated. The size of the majority of the agglomerates was less than 0.25 μm, however, the powder contained
interparticle agglomerates and large spherical particles of size up to 6 μm. The crystallite size distribution in ZrO$_2$ powder obtained by TEM can be characterized as “wide”: dispersion comprises $o = 11.1$. The size of largest (more than 30 nm) crystallites amounts to 80 nm, though their contribution is not significant and does not exceed 10 %. The average crystallite size defined by electron microscopy coincides with the average size determined by X-ray diffraction (20 nm) and is close to the average crystallite size (22 nm) observed in similar ZrO$_2$ powders [12]. X-ray diffraction examination showed that the main phase in the powder was high-temperature cubic zirconia. The net fraction of the tetragonal and monoclinic phases was within 8%. The average crystallite size of the cubic zirconia was 25 nm as determined from the width of its X-ray lines.

During milling, a transition from one competing process to another was observed: from aggregation to disaggregation. In the initial stage of milling, aggregation prevailed. After 5 h of milling, the powder contained few or no separate particles: it consisted of aggregates with an average size above that in the as-prepared powder (Fig. 1a). At the same time, further milling led to disaggregation of the powder, breaking both the aggregates that had already been present before milling and those that had been formed during milling. After 25 h of mechanical processing, the powder was the least aggregated. The average particle size was 0.13 μm, the powder contained a much smaller percentage of electron-opaque particles, and there were no thin-walled spherical particles.

Milling for more than 25 h led to re-aggregation of the powder (Fig. 1b), but the resulting aggregates consisted of particles more uniform in size compared to the unmilled powder. After milling for 50 h, the powder consisted of spherical aggregates (granules) 0.12 μm in average size (Fig. 1c).

In an earlier study [1] and [13], powder disaggregation during milling was accompanied by an increase in the percentage of an X-ray amorphous (quasi-amorphous) phase: the X-ray diffraction pattern of the powder showed an increased background at small diffraction angles, and the particles in electron-microscopic images had a halo.

The disaggregation of the powder during milling was accompanied by an increase in its specific surface area and bulk density. Re-aggregation also led to an increase in the bulk density of the powder. In particular, the powder had the highest bulk density (0.2 $p_{\text{theor}}$) after milling for 50 h. After 25 h of milling, its bulk density was 0.1 $p_{\text{theor}}$.

The ratio of the integral intensity of the strongest reflection of the zirconia cubic phase I to the background radiation intensity $I_b$ was calculated. Similar phase transformations into cubic phase were observed after high energy high speed collisions in Si$_3$N$_4$ particles embedded in alumina matrix [14] and in NiO-Al-Al$_2$O$_3$ system after high temperature synthesis [15]. The calculation shows that for the time of powder refinement up to 5 h this ratio remains almost unchanged and decreases at further increase of the mechanical treatment time (Fig. 2). It is significant that the kink in the
time dependence of background intensity coincides with the beginning of powder separation in two independent subsystems and appearance of an ultrafine fraction with the “halo” around particles.

![Graph](image1)

Fig. 1. Average size distributions of powder particles at increasing time of treatment after ball-milling processes: a - initial state, b - 10h, c - 50h

![Graph](image2)

Fig. 2. The ratio of the (111) reflection intensity of cubic phase to the background radiation intensity in X-ray diffraction patterns of powder after mechanical treatment of different duration
The estimation of the crystallite size and lattice microdistortion of the cubic phase in the activated powder shows that the average crystallite size remains almost unchanged under mechanical treatment, but lattice microdistortion grows proportionally to the treatment time and is evidently induced by microstresses. A different character of the dependence of fine structure parameters on the time of refinement is observed for the zirconia monoclinic phase. With increasing mechanical treatment time the crystallite size reduces, while the lattice microdistortion value increases.

Fig. 3 gives the diagram of powder compaction under continuous loading and the compacting pressure dependence of the relative compact volume in double logarithmic scale (measurements were made after the removal of specimens from the mold). In the diagram three linear portions with different slopes are well pronounced. A kink is also observed in the compacting pressure depending on the relative compact volume, though at a higher applied pressure. The portions with different slopes in the given dependences reflect the change of the prevailing mechanisms of powder compaction. The difference of pressure under which the diagram of continuous powder compaction and the compacting pressure depending on the relative compact volume, though at a higher applied pressure. The portions with different slopes in the given dependences reflect the change of the prevailing mechanisms of powder compaction. The difference of pressure under which the diagram of continuous compaction and the compacting pressure dependence of the relative compact volume kink stems from a decrease in the actual compact density due to elastic aftereffect after specimen removal.

Fig. 3. Plot of relative density vs. compaction pressure for the compaction curve (1) and densification body (2) of powders

The X-ray phase analysis data show that the monoclinic phase content in compacts constantly increases starting from a minimum pressure. Despite the fact that the phase composition analysis was performed on the compact surface from the active die side and therefore data on the monoclinic phase content were somewhat increased relative to the entire volume (owing to a nonuniform application of pressure to different
specimen volumes at the cost of interparticle friction and friction of powder particles on the mold walls), it can be observed that the monoclinic phase during compaction is formed already at low pressure (less than 50 MPa) whose value is much lower than the strength of macroscopic zirconia specimens under compression (above 500 MPa). This is due to the fact that in nanocrystalline powder with a very complex morphological structure stress localization can occur, considerably exceeding the average stress level already at the initial loading stage. Thus, even at the initial stages of powder compaction the transfer of particles to the free pore space is accompanied by their failure.

The increase of the zirconia monoclinic phase content in powder at compaction is not monotonic; the most intensive failure of powder structural elements takes place in the compacting pressure interval from 50 to 100 MPa. The pressure value at which a kink occurs in the dependence reflecting the ZrO₂ monoclinic phase content growth during compaction corresponds to the pressure under which the compacting pressure dependence of the compact density kinks. Since the failure of powder particles was observed in the whole compacting pressure interval, the kinks in the compaction diagrams are probably related to the beginning of failure of stronger structural elements of powder.

The constructed dependences of compact density variation at sintering show that the most intensive compaction of specimens for all temperature conditions takes place at the heating stage, while isothermal aging for 7 h allows ceramics density to increase by no more than 5..7%. Rapid shrinkage of nanocrystalline powders at the nonisothermal sintering stage was already discussed in papers [16, 17] where the mechanism of mutual slipping of powder particles and compaction at the cost of recrystallization-induced grain growth are considered as the mass transfer mechanisms.

Analysis of shrinkage value dependences at the isothermal sintering stage (Fig. 4) reveals that the exponent $n$ of the shrinkage kinetics equation where $AL/L$ is the relative shrinkage, $K$ is the kinetic coefficient of the process rate, and $n$ is the constant reflecting the compaction mechanism), first, is almost the same for the sintering regimes at homologous temperatures 0.56 and 0.63 and, second, exceeds a few times the exponent for the sintering regime at homologous temperature 0.63. This might result from the fact that at the stage of compact heating a strong matrix stable to further compaction at isothermal aging is formed. In this case, the higher the sintering temperature, the more stable the material to compaction at isothermal aging. The temperature gradient existing in compacts at heating evidently promotes the failure of barriers and displacement of powder particles, whereas the established thermodynamic equilibrium at isothermal aging hinders active displacement of particles.
Fig. 4. Plots of relative density for samples sintered at different homologous temperatures

By the dependence of the exponent $n$ from the shrinkage kinetics equation on the shrinkage value $AL/L$ one can determine the value of $n$ at which no shrinkage at all would occur at isothermal aging. Fig. 5 illustrates the obtained dependence. The experimental points with high correlation coefficient are approximated by a linear functional dependence by which one can easily define the heating temperature prior to isothermal aging, at which no compaction of ceramics would take place; this corresponds to temperature 1700°C. Certainly, at a varying density of sintered compacts the temperature of isothermal aging without compaction would be different. It is thus possible to govern the process of structure formation in ceramics both at the heating stage and isothermal aging stage as well as if it is necessary to obtain a developed porous structure in the material. The porous matrix formed during heating would provide porosity in the material, while isothermal aging would increase the strength of interparticle bond.

As would be expected, the disaggregation of the powder led to an increase in the density of the ceramics produced from it (Fig. 6). The highest density was realized by the ceramic produced after milling the powder for 25 h, which ensured the lowest degree of aggregation. The density of that ceramic considerably exceeded that of ceramic samples produced from the as-prepared powder. The ceramic prepared from the powder consisting of spherical granules (after milling for 50 h) had considerable residual porosity both within and between the granules, even though the powder had the lowest bulk density. The ceramic produced after milling the powder for 5 h (the highest degree of aggregation) had the lowest density.
Milling also influenced the grain size of the ceramics. The average grain size determined on fracture surfaces increased with an increase in the degree of aggregation during milling and decreased upon disaggregation. Owing to powder disaggregation, we were able to reduce the grain size in the ceramics by almost a factor of 2 (Fig. 6): the average grain size in the ceramic produced from the unmilled powder was 0.6 μm, and that in the ceramic produced after milling the powder for 25 h was 0.3 μm.

Milling the ultrafine ZrO$_2$-3wt.%MgO powder markedly increased the strength of the ceramic produced from it. According to the three-point bending test results, the strength of the ceramic produced after milling the powder for 25 h was 640 MPa, exceeding that of the samples prepared from the unmilled fine powder by more than a factor of 2. Even though the ceramic produced from the powder reaggregated during
milling had considerable residual porosity, its strength was comparable to that of the ceramic fabricated from the powder with the lowest degree of aggregation and its density was higher.

4. Conclusions

The structure and phase composition of zirconia-based nanosystems was studied. The present results demonstrate that, during low-energy milling in a tumbling mill, ultrafine ZrO$_2$-3wt.%MgO powder prepared by decomposing liquid precursors in an HF-plasma undergoes first aggregation and then disaggregation. Powder disaggregation during milling leads to an increase in the density, a reduction in the grain size, and a marked increase in the strength of the ceramics produced from the powder. The morphological structure of ultrafine-grained ZrO$_2$ powder as well as its variation under mechanical activation, compaction and annealing was investigated. It was shown that in the course of mechanical activation the given nanosystems are divided into two subsystems with the average size of structural elements differing by two orders of magnitude. The fraction of a quasi-amorphous (X-ray amorphous) phase therewith increases. This enables purposeful variation of the characteristics of sintered materials.

It was shown that through heating rate variation at sintering of such a nanosystem one can purposefully vary its shrinkage at the isothermal sintering stage. The higher the sintering temperature, the slower the compaction process at the isothermal stage. This allows producing materials with various porosity values but high strength of sintered material.

References


Restructuring of Ceramics Features with Changes in the Large and Nanocrystalline Ceramic System ratio

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Abstract. The structure and properties of ceramic based on alumina powders systems produced by the method of thermal decomposition of hydroxide aluminum and the plasma-spray pyrolysis method has been studied. It is shown that at the maintenance of 60 % plasma-chemical powder Al₂O₃ in mix sharp change strength characteristics which those more than have less porosity is observed. Approximation of strength dependence vs. average pore size to porousless state shows a possibility of obtaining material with almost theoretical strength. Correlation between microstresses in crystallites and macrostrength in sintered ceramics was found.

Keywords: alumina, ceramic powders, microstructure, nanocrystalline, plasma-spray, pyrolysis, strength, stress

1. Introduction

Using nano-sized ceramic powders which are not in equilibrium opens up entirely new opportunities to obtain highly porous ceramics [1-5]. Due to the developed surface of the nanocrystalline particles, special nanocrystalline structures are formed with a high bonding strength at the grain boundaries, providing high strength for the ceramics [6-8].

A promising method for creating permeable ceramic materials with high porosity is the mixing large-fractured and ultrafine powders [9], and the geometry of the pores obtained in such a way is determined by the size and shape of large-fractured powder particles [10]. However, when creating a porous ceramic material in this manner ultrafine powder is used only as an additive (as a rule up to 10 %) [11], in other words, the pattern formation in ceramics porous structures with ultrafine powders, over a wide range of content, are not well understood. However, the data on the pore structure of those materials and its relation to the fine crystal structure parameters have a
fundamental importance in the analysis of the deformation behavior [12, 13].

The aim of this paper is to investigate the crystal structure of the thin porous alumina ceramics synthesized from powders with different particle sizes (dispersion).

5. Materials and methods

To obtain porous ceramic mixture powders, mixtures of powder were prepared in a wide range from technical alumina (GOST 30558-98) to plasma chemical Al₂O₃ (TU 2320-00107622928-96). Sintering is performed at temperatures of 1200, 1300, 1400, 1500, 1600 and 1650°C for duration in the isothermal hold of one hour.

X-ray diffraction analysis was performed on ceramics (DRON UM1) with filtered CuKa radiation. The average crystallite size was calculated from the broadening of the reflex to small angles. The values of micro distortions crystal lattice were calculated from the broadening of the reflex to the far corners of the diffraction pattern.

Analysis of the morphology of the pore structure was carried out by scanning electron microscopy by QUANTA 200 3D microscope. The pore size was determined by random secants, the number of measurements was at least 300.

6. Results and discussion

Research was conducted on the polished surface of the ceramic samples sintered at 1650°C and holding 1:00 hour (Fig. 1). It was found that the pore structure of the commercial alumina sample is a system of continuous long channelization and disordered forms of dense portions corresponding to the alumina agglomerates, in which at higher magnification there can be seen varying forms of closed pores larger than 5 microns. In fact, this structure corresponds to two interpenetrating components: substance and pore.

In contrast to the ceramics consisting of industrial alumina, the pore structure of the plasma-chemical sample Al₂O₃ powder represented as mainly isolated pores with a random pore shape and distinct clusters of various sizes (Fig. 2). Mostly, the amount of isolated pores had a size of less than 2 microns. The average pore size of the clusters was 10 microns.

In the studied ceramics, bimodal distribution of pore size is observed. The first maximum (d1) is due to pores in size less than 5 microns, the size of which is commensurate with the size of grains. A second maximum (d2) forms macropores ranging in size from 5 to 100 microns. Such large voids in ceramics are due to the formation of lasting frameworks made of used agglomerates powders during pressing, the dimensions of which determine the size of macropores between them. In coarse fraction ceramic powder, the ratio of pore size of 0.5 microns is substantially lower than the ceramic powders of the nanocrystalline plasma-chemical Al₂O₃.

With the increase of the content of plasma chemical powder in the starting mixture the communicating pore space starts to decrease, and thus, the reduction in the size of channelization is considerable. This is evidenced by reduction of the average pore size
from 53 to 9 microns for maximum d2. However, in ceramics that contains only plasmochemical powder, the porosity is again increasing. In ceramics containing 90% plasma chemical powder, the densest structure occurs, and there are isolated pores with random shapes and pores separate clusters. Apparently, this is due to the fact that the alumina 10% additive added to the plasma chemical Al₂O₃ powder destroys the foam-like agglomerates plasma chemical powder on the pressing stage, wherein the particles and agglomerates of industrial alumina are not enough to form a lasting framework on their base.

![Fig. 1. The microstructure (a) and pore size distribution (b) for industrial ceramics based on alumina, sintered at 1650°C and holding for 1 hour](image1)

![Fig. 2. Microstructure (a) and pore size distribution (b) for plasma chemical based ceramic powder Al₂O₃ sintered at 1650°C and holding for 1 hour](image2)

Research on the influence of the crystallite size on micro distortions crystal lattice showed that the latter decreases with the increase of crystallite D (Fig. 3). Built dependence is described by the following formula:
The case when $\epsilon^{2/1} \sim D^{-1}$ proves that the main contribution to micro distortions lattice in the studied ceramics is made by the interfaces, which are always present in such systems. In this regard, the smaller are the crystallites, i.e. the length of the border, the higher is the level of micro distortions.

The relationship was investigated between the fine crystal structure parameters and the sintering temperature, which indicates that, with an increase in the sintering temperature, the average crystallite size increases linearly, and the level of the crystal microstrains lattice decreases.

An estimation was made for the diffusion activation energy, which is equal to $97 \cdot 10^3$ J/mol or 23 kcal/mol, which is 5 times less than the activation energy of self-diffusion of aluminum and oxygen in polycrystalline oxide, from which we may suggest that the main mechanism of mass transfer during sintering is grain boundary diffusion.

We found that the increase in porosity is accompanied with a decrease in crystallite size and microstrain growth. Dependence of crystal lattice micro distortions porosity in alumina ceramics has a pronounced kink in the porosity of about 50% (Fig. 4).

Investigation of the effect of porosity on the strength of the ceramic showed that the strength of the samples decreases significantly with increasing porosity, when porosity is in the range of about 50%, the angle of inclination of the approximating line is changed (Fig. 5). Primarily, it is due to the fact that there is a change in the nature from the isolated pores structure and pore clusters of various shapes and sizes for a ceramics structure consisting of two interpenetrating component, i.e. substance and pore.

![Fig. 3. Dependence of the average level of micron-sized crystallites in alumina ceramics made from powders with different particles](image-url)
Thus, the changing of the pore structure nature is accompanied with a sharp decrease in the strength and growth of the crystal lattice microstrain, which corresponds to the percolation transition in the ceramics under examination.

Type pore volume and pore size also significantly affect the strength of the material. It was found that the tensile strength is greater, the smaller the average pore size and dispersion, and the extrapolation of this dependence to zero porosity showed that the strength of the studied ceramics will be about 3.5 GPa, which corresponds to the estimated strength of alumina that is available in the literature [14, 15].
7. Conclusions

It was found that in the ceramic-based powders with different particle pore structures, the change in the nature of the ceramic frame and the large pore space to isolated pores and pore clusters coincides with the increase of the nanocrystalline powder in the initial mixture of powders.

Pore structure type changes with a porosity of about 50% and is accompanied with a sharp decrease in strength and a decrease in microstrain, which corresponds to the percolation transition in the ceramics under examination.

Pore size distribution is bimodal. The first maximum is due to pore size of less than 5 microns, the second is a pore size of 5 to 100 microns.

The estimation of the activation energy of the grain growth process during sintering is 23 kcal/mol. This value is showing that the main mechanism of sintering is grain-boundary diffusion.

The determined relationship between crystallite size and crystal lattice microdistortions indicates that the examined ceramics’ main defect part is located at the grain boundaries.

Thus, the obtained results enable a directional adjusting of the structure and properties of ceramic materials based on aluminium oxide powders with different particle sizes. This makes possible to practically obtain a variety of structures either as highly porous and substantially zero porosity with a set complex of physical and mechanical properties.

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References


Thermal expansion of oxide systems on the basis of ZrO$_2$

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Abstract. The structure and phase composition of the ceramic-based system ZrO$_2$-MgO is studied. The dependence between the structural-phase state and the coefficient of thermal expansion of ceramic materials based on solid solutions ZrO$_2$-MgO is demonstrated. The coefficient of thermal expansion of the system increases proportionally to the increase of the MgO content. The thermal expansion of the ZrO$_2$-MgO ceramic materials can be described in the framework of the mixture rule taking into account the phase composition of ZrO$_2$ and the amount of magnesia grains in the matrix. keywords: ZrO$_2$-MgO solid solutions, coefficient of thermal expansion, mixture rule

1. Introduction

Today’s industrial progress leads to the need for materials that retain their functional properties when operating under high temperature conditions [1-6]. Good candidates in this respect are the oxide ceramic materials, particularly the ones on the basis of ZrO$_2$-MgO solid solutions. Materials of the ZrO$_2$-MgO system are known to have high melting temperature, chemical resistance, crack resistance and strength, which make possible their operation under high temperature conditions in aggressive media. Of particular importance in such conditions is the thermal expansion of the material. The literature provides the values of the coefficient of thermal expansion for stabilized ZrO$_2$ [7-10], but neither the qualitative nor the quantitative composition of the materials is considered. It is therefore pertinent to study the thermal expansion of the ZrO$_2$-MgO systems of variable composition.

The aim of this paper is to study the structure and phase composition and their relation to the coefficient of thermal expansion of the ZrO$_2$-MgO ceramic materials.
8. Experimental procedure

ZrO$_2$-MgO ceramics of the following compositions have been studied: ZrO$_2$ + 8.6 mole% MgO (hypoeutectoid); ZrO$_2$+13.9 mole% MgO (eutectoid); ZrO$_2$+25.4 mole% MgO, ZrO$_2$+35 mole% MgO, ZrO$_2$+43.3 mole% MgO (hypereutectoid).

Specimens were compacted from powders produced by thermal decomposition of salt solutions in low-temperature plasma. Powder compaction was carried out under a pressure of 70 MPa. The compacts were sintered at 1650°C and then subjected to one hour of isothermal exposure in air.

The structure of the obtained ceramics was analyzed by scanning electron microscopy on a microscope Philips SEM 515. The accelerating voltage was 30 kV. Specimens for SEM examination were mirror polished with diamond pastes of different sizes.

The phase composition and crystal structure parameters were studied by X-ray diffraction patterns obtained using filtered CuK$_\alpha$ radiation. The zirconia phase content was estimated by the ratio of the integral intensities of the tetragonal and cubic diffraction lines $I(111)$, and the monoclinic diffraction lines $I(111)$, $I(-111)$.

Thermal expansion was measured using a mechanical dilatometer in air. The specimen temperature was increased at a rate of 10 °C/min. The specimens were heated up to 1100 °C, which, according to the phase diagram of the ZrO$_2$-MgO system, corresponds to the temperature of transition from the low-temperature monoclinic ZrO$_2$ phase to the high-temperature tetragonal modification of ZrO$_2$.

9. Results and discussion

The SEM images of the ZrO$_2$-MgO ceramics structure with different magnesia content are given in Fig. 1. The structure of the specimens of the hypoeutectoid composition shows lenticular grains of the tetragonal ZrO$_2$ phase, along with grains of the cubic ZrO$_2$ solid solution (Fig. 1a). The structure of the ZrO$_2$ (13.9 mole% MgO) ceramics is represented in Fig. 1b. This composition is characterized by grains of the cubic modification of ZrO$_2$ [11, 12]. The specimens of the hypereutectoid compositions have magnesia inclusions in the ZrO$_2$ matrix. In this case, the content of MgO inclusions increased from 9 to 22% with the magnesia content growth in the ZrO$_2$-MgO system from 25.4 to 43.3 mole%, respectively.

According to X-ray phase analysis data, the X-ray diffraction patterns of the hypoeutectoid ceramics have reflections from three zirconia phases, namely, cubic (C-ZrO$_2$), tetragonal (T-ZrO$_2$) and monoclinic (M-ZrO$_2$) (Fig. 2), with the monoclinic phase content increasing with the growing magnesia content in the initial mixture.

The phase composition of the eutectoid ceramics is represented by the high-temperature cubic modification of ZrO$_2$. The X-ray diffraction patterns of the hypereutectoid ceramics have, along with the ZrO$_2$ reflections, diffraction maxima corresponding to MgO.
Fig. 1. SEM images of the ceramics structure
(a) – ZrO$_2$ (8.6 mole% MgO), (b) – ZrO$_2$ (13.9 mole% MgO), (c) – ZrO$_2$ (25.4 mole% MgO),
(d) – ZrO$_2$ (35 mole% MgO), (e) – ZrO$_2$ (43.3 mole% MgO)
Fig. 2. X-ray diffractograms of the ceramics of the ZrO$_2$-MgO system:
1 — ZrO$_2$ (8.6 mole% MgO); 2 — ZrO$_2$ (13.9 mole% MgO); 3 — ZrO$_2$ (25.4 mole% MgO);
4 — ZrO$_2$ (35 mole% MgO); 5 — ZrO$_2$ (43.3 mole% MgO)

Measurements of the coefficient of thermal expansion of the studied materials (Fig. 3) showed that the coefficient of thermal expansion measured in the temperature range 400-1250 K depends linearly on the magnesia content in the initial mixture. The measured thermal expansion coefficients agree well with the values calculated by the mixture rule taking into account the phase composition of the studied materials: the content of the monoclinic ZrO$_2$ modification for the composition with 8.6 mole% MgO is 15%, which determines low values of the coefficient of thermal expansion equal to 6.7 • $10^{-6}$ K$^{-1}$, since, according to the literature data, the coefficient of thermal expansion of the monoclinic ZrO$_2$ phase is 6 • $10^{-6}$ K$^{-1}$ and that of the cubic ZrO$_2$ phase is 8 • $10^{-6}$ K$^{-1}$. The coefficient of thermal expansion of the eutectoid specimens is defined by thermal expansion of the cubic ZrO$_2$ phase, while the main factor that contributes to the thermal expansion of the hypereutectoid specimens is an increase in the amount of magnesia grains in the zirconia matrix.

In extrapolating the obtained dependence to the zero MgO content, the coefficient of thermal expansion corresponds to the thermal expansion of the monoclinic ZrO$_2$ modification. In extrapolating the obtained dependence to the 100% magnesia content, the coefficient of thermal expansion is 14.9 • $10^{-6}$ K, which is close to the thermal expansion of magnesia equal to 14.4 • $10^{-6}$ K. So, the coefficient of thermal expansion of the ZrO$_2$-MgO system is defined by the mixture rule taking into account the phase composition and amount of magnesia inclusions in the ZrO$_2$ matrix.
10. Conclusions

It is found that the coefficient of thermal expansion is governed by the phase composition of the sintered ceramics, with a ratio of the fractions of the high- and low-temperature ZrO$_2$ modifications and the amount of magnesia grains in the ZrO$_2$ matrix. The coefficient of thermal expansion of the system increases proportionally to the increase of the MgO content. The thermal expansion of the ZrO$_2$-MgO ceramic materials can be described in the framework of the mixture rule taking into account the phase composition of ZrO$_2$ and the amount of magnesia grains in the matrix.

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References


Investigation and optimization of homogeneity of ceramic injection molding raw material to improve crack toughness of end product

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Abstract. This study used capillary rheometer, gas densimeter and injection molding pressure measurement to quantitatively analyze the homogeneity of alumina based injection molding feedstock, and presents the report of the relationship between material homogeneity and kneading parameters, and the ration of different raw components. The researchers found as main result that the flux material has the highest effect on the homogeneity, since increasing the amount of this material can help in the equable mixing of alumina powder and paraffin wax. Furthermore, increasing the mixing time has positive effect on the homogeneity of the material, but much less than the amount of flux.

Keywords: alumina powder, paraffin wax, ceramic injection molding, densimeter, capillary rheometer, feedstock

1. Introduction

The procedures of ceramic injection molding (CIM) include four steps: kneading process, injection molding, debinding, and sintering. The CIM technology offers the opportunity to make complex and near-net-shape of ceramic parts. The kneading process is an important step in ceramic injection molding. The kneading stress offered by a sigma-blade kneader is quite enough, but in special cases with other kneaders it may be not enough to break down the powder agglomerates in the ceramic feedstock, especially, if the agglomerates are consisted of ultra-fine powder. The agglomerates are retained until sintering and become the fracture origin if the effective size of the defects is too large to withstand fracture stress [1, 2, 3]. Evans [4] reported a result of zirconia, which was fractured in a defect size greater than 10 ^m. The fracture strength is not affected, if the agglomerates are smaller than 10 ^m [4]. Recently, the fundamental and application issues of nanotechnology and micro-electromechanical system (MEMS) have evoked the interest toward ceramists. The precision microinjection molding makes the
manufacturing of small parts possible for many advanced applications. The powder size must be reduced to produce thin and complex parts. The nanopowder tends to agglomerate due to van der Waal force. However, little attention for the kneading behavior of ceramic feedstock have been given in literature by using ultra-fine or nanopowder [5].

For producing ceramic arc tube parts (plugs), there are three different major components used for producing injection molding raw material (hereinafter feedstock): high purity alumina powder as the main component, an organic paraffin wax as a binder material, and flux material as surfactant.

After selecting a suitable powder and a binder system, the first processing step in CIM is to mix them to prepare an appropriate feedstock for molding and subsequent processing.

A homogeneous feedstock having high powder content is required to achieve a low shrinkage during binder removal and sintering. The feedstock should have the particles separated with a very thin layer of binder. To achieve this, powder agglomerates have to be dispersed in the binder [1, 2, 6].

With a homogeneous feedstock, in this experiment the main goals were to improve the quality of end product and to avoid the cracks and material discontinuities in the sintered ceramic parts (Fig. 1).

Fig. 1. Cracked (left) and intact (right) sintered alumina ceramic

1.1. Possible options to determine the homogeneity of ceramic feedstock
In the case of the present experiments, the following measurement methods were chosen as output parameters of the grade of homogeneity: capillary rheometry, densiometry and pressure during injection molding. Literature mentions viscosity as a tool to determine the grade of homogeneity [7, 8, 9], but regarding the other two measurements it was not found to be advantageous for the determination of homogeneity during the present studies.

In the case of all three methods (described below) the same evaluation principle was followed: several samples were taken from the prepared material cell, and the standard deviation of the measured values were investigated as an output parameter that can show the picture about the grade of material homogeneity and internal diversity [10].
1.1.1 Capillary rheometry

The shape of material is changing by the effect of external forces. Two ideal cases of deformation are known: elastic and viscous, which states can be mathematically well described by rheological state equations (constitutive equations) [11,12]. The Ostwald de Waele power law can follow the behaviour of injection molding feedstock, where the raising tension (t) and the deformation speed (y) are proportional to a power of n>0 natural number; see Eq. (1). Generally, in most of the cases n<1, so the viscosity of molten material decreases with the increasing deformation speed, at constant temperature (Fig. 2). This kind of material behaviour is pseudo-plastic: in this case the material is thinning by the shear stress.

\[ \tau = K \cdot \dot{\gamma}^n \]  

(1)

Fig. 2. Typical viscosity curve of pseudo-plastic materials

The principle of capillary rheometry is the following: the measured material flows through a small diameter tube with relative small flowing velocity. Knowing the amount of material flow over given time, the pressure difference, and the geometry of the capillary (radius, length) the viscosity can be defined according to the Hagen-Poiseuille law; see Eq. (2) [13,14].

\[ v = \frac{\pi (p_1-p_2)}{8\eta l} r^4 t \]  

(2)

where:
- \(v\): velocity of flow
- \(p_1\) and \(p_2\): the pressure on the two ends of the capillary \(r\)
- \(\eta\): viscosity \(l\): length of capillary
- \(r\): capillary radius
- \(t\): time

Considering the theory of determining homogeneity using viscosimetry, if the homogeneity of the material is increasing then the standard deviation of the viscosity values of samples is decreasing under constant temperature.
1.1.2 Densiometry
To determine the real density of ceramic feedstock a Quantachrome Ultrapyc 1200e densitometer (Fig. 3) was used with He gas system. The He gas for density measurements is used due to its small atomic size and high diffusion ability since it is able to penetrate into the smallest pores, even up to 0.2 nm. The densiometry is based on pycnometer volume determination, which is equal to the volume of displaced gas by the feedstock material (Archimedes law) and to the gas expansion technique (Boyle law). The volume of open pores can be defined with this method, but the closed or impenetrable pores can not be measured [15,16].

Fig. 3. Quantachrome 1200e type densitometer (left) and measuring cells (right)

The standard deviation of measured density values can refer to the grade of homogeneity of feedstock since the mixed injection molding raw material consists of several components of different density. Namely, if some component did not mixed properly in the feedstock, then there can be a local enrichment from it, and so the measured density can be comparable with other samples, where there is no component enrichment; that may be considered a properly mixed raw material [16].

1.1.3 Injection molding pressure
The injection molding pressure is a parameter, which arises when the injection switches to holding pressure. In other words, this parameter is the maximum injection molding pressure during the injection process, which is needed for the filling of molding tool with a given quantity of material. The maximum speed of the material is defined by the gate between the injection unit and the injection tool, as a minimum crosssection (bottle-neck) [17, 18].

Since the temperature, the minimum cross-section and the amount of material are constant, only the properties of material has influence on the flow of molten material, the change of the resistant force and so the injection molding pressure depends only on the flow behaviour of the material. In this way, one can get a similar capillary
viscosimeter, in which the viscosity from the pressure against to the material flow can be estimated. And thus, from the standard deviation of pressure values, the homogeneity of feedstock can be determined as well.

The relationship between the two parameters is linear (Fig. 4).

![Fig. 4. The determined relationship between the capillary viscosity and injection molding pressure](image)

The describing equation of the relationship with 92% probability is given by Eq. (3):

\[
y = 2.2488x + 56.287
\]  \hspace{1cm} (3)

This linear relationship between the two outputs shows, that one can get data about the homogeneity with the standard deviation of injection molding pressure of the feedstock produced with the given mixing parameters.

2. Experimental

The primary standpoint of the experiment is to discover the connection between the homogeneity of feedstock and the quality of end product, and to determine the homogeneity at all. To reach this goal, different mixtures were made with different processes and amounts of components.

To research the properties of homogenous feedstock, a design of experiment was made, using the MINITAB statistical software.

To analyse the main effects, the Plackett-Burman III resolution fractional factorial design of experiment was used [19, 20, 21]. Considering this, 4 factors were investigated at two levels: amount of flux material, mixing time, mixing temperature and the dosage of alumina powder during mixing.

In favor of control of reproducibility, repeatability and linearity, the centre point was repeated three times according to the design of experiment, and the full test was consisted of 15 different runs.

There were constant mixing volumes and weights run by run. The determination of the factor values was made by the operating levels and literature research. After the mixings, 5 samplings were carried out for each run.
3. Results and discussion

3.1. Determination of homogeneity

3.1.1. Results of capillary viscosimetry

The most important properties of an injection molding feedstock are the viscosity and homogeneity. According to the literature review, the high quality feedstock has low viscosity, and the viscosity does not change within manufacturing batch, that means the viscosity has low fluctuation, it was homogenously mixed [22,23].

The capillary viscosimetry measurements were carried out by a laboratory Dynisco LMI 4000 type capillary rheometer, the measuring temperature was set to 68 °C, and the melting time was 360 seconds (Fig. 5). The measuring temperature was chosen to that of the temperature of injection molding of the test materials, to help the comparison of different test results. For the measurements, 3700 g pressing weight and 1.042 mm capillary diameter were chosen.

![Dynisco capillary rheometer](image)

Fig. 5. Dynisco capillary rheometer (left) and the viscosity measurement of feedstock (right)

After the measurement, the equipment automatically displays the viscosity value based on the MFR (Melt Flow Rate). The measurements were repeated on five samples per batch, in this way the standard deviation values were possible to be determined. Fig. 6 shows the influences of input parameters on the standard deviation of viscosity - so the dependence of homogeneity on the input parameters of mixing.

It can be seen, that the flux material has the strongest effect on the homogeneity, so if more flux is added into the feedstock, the standard deviation of viscosity becomes lower. The flux is a surfactant in the system, so if the amount of alumina powder and paraffin wax is increased, then the components can be mixed with each other more effectively. Consequently, the wax can be able to coat the alumina more, and this can decrease the powder-powder friction, and the focus is placed to the wax- wax friction [24].

In addition, it can be observed, that the homogeneity is decreased with the increasing...
mixing time, but not so strong effect can be observed with the narrow variation intervals chosen, however, it is visible that with the increase of mixing time the components can mixed better with each other.

![Fig. 6. Influences of input parameters on the standard deviation of viscosity](image)

The dosage of alumina shows weak negative effect, however, it would be logical that the homogeneity is increasing if the dosage of powder is increasing. It can be noticed that the results are probably distorted by the noise of applied dosage method, namely, if there were more steps of dosage then more stops appeared in the mixing process and it would have a negative effect on the homogeneity and the efficiency of mixing. Nevertheless, it can be concluded that the continuous mixing is more important than the dosage in more steps. The dosage in more portions with continuous mixing together can improve quality.

### 3.1.2. Results of density measurements

The method of density measurement was the following. Sample was placed into the sample holder with constant weight, measurement was performed with 20 psi constant He gas pressure. Before the test 90 cleaning rinse were applied to eliminate the stuck air particles in the pores and on the surface of feedstock.

The equipment records 3 density values, and calculates the average of those. Five samples were taken and measured from the different feedstock runs, to be able to study the homogeneity of the composition of material from the standard deviation of the measurements. *Fig. 7* shows the dependence of the standard deviation of density on the input parameters of mixing.

It can be seen in case of this measurement method as well that the increase of flux material amount and mixing time results the standard deviation of density values to decrease, so the homogeneity of the feedstock increases. However, it can be seen here as well, that more steps of dosage does not result positive effect in the homogeneity, due to the same reasons mentioned above.
3.1.3. Evaluation of injection molding pressure measurements

The value of pressure during injection molding would be theoretically equal to the other two measurements before, since this measurement is an alternative capillary viscosimetry on account of constant and fixed cross-section, temperature, material velocity and material properties. In this case, the resistance of material was also measured during forcing through the capillary. As it was expected, the pressure results are comparable to the results of the other two measurements (Fig. 8).

In this case as well, the amount of flux dominates, although in this case one could observe the highest positive effect of the mixing temperature on homogeneity. However, this effect is not significant enough to enunciate that the mixing temperature has an influential role on the homogeneity within the interval variation studied.

3.1.4. Results of injection molding experiments

As a second step, after the determination of the homogeneity of different feedstocks, the injection molding was carried out. In this case the main question was the effect of homogeneity on the quality of the sintered end product, especially on the occurrence of
cracks in the ceramic.

The samples of different runs were classified after the presintering and sintering processes, which results can be seen in Fig. 9.

![Fig. 9. Susceptibility of cracking, depending on the input mixing parameters](image)

In this case as well, the positive effect of the amount of flux is noticeable. The explanation is the same as before: the homogeneity of feedstock was improved, hereby less separated component remained in the mixture (whether powder or paraffin wax), which can cause cracks, voids or any heterogeneity in the sintered end product [25,13,14]. The other three factors did not have any significant effect on the amount of cracked products within the variation interval studied, except for the weak positive effect of mixing time.

4. Conclusions

The introduced test methods can be suitable to determine the grade of homogeneity of the ceramic injection molding raw materials.

With the defined mixing settings the homogeneity of raw material can be improved.

The flux material has the strongest effect on the homogeneity, since increasing the amount of this component can help homogeneous mixing of alumina powder and paraffin wax.

Increasing the mixing time has positive effect on the homogeneity of the material, but in a much less pronounced fashion than the amount of flux.

In the decrease of the amount of cracked ceramics, the mixing time and the amount of flux material were found to be the most effective input parameters.

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Foam Glass Ceramics as Composite Granulated Heat-Insulating Material

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Abstract. Manufacturing technology for granulated glass-ceramic heat-insulating material made from crushed glass, clay and organic additives was developed. The effect of the basic physical characteristics of the components of the charge on the process of pore formation is studied. According to the research results, the basic parameters affecting the sustainability of the swelling glass are specified. A rational charge composition, thermal and gas synthesis mode are chosen such that the partial pressure of gases is lower than the surface tension of the melt. This enables the formation of granules with small closed pores and a vitrified surface. The regularities of the effect of composition and the firing temperature on the properties of the granules are determined. The resulting granulated heat-insulating material is produced with a bulk density of 260-280 kg/m³, and pellet strength of 1.74 MPa, thermal conductivity of 0.075 W/m °C, and water absorption of 2.6% by weight. The results are given of the study of the dependence of the thermal conductivity coefficient and mechanical strength of the granules on the bulk density. Keywords: Carbon, clays, crushed glass, density, durability, granulate, glass-ceramics, heat-insulation, sawdust, thermal conductivity, water absorption.

1. Introduction

The advantage of foam glass compared to other well-known insulating materials is its unique combination of insulating and functional characteristics [1, 2], which enables the use of this material in various industrial spheres [3, 4] including heat insulation lightweight aggregate concretes as well [5, 6, 7].

The aim of this research is the experimental and theoretical justification of the feasibility of producing a competitive environmentally friendly insulation - granulated
foam glass ceramic, which would provide effective thermal and physical characteristics for the construction industry and thermal engineering. For achieving this goal, the following tasks were set:

a. Experimentally validate an increase in the functional, thermal and physical characteristics of foam glass ceramics by means of selection and optimization of the structural phase condition of granulated material.

b. Study the physical and chemical processes of pore formation and crystallization of aluminum silicate hot melt during the formation of the phase composition and foam glass ceramic structure.

2. Materials and experiments

Crushed glass, clay, carbon and sawdust were used as the material for the production of granulated foam glass ceramic. In order to increase the mechanical strength of interpore partitions and the surface of granules and, consequently, the granule mechanical strength in general, clay was added to the composition, and as it decreased the hot melt viscosity, an organic additive - sawdust - was used to enable stable foaming with a gassing agent. Glass types with high foam glass production characteristics include: SiO₂ - 60...72.5%, Fe₂O₃ - 0...2.5%, CaO - 4...6.0%, MgO - 1,5...2.5%, Na₂O - 12,5...15.0%, Al₂O₃ - 1,2.1.57 [8].

2.1. Glass

Three types of glass (Table 1) were used in the experiments. The first type of the crushed glass was float (window) glass.

Chemical composition of windowpanes is the closest to this. Their distinctive characteristic is a low level of Al₂O₃ compared to other types of glass.

The second important source of crushed glass was green bottle glass. This type of glass has a high level of Fe₂O₃ - 0.65%, Al₂O₃ - 4.0%, Na₂O - 14.5%, which is an important factor for the process of foaming.

The third source of crushed glass was electric bulb glass SL96-1 from the Tomsk Electric-Bulb Factory with chemical composition described in Table 1.

Table 1. Chemical composition of the used crushed glass types

<table>
<thead>
<tr>
<th>Glass chemical composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of glass</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Window glass</td>
</tr>
<tr>
<td>Bottle glass</td>
</tr>
<tr>
<td>Lamp glass</td>
</tr>
</tbody>
</table>
During the production of granulated foam glass ceramics it is necessary to carry out the correction of the functional composition of a charge taking into account every type of glass used.

2.2. Clay
A range of clay deposits was studied in order to determine the local raw material base for the production of foam glass ceramics [9].

The best results were obtained using clay that is classified as pulverous loam, with a domination of SiO$_2$ - 70.73%; Al$_2$O$_3$ - 17.12% and Fe$_2$O$_3$ - 5.68% in its chemical composition. The presence of this type of clay in the charge leads to a decrease of water consumption to 3-4%, increasing the mechanical durability and fire resistance of the granules of foam glass ceramics (Table 2).

Table 2. Granulometric characteristics of particles

<table>
<thead>
<tr>
<th>Type of particles</th>
<th>Size of particles, mm</th>
<th>Particle content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>&lt;0.005</td>
<td>20.32</td>
</tr>
<tr>
<td>Silt</td>
<td>0.005...0.05</td>
<td>68.80</td>
</tr>
<tr>
<td>Sand</td>
<td>0.05...1.0</td>
<td>absent</td>
</tr>
</tbody>
</table>

2.3. Organic additive
In contrast to traditional foam glass compositions, the distinctive characteristic of the charge composition proposed for the production of foam glass ceramics was using sawdust as an organic element of the charge.

Softwoods and hardwoods contain pentosans (a type of hemicellulose) that hydrolyze in the presence of water and turn into simple sugars that are soluble easily in water. Simple sugars prevent good adhesion of the charge particles with sawdust. Therefore, preference was given to softwoods as they contain 2-3 times more pentosans than hardwoods.

The balance of chemical agents in sawdust was about 50% carbon, 6.0% hydrogen, 44% oxygen and approximately 1.0% nitrogen.

2.4. Gassing agent
When justifying the choice of gassing agent, the conjunction of temperature intervals of hot melt appearance with required viscosity and formation of the peak partial pressure of gaseous products in organic burn off were taken into account. Carbon was used as the gassing agent.

In the course of the study the following charge composition was used (% by weight): crushed glass 67 - 84; clay 8 - 25; carbon 5 and sawdust - 3. The charge degree of fineness was 0.45-0.15 mm.

The granules were made in the following way: glass cullet was further crushed in a grinder to 1.5-3.0 mm, and then in a ball mill combined with sawdust to the particle
specific surface area of 300-350 m$^2$/kg. In such a way the sawdust was added to the charge during the moment of glass grinding, which enabled their pulverizing to a wood powder with an obtainment of a high shape factor of wood fiber (length-to-thickness ratio) equal to 4 and the size of particles no more than 560 microns. Grinding process of carbon and clay was also performed in the ball mill.

The obtained glass-wool and carbon-clay powders were dosed and loaded in a rod vibrating mill where they were jointly mechanically activated to a specific surface area of 400 m$^2$/kg. The obtained charge was gaged with water (10-15% of the charge mass) for gaining the required plasticity, and then was formed into granules of 3-8 mm in size.

The experiments were carried out with a permanent carbon value of 5% and organic additives (sawdust) of 3%, as it was described above.

### 3. Results and discussions

Granule burning was carried out at a temperature of 830-850°C within a sintering range of foaming mixtures equal to 4-6 minutes. When the charge contains 8% of clay there commences a formation of granules consisting of cells ranging from 0.135 to 2.7 mm in size, and occasionally connected with communicated channels (Fig. 1) and with an interpore partition thickness of 0.07-0.1 micrones. The granule density was 200 kg/m$^3$.

![Fig. 1. Histogram of pore dispersion in quantity and size and pore structure of foam glass ceramics with 8% clay containment in the charge. Granule density is 200 kg/m$^3$.](image)
The formation and steadiness of the foam depends on the surface energy at the boundary between gas and liquid. When adding 10% of clay to the charge, the surface tension and free energy of the system, which forms fragile foam, start to increase. As the proportion of clay starts to increase beyond 25%, the boundary surface between phases starts to decrease; the pores and the gas emission mutually combine, and the foam settles.

In order to overcome this challenge the decision was made to use sawdust as an organic additive in the charge. It was estimated experimentally that adding up to 3% of sawdust with a simultaneous increase of the foaming temperature up to 830 °C and the time of pore formation up to 5 minutes, the amount of gases and their partial pressure would increase. Furthermore, the viscosity of the hot melt begins to decrease and the particle sintering commences, leading to the formation of glass ceramic mass.

When increasing the temperature by 70-110 °C higher than the glass softening point, sodium sulphate reacts with coke carbon and the carbon of burning organic additives (sawdust) with the formation of carbon monoxide:

\[ \text{Na}_2\text{SO}_4 + 4\text{C} = \text{Na}_2\text{S} + 4\text{CO} \]  

(1)

The presence of clay facilitates an increase of the glass softening point and the bloating phase, and containment up to 5.0% of carbon and up to 3% of sawdust enables the formation of a rather large amount of gas with high partial pressure. The charge composition is made in such a way that the gas partial pressure is lower than the surface tension of a hot melt, which enables an increase in the dividing surface between phases and equal distribution of pores in a hot melt.

In the process of foaming, the pores mutually combine at a low rate. The gases in the pores work against the energy caused by surface tension. The presence of clay in a hot melt significantly increases the energy of the surface tension, and the gas pressure in pores decreases as the pores diminish. As a result there are up to 92% of closed pores of 0.2-0.4 mm in size, with a thickness of the dividing partition within the bounds of 0.07-0.1 micron up to 12 microns.

According to the silicate foam formation mechanism, a maximum of closed cells is formed under the foaming of homogeneous systems with an optimal viscosity of hot melts, in which smooth foaming, and, at the same time, a high fixity of formed foam caused by its structural-mechanical factor are provided (Fig. 2). The granule density is 260 kg/m³.

Mutual combination and formation of open pores occurs in the initial foaming period - the period of free gas exit. This process stops as the gas pressure in the system equalizes. Under a relatively high hot melt viscosity, the equilibrium state of the system is gained much slower. The formation of closed pores in foam glass ceramics is enabled by adding fusible clay into the charge, which decreases the viscosity of a hot melt and significantly increases its plasticity, and at the same time raises the mechanical strength of pore partitions. As a result, the pore partitions are not pierced and the formation of
new pores occurs independently, without the impact of gassing processes in neighboring pores.

Fig. 2. Histogram of pore dispersion in quantity and size and pore structure of foam glass ceramics with 10% clay containm

Clay as a fusible additive in the rational composition of a charge plays the role of stabilizer. The stabilizing action of clay enables the formation of a so-called energy barrier, which increases the mechanical strength of partitions with the narrowest thickness. Increasing the clay proportion up to 25% enables the rise of the hot melt viscosity, and an increase in the thickness and mechanical strength of the walls. Gas pressure in pores is not enough for their size increase. As a result small pores start to appear - from 0.036 to 0.135 microns, and the thickness of pore partitions expands and varies from 0.07-0.1 micron to 50 microns (Fig. 3). The granule density is 290 kg/m³.

The glassy layer formed on the granular surface enables the formation of a solid surface at the stage of bloating, as a result of which the mechanical compressive strength is increased and the water absorption decreases.

The formation of a porous structure during heating is divided into the following stages:
- Synthesis - formation of sintered material during heating to the sintering temperature range;
- Bloat - the process of volume and structural changing of material;
- Annealing - a special mode of cooling.

As follows from the study, an optimal thermal profile for the sintering regime and granular porization was determined (Fig. 4).

![Fig. 3. Histogram of pore dispersion in quantity and size and pore structure of foam glass ceramics with 25% clay containment in the charge. The granule density is 290 kg/m$^3$](image)

![Fig. 4. Optimal scheme of thermal cycle of foam glass ceramic granule sintering and porization](image)
A thermal shock in the zone of high temperatures (830°C) in a reductive conditions with 3.0% CO containment is characteristic for granular thermal processing. Furthermore, the mechanical strength comes to the maximum while granules are in the high temperature zone for 5-6 minutes. Thermal cycle foaming → pore formation → annealing (Fig. 4) provides an optimal time for granules in the foaming zone, regulating the size and the quantity of pores and prevents the process of bubble coalescence (increasing of pore size), for which greater time in the high temperature zone is required.

When granules stay in the high temperature zone more than 10 minutes, the probability of dissipative phenomena is increased, i.e. the extension and collapsing of pores. As the quantity of pores decreases, they start to expand by up to 2 mm, and the partitions become fragile and thin. When foam glass ceramic is foaming, the structure of the pores being formed is mainly determined by rheological characteristics of an alumina-silicate melt. The strength of pore membrane during the extension depends upon the viscosity of the melt, which provides the solidity of partitions and the surface strength in the high temperature zone.

Annealing is necessary to fix the pore structure and to relieve temperature stresses in the pores. Experiments have shown that the best result is achieved when annealing starts at a temperature of 300°C and ends at 90°C. The rate of the temperature decrease is 11.6 degree/min. Such a high rate, without granule breakage and shelling of the surface, is enabled by the presence of clay in the charge and a long period of crystallization. Clay enables the formation of fire resistant alumina-silicate matrix.

To study the dependence of the thermal conductivity coefficient on medium density and compressive strength, studies with a change of rational composition of a charge were conducted. As the studies showed (Fig. 5) all three criteria - mechanical compressive strength, density and thermal conductivity - depend on the size and the quantity of pores, and on the thickness and the composition of partitions. When density is increased the thermal conductivity and the granular mechanical strength grow by means of increasing the percentage of clay in the composition of charge. As the temperature increases, the melt viscosity decreases. Gas pressure rises and the shear action of capillary forces develops. The pores get filled with a fluid phase, which leads to a thickening of the material.

The studies of temperature-time regimes within space factors determined an optimal component proportion in the charge for obtaining the required porous structure. Moreover, small closed pores equally dispersed over the granule surface appear (Fig. 2). The granular mechanical strength is between 0.82-1.74 MPa.
Foam glass water absorption depends upon the pore characteristics: their size, quantity and structure (closed and open). Low water absorption is one of the most important factors in choosing the composition of a charge, as this parameter is inversely dependent both upon the density (Fig. 6) and thermal conductivity coefficient.

The results of the water absorption test for foam glass ceramics are shown in Fig. 7.
During the tests of granular foam glass ceramics with 260 kg/m$^3$ density to determine thermal conductivity, strength, water absorption and operating temperature, physical technical characteristics were obtained, with a significant difference from expanded clay and other insulating materials of the same density (Table 3).

Table 3. Results of comparing granular foam glass ceramics with 260 kg/m$^3$ density and expanded clay gravel fractions of 5-10 mm

<table>
<thead>
<tr>
<th>No.</th>
<th>Factor</th>
<th>Expanded clay</th>
<th>Granular foam glass ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pour density, kg/m$^3$</td>
<td>500 - 550*</td>
<td>260</td>
</tr>
<tr>
<td>2</td>
<td>Flammability</td>
<td>Non-flammable</td>
<td>Non-flammable</td>
</tr>
<tr>
<td>3</td>
<td>Thermal conductivity, W/m. °C</td>
<td>0.065 - 0.097</td>
<td>0.075</td>
</tr>
<tr>
<td>4</td>
<td>Compressive strength, MPa</td>
<td>1.7 – 2.5</td>
<td>1.74</td>
</tr>
<tr>
<td>5</td>
<td>Water absorption, m%</td>
<td>8 - 20</td>
<td>2.6*</td>
</tr>
<tr>
<td>6</td>
<td>Upper operating temperature, °C</td>
<td>Up to 600</td>
<td>620</td>
</tr>
</tbody>
</table>

4. Conclusion

It has been established that the products are fragile when the clay content in the charge is lower than 8%, with a low mechanical strength and large pores; if the clay content is higher than 25% then the granules are close in their physical and technical properties to expanded clay.

Granulated foam glass ceramics with a density of 260 kg/m$^3$ have low thermal conductivity and water absorption, and high compressive strength and operating temperature.

The developed technology provides the opportunity to produce granulated foam glass ceramic products of various geometric shapes - plates, blocks, segments, shells and enables them to be recommended as an effective heat-insulating material not only in construction but also in thermal engineering [10, 11].

Acknowledgement

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The Influence of Porosity on the Elasticity and Strength of Alumina Ceramics

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Abstract. This work investigates the behavior of porous alumina ceramics (within the porosity range of 18% to 70%) when subjected to deformation by compression and shear. The analysis of strain-deformation curves showed that there was a transition from a typically brittle state for relatively dense ceramics (<20% porosity), to a pseudo-plastic one with a high rate of porosity (above 50%). The values of the modulus of elasticity, shear modulus and Poisson's ratio decrease with an increase in volume in the pore space of Al₂O₃ ceramics, which correlates with the appearance of multiple cracking during the deformation of ceramics with a high level of porosity.

Keywords: Alumina, deformation, modulus of elasticity, plasticity, porosity, shearing, strain, strength, stress.

1. Introduction

It is 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 [1-3]. In addition, the macroscopic behavior of ceramics can vary from brittle to quasi-plastic depending on the pore space volume [3]. 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 [4-9] in terms of the emergence of a structural hierarchy of deformation and failure in similar brittle materials (ceramics, stones).

The objective of the work is to study the relations between parameters such as porosity, compressive strength, Young’s modulus, shear modulus, measured in the process of mechanical loading under compression and shear, as well as structures of damage and deformation in alumina ceramics.
2. Experimental materials and methods

$\text{Al}_2\text{O}_3$ ceramics with different porosity values (18%-70%) were made of powders obtained via thermal decomposition of aqueous nitric-acid metallic salt solutions in high-frequency discharge plasma [10]. The initial powders and a 3% polyvinyl alcohol solution were pressed by a hydraulic press under 10 kN/cm$^2$ pressure in steel die molds in order to obtain cylindrical (10 mm in diameter, 15 mm in height) and cubic (10 mm each side) shapes.

Sintering was performed in air at temperatures ranging from 1000 to 1650°C with an isothermal exposure time of one hour. The density of the sintered specimen was measured using the geometrical method. Residual porosity was calculated from the ratio of theoretical density to measured density, considering the phase composition of the obtained materials. The material structure after sintering was studied by optical metallography.

The specimens were exposed to mechanical tests in compression and shear by a universal testing machine Instron 1185, with simultaneous recording of the loading diagram. The traversal (loading) rate was 0.2 mm/min. On the $\sigma$-$\varepsilon$ curves, a straight-line segment was outlined which corresponded with elastic deformation. Effective modulus of elasticity ($E$) and shear modulus ($G$) were defined as the angle of a tangent line slope to a straight-line segment of the $\sigma$-$\varepsilon$ function curve.

3. Results and discussion

Investigations of ceramics structure after sintering showed that in specimens sintered at low temperatures, high porosity was observed and these pores were advantageously interpenetrating. The pore structure of $\text{Al}_2\text{O}_3$ ceramics 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 (Fig. 1.c,d) due to the consolidation of fine pores into larger ones. According to X-ray structure analysis data, at all sintering temperatures $\text{Al}_2\text{O}_3$ is in a stable $\alpha$-phase.

The comparison of $a$-$e$ diagrams, obtained after testing ceramics with different porosity levels in compression, showed that their behavior depends on the pore space volume. The $a$-$e$ curve analysis of 20% porous ceramics proved that they are linear functions until material destruction, (Fig. 2.a) while deviations from the linearity (Fig. 2.b) are observed in ceramics with a higher porosity of 20% to 50% in the area of high stresses.

Stress-strain diagrams obtained by tests in compression (curve 1) and shear (curve 2) for Al2O3 with porosity of: (a) 20% (b) 50%. (c) Stress-strain diagram obtained by tests in compression for alumina ceramics with a pore space volume over 60%. (d) Stress-strain diagram obtained by tests in shear for alumina ceramics with a pore space volume over 60%.
Deformation diagrams of ceramics with porosity over 50% had a more complex behavior. The compression test curves mostly had a gradually descending stress arm (Fig. 2.c) which appear due to microdamages accumulated in the samples whereas the shear test curves had a slightly ascending arm after the stress fall curve portion which resulted from the stress growth (Fig. 2.d).

Observations of specimen structure after compression tests identified some differences in the nature of damage of ceramics with different porosities. In specimens with 18%-20% porosity, brittle fracturing of elastic specimens occurs after elastic energy accumulation. Due to elastic energy release, the specimen fully breaks down after reaching the compression strength limit. With a growth in pore space volume, damage of more localized nature is seen in ceramics and specimens do not fully break down after reaching the compression strength limit and, in general, do not lose the ability for future deformation. Specimens with a porosity near 40% after compression tests are shown in Fig. 3.a,b. It is visible that on the lateral surface of cylindrical specimens, cracks formed at a 45° angle to the applied load axis (Fig. 3.a). In such ceramics, a damage zone in the form of a truncated cone with a cone angle of about 45° forms after compression, while the cone basis lies almost in a static capture plane (Fig. 3.b). The deformation process of 50%-70% porous ceramics is accompanied with the appearance of multiple cracks directed primarily parallel to the loading axis (Fig. 3.c) on the lateral surface of the cylindrical specimen. In addition, the base diameter of the cone forming in the deteriorating specimen was relatively smaller in size compared to denser ceramics (Fig. 3.b), while the cone’s taper angle was approximately 45° (Fig. 3.d).
Fig. 2. Stress diagrams obtained by tests in compression (curve 1) and shear (curve 2) for Al₂O₃ with porosity of (a) – 20%, (b) – 50%, (c) – stress strain diagram obtained by tests in compression for alumina ceramics with a pore space volume over 60%, (d) – stress-strain diagram obtained by tests in shear for alumina ceramics with a pore space volume over 60%
Fig. 3. The failure shape of Al$_2$O$_3$ specimens with porosities of: (a, b) 40%, (c, d) 55% after a test in compression. The failure shape of Al$_2$O$_3$ specimens with porosities of: (e) 40%; (f) 69% after a test in shear.

In the course of shear tests, specimens with <40% porosity demonstrated the emergence of a main crack which was angled 45° towards the applied load (Fig. 3.e). The main crack appeared at the deformation stage right after the elastic part on the strain-deformation curve. In specimens with porosity over 40%, the deformation process was accompanied with the emergence of many fine cracks in different directions without the explicit main crack until the stage of complete destruction (Fig. 3.f). Fig. 3.b shows that on the edges of the specimen there are areas of material separated by developing cracks from the ceramic base, in which deformation from compression occurs.

It is known that cracks appear at the location of deformation, in the most damaged areas of the material [11]. In the case when stress is formed by an incline towards the compression of the damaged area, tension related to the presence of friction between the grip (plate) of the testing machine and adjacent ends of the sample plays a significant role in the failure [12]. Accordingly, the formation of cones inside of the
collapsed samples (Fig. 3. c,d) due to the presence of friction forces and the destruction of ceramics under compression is controlled by shear stresses.

It is also known that the orientation of cracks depends on the accumulated strain limit value, or dilatancy (micro-crack saturation and their openings) [11]. As each pore is a potential source of microcracking in a porous material, and with the increase in the number of pores in a specimen, the number of such sources naturally grows, then the observable distinctions in the direction and behavior of crack spread in different porosity level ceramics (Fig. 3) are apparently the result of differing levels and natures of accumulated deformation in the form of microcracks that appear after compression and shear.

Studies of the mechanical and elastic properties of ceramics showed that within the studied intervals of pore space volume (from 0.18 to 0.72), the strength limit in compression and shearing, as well as the modulus of elasticity and shear modulus decrease with an increase in porosity (Fig. 4). In addition, the dependency of changes in strength properties on porosity is well-described by the law, and is near exponential.

As it is seen in Fig. 4.c, the absolute values of the modulus of elasticity and shear modulus grow closer with an increase in porosity, which shows a decrease in Poisson's ratio. It should be noted that in our case there is only a decrease in Poisson's ratio values. Determining the absolute values of Poisson's ratio in the process of mechanical testing was complicated, as experimental error constituted a value of ±0.3. An identification of Poisson's ratio by measuring the rate of longitudinal and latitudinal sound waves [13] in the ceramics performed with the use of an ultrasound flaw detector showed that values for Poisson's constant decreased from 0.21 to 0.15 with a growth in pore space volume of 20% to 40%.

The fact that Poisson's ratio decreases with an increase of pore space volume was previously noted in several publications [1, 13]. In [13, 14] it was shown that for porous isotropic bodies, the values of Poisson’s ratio depend on the pore space volume, pore geometry and Poisson's ratio values for a pore-free material state (μ₀). For materials with μ₀>0.2 (including alumina ceramics), it is theoretically predicted and experimentally proven that there is a decrease in the values of Poisson's ratio with an increase in pore space volume for ceramics with different pore geometry [13, 14].

The decrease of values for Poisson's ratio with an increase in pore space volume can be explained by nonlinear elasticity, which similar porous ceramics display under mechanical loading [15, 16]. Furthermore, local deformations due to relative movements and deformations of its structural components play an essential role in the deformation of objects with a similar complicated internal structure, noticeably changing the elastic properties of metals [1].
Fig. 4. Dependence of (a) compressive strength, (b) shear strength, (c) modulus of elasticity and shear modulus values on pore space volume of alumina ceramics

4. Conclusions

The analysis of stress-strain curves of porous alumina ceramics (within the porosity range of 18% to 70%) showed that during deformation in compression and shear, there was a transition from a typically brittle state for relatively dense ceramics (<20% porosity), to a pseudo-plastic state with a high porosity level (over 50%).

The values of the modulus of elasticity, shear modulus and Poisson’s ratio all decrease with an increase in pore space volume of $\text{Al}_2\text{O}_3$ ceramics, which correlates with the appearance of multiple cracking in the course of the deformation of highly porous ceramics.

It was shown that during deformation in compression, the failure process was
controlled by shear stresses, which leads to the formation of damage in the shape of cones in the internal volume of the specimen, the size and location of which depend on the pore space volume.

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References
Methods and equipment for investigation rheological properties of complex materials like convectional bricks and ceramic reinforced composites

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Abstract
In the present work two special instruments are described and introduced which were developed for the rheological tests of materials like minerals, raw materials and semi-finished products of ceramic industry or complex materials like ceramic particles and fibers reinforced metal alloys and hetero-module, hetero-viscous and hetero-plastic materials with increased dynamic strength. The working principles of introduced ‘rheotesters’ are relatively simple and easy for using to determine rheological parameters like instantaneous elastic module, delayed elastic module or viscosity of damaged and undamaged material structures. The instruments have given opportunity to prepare easy and quickly the rheological model of tested material.

Keywords: ceramics, composites, instrument, material, module of elasticity, rheology, test, viscosity

1. Introduction

There are many scientific works can be find in accordance to investigation of rheological properties of materials in nanoscale [1-4] in our days. In spite of this it is quite difficult to determine in macro-scale the most important rheological parameters of complex materials like
- mined convectional brick clays
- concrete mixtures reinforced with graves and fibers
- asphalt pavements and asphalt concretes
- ceramic particles and ceramic fiber reinforced metallic matrix composites
- hetero-module, hetero-viscous and hetero-plastic complex materials.

During production of ceramics and ceramic reinforced composites it is obvious that the chemical and structural transformations in the materials are taking place as reactions in solid phase [5-10]. At a certain temperature and chemical or mineralogical composition the speeds of these solid phase reactions are very strong depended on the concentration of components and the volumes of their contact surfaces. Because of these during the production of convectional bricks, ceramic roof tiles, technical ceramics and ceramic reinforced composite materials one of the most important technological goals is to give as larger as possible specific surface to the used raw materials during their crushing and comminution. The achieved specific surface of the components is very strong influence not only on forming process and quality but on the required energy consumption of heat treatment or firing [11-15]. To get the necessary volume of specific surfaces of the raw materials the required energy consumption depends not only on their chemical and mineralogical composition and working principles of crusher and mixture machines and equipment but also on physical, mechanical and rheological parameters of the used materials.

The importance of rheological properties of raw materials during production of convectional bricks and ceramic roof tiles was first declared by Hallmann [16]. By his determination most of the raw materials used in the building material industry can be determined with rheological equation (1) as:

$$ (\tau - \tau_0)^m = \eta(\dot{\varepsilon})^n \quad [\text{Pa}] $$  \hspace{1cm} (1)

where:
- $\tau$ – the shear stress developed in the materials during processing (Pa);
- $\tau_0$ – the yield stress or static yield point of used materials (Pa);
- $\eta$ – the dynamic viscosity of materials during processing (Pas);
- $\dot{\varepsilon}$ - the shear rate developed in the material (s$^{-1}$);
- $m$ és $n$ – power law exponents.

Later many of the authors have confirmed the above declaration of Hallmann during their investigation of rheological parameters of raw materials used for production different kind of building materials. For example the melted glasses, cement pastes with high water content, mortars, porcelain and china slurries for slip casting can be determined as:

$$ \tau = \eta \dot{\varepsilon} \quad [\text{Pa}] $$  \hspace{1cm} (2)

It is obvious that equation (2) is generated from equation (1) under the following conditions:
m = 1, n = 1 and \( t_0 = 0 \) \hspace{1cm} (3)

Meanwhile by [17] the well prepared convectional brick clay during its extrusion can be characterized with rheological equation (4):

\[
\tau - \tau_0 = \eta \dot{\varepsilon} \quad \text{[Pa]}
\]

which is also generated from eq. (1) at boundary conditions:

\[
m = 1 \quad \text{and} \quad n = 1
\]

In the 1970s the Russian scientists [18-21] have achieved remarkable results in investigation of mined convectional brick clays with relative water containment \( W_r \geq 15 \) m\%. From the beginning of 1970s the researchers have more and more intensively investigated the physical, mechanical and rheological properties of clay minerals. For example [22] has shown that the convectional brick clays with water containment more than 12-15 m\% have lost their mechanical strength and elasticity and they have turned into plastic materials. On this basis [23] has supposed that the convectional clays with mined moisture (water containment) are viscous-plastic materials which can be characterized with rheological equation (6) as:

\[
\tau + \tau_0 + \eta \frac{dv}{dx} \quad \text{[Pa]}
\]

where \( \eta \) is the dynamic viscosity and the deformation speed gradient ‘\( dv/dx \)’ is the shear rate during crushing the materials on high speed smooth rollers. This conception was later confirmed experimentally (Fig.1) by [24].

Taking into consideration the rheological properties of mined convectional brick clays as non-Newtonian materials gave new opportunities to authors [25-31] to determine and optimize technological parameters of processing machines like crushers, extruders, etc. So on the basis of non-Newtonian rheological properties of ceramic raw materials and achieved results in theory of continuum mechanics gave also opportunities to develop mathematical methods for design smooth high speed rollers [32-35] and vacuum extruders for forming ceramic building materials and asbestos cement wall panels [36]. To examine the rheo-mechanical properties of elastic fibers reinforced viscous-plastic complex materials, new universal ‘rotovisco’ equipment was also developed [37].
Fig. 1. The dynamic (effective) viscosity of mined clay minerals as function of shear rates (taking from [29])

The knowledge of rheological properties and parameters of convectional brick clays is required to understand the physical and mechanical processes taking place during crushing, comminution and forming of ceramic materials as well as to increase the efficiency of the machines used in ceramic technologies and industries [38–46]. For example [47] recommends use rheological model:

\[ \eta_g = a^n \eta_m \]  

\[ \text{(7)} \]

to investigate and determine the physical and mechanical processes taking place in the materials in the working ‘gaps’ of pan mills; where

- \( \eta_g \) – the dynamic viscosity of materials in the working gap of pan mill (Pas)
- \( \eta_m \) – the measured dynamic viscosity of materials by the laboratory equipment (Pas)
- \( a \) – coefficient the value of which for ‘Malyi-clay’ is: 0.5–0.6
- \( n \) – power law exponent

The value of the power law exponent can be determined as:

\[ n = \frac{\lg \dot{\varepsilon}_g}{\lg \dot{\varepsilon}_m} \]  

\[ \text{(8)} \]

where

- \( \dot{\varepsilon}_g \) – the shear rate developing in material during its processing on the industrial equipment (Pas)
- \( \dot{\varepsilon}_m \) – the shear rate developing in material during rheological tests on laboratory equipment (Pas)
2. Traditional methods and equipment

There are many relatively simple methods and equipment to determine and measure certain physical and mechanical properties of materials but it is quite difficult to measure and determine the physical, mechanical and rheological properties of complex materials like ceramic raw materials and ceramic particles or fibers reinforced composites [48-52]. The reason is that the instruments which are successfully working for rheological test of materials in chemical, plastic, pharmaceutical, dairy and food industry cannot be used for tests of ceramic raw and semi-finished green materials because of their abrasivity, hardness, strength, etc. The advantages of these traditional rheotesters and instruments are their shortage in development the required shear stresses, mechanical pressures and/or temperatures or shear rates. Because of these for the rheological test of raw materials of ceramic and building materials industry are generally used so-called capillary viscometers (Fig.2) with high value of mechanical pressure [39, 41, 53].

![Idealized diagram of capillary rheometer](image)

Fig.2. The principle of capillary rheometers and the generated by them curves of volume flow ($V(t)$), pressure stress ($p(t)$) and shear stress ($\tau(\dot{\gamma})$)

Using the capillary viscometer first necessary to determine the volume flow ($V(t)$) and saw pressure ($p(t)$) as function of time and further from these data can be determined the shear stress and shear rate in the materials passing through the capillary with $D$. So, from the determined by experiment the values of shear stress as function of shear rate:

$$\tau = f(\dot{\gamma}) \quad [\text{Pa}]$$

already can be determined the effective viscosity of materials as:

$$\eta_e = \frac{pR}{2L} = \frac{\pi R^4}{8LV} \quad [\text{Pas}]$$

(10)
where:
\( L \) – the working length of capillary viscometer (m)
\( P \) – the mechanical pressure stress at the working length of capillary (Pa)
\( R \) – the radius of capillary (m)
\( \dot{V} \) – the volume speed of tested material in the capillary (m³/s)

The advantages of the capillary viscometer are the simplicity of construction, the optional value of pressure strength thanking to the hydraulic movement of the stamp in the cylinder, working ability at wide range of moisture or plasticizer. The main disadvantages of these kind of rheometers that the pressure stress \( p_{ny} \) at the capillary is not permanent as its value during the measurement is changing as:

\[
p_{ny} = p_b \cdot e^{-\frac{4\mu H}{D_0}} \quad [\text{Pa}]
\]

where:
\( \mu \) - coefficient of external friction of tested materials at the walls of instrument
\( D_0 \) – diameter of the saw stamp (m)
\( H \) – height of tested material in the ‘cup’ of viscometer (m)
\( p_b \) – pressure stress at the surface of the saw stamp (Pa)

During the rheological tests the heights of the tested materials in the ‘cup’ of viscometer are changing as shown in eq. (12):

\[
0 \leq H \leq H_0 \quad [\text{m}]
\]

and its value in a certain moment can be determined as:

\[
H = H_0 - v_0 t \quad [\text{m}]
\]

where
\( H_0 \) – the starting height of the tested material in the ‘cup’ (m)
\( t \) – the time of measurement from the starting (s)
\( v_0 \) – the speed of the saw stamp in the ‘cup’ (m/s)

3. The developed new instruments and applied methods

During the rheological investigation of ceramic raw materials, semi-finished products and ceramic particles or fibers reinforced metal matrix composites the rheotester must be reliable, relatively poor and must be satisfied the following requirements:

a. the instrument must be capable to measure and determine the rheological parameters of more frequently used raw materials and/or semi-finished products in wide range of technical and technological conditions in different sectors of silicate industry
b. the instrument must be capable to develop the mechanical stresses and shear rates in the materials which are happen during their passing through machines and mechanical equipment of technology lines

c. the instrument must be capable to develop temperature used to be in technological process in the silicate industry and must be controllable inside of the materials during the whole testing process

d. it must be capable to measure also the compaction ratio, external friction coefficient and effective viscosity of tested materials under variation of mechanical stresses, temperature and shear rates

e. the developed new construction must be simple, easy to produce and use

f. the new instrument must be capable for “quick” test of rheological parameters and the measured data must be reproducible

So, the above requirements must also satisfy the following mathematical functional relationship for the compaction ratio:

\[ \frac{\Delta H}{H} = f(\sigma, H_\sigma, P, Q, T, W) \quad [m] \quad (14) \]

and for the external friction coefficient

\[ \mu = F(\sigma, n, P, Q, T, W) \quad (15) \]

as well as effective viscosity

\[ \eta_e = \Phi(\phi, \sigma, P, Q, T, W) \quad [\text{Pas}] \quad (16) \]

Where:

- \( \sigma \) – the normal mechanical pressure acting on the working surface of the tested material (Pa)
- \( H_\sigma \) – the filling heights of material in the instrument (m)
- \( P \) – the volume of used plasticizer (%)
- \( Q \) – the chemical or oxide composition of the tested material
- \( T \) – the temperature of material during the measurement (\( ^\circ \text{C} \))
- \( W \) – the moisture of tested material (%)
- \( n \) – axis turn number (rpm)
- \( \gamma \) – shear rate (s\(^{-1}\))

To satisfy the above requirements a universal ‘rotovisco’ (Fig.3) and a combined rheo-tribometer (Fig.4) were developed partly in Russia and at Igrex Engineering Service Ltd. in Hungary.
The universal ‘rotovisco’ can be successfully used to the rheological tests of plasticized cement pastes and concretes reinforced with mineral graves and fibers [51-54] as function of setting time and temperature [55]. The combined rheotribometer can be successfully used for rheological tests not only asphalt mixtures and pavements [56-57] but for different silicon-carbide composites [58-59] and for aluminum-titan alloys [60-61]. The complex rheological and mechanical test of so complex materials like mined convectional brick clays also available on this instrument [62]. During the rheological test the instrument measures the shear rates ($\dot{\gamma}_0$), shear stress ($\tau$) and effective viscosity ($\eta_e$), and computes their values by equations (17)-(18)-(19) as the followings:

$$\dot{\gamma}_0 = \frac{\omega R_0}{H} \quad [s^{-1}] \quad (17)$$

$$\tau = \frac{M}{A R_0} = \frac{M}{\pi (R^2 - r^2) R_0} \quad [Pa] \quad (18)$$

$$\eta_e = \frac{H M}{\pi \omega (R^2 - r^2) R_0^2} \quad [Pas] \quad (19)$$

Where:

$\dot{\gamma}_0$ – the shear rate developed in the materials in the ring-shaped pot

$\eta_e$ – the effective viscosity of the material

$\omega$ – the angular speed of ring-shaped container (s$^{-1}$)
A – the volume of sheared surface (m²)
H – the height of the tested materials in the ring-shaped pot
M – the value of the measured torque (Nm)
r – internal radius of ring-shaped pot (m)
R – external radius of ring-shaped pot (m)
R₀ – the radius belongs to the average volume speed of materials in the pot (m)

The working principle of the patented in Hungary combined rheotribometer is even more simple. The rheological parameters of tested materials also can be measured as function of chemical and mineralogical composition (Q), temperature (T), developed mechanical stress (σ), moisture (W) and volume ratio of used plasticizer (P), etc. During the rheological tests the instrument measures and computes the values of shear rates (\( \dot{\gamma}_0 \)), shear stress (τ) and the effective viscosity (\( \eta_e \)) as:

\[
\dot{\gamma}_0 = \frac{V}{H} \text{[s}^{-1}] \quad (20)
\]

\[
\tau = \frac{F}{A} \text{[Pa]} \quad (21)
\]

\[
\eta_0 = \frac{\tau}{\dot{\gamma}_0} = \frac{FH}{AV} \text{[Pas]} \quad (22)
\]

where:
A – the volume of sheared surface (m²)
F – the pulling force (N)
H – the working height of the tested materials (m)
V – the speed of batching car with the shearing plate (m/s)

Converting the batching car with shear plate into ‘Tolstoi-instrument’ (Fig.5) it is possible to get the deformation-times curves (Fig.6) of the tested material as function of their compositions, temperatures, and loading forces.

Fig.5. Schematic draw of Tolstoi’s instrument
1-loading force, 2-rope pulley, 3-lower tool, 4-upper tool, 5-hold-down roller, 6-displacement beacon, 7-printer, 8-material
Fig. 6. Typical deformation of plasticized asbestos cement pastes as function of time

On the basis of the deformation-time curves created by combined rheotribometer is it possible to determine the instantaneous elastic module \( E_1 \), the delayed elastic module \( E_2 \) and viscosity of damaged \( \eta_1 \) and undamaged material structures \( \eta_2 \) as well as their static yield points \( \tau_0 \) of so complex hetero-modulus, hetero-viscous-plastic materials like ceramic reinforced metal alloys and shield materials with extreme dynamic strength [63] in functional relationship as:

\[
E_1 = f(\tau, p, Q, T, W), \quad [\text{Pa}] \quad (23)
\]

\[
E_2 = f(\tau, p, Q, T, W), \quad [\text{Pa}] \quad (24)
\]

\[
\eta_1 = f(\tau, p, Q, T, W), \quad [\text{Pas}] \quad (25)
\]

\[
\eta_2 = f(\tau, p, Q, T, W), \quad [\text{Pas}] \quad (26)
\]

\[
\tau_0 = f(\tau, p, Q, T, W), \quad [\text{Pa}] \quad (27)
\]

Where:
\( \tau \) – the shear stress developed in the tested material by loading force \( F_1 \) (Pa);
\( p \) – the pressure stress developed in the tested material by loading force \( F_2 \) (Pa);
\( Q \) – the mineralogical, chemical and grain structure of the tested material;
\( T \) – the temperature of the tested material during the measurement (°C);
\( W \) – ratio of the moisture or quantity of used plasticizer in the tested material (m\%).

On the basis of the deformation-time curves it is quite easy to determine and find the rheological parameters of tested materials and create their rheological models [64]. So for example
4. Conclusions

The developed universal ‘rotovisco’ and combined rheotribometer fully satisfied the requirements explained above in section 3. The instruments are not complicated and easy to use them to measure the most important rheological parameters of complex materials like convectional brick clays, asphalt pavements or other raw materials and semi-finished products of building industry. By the requirements the instruments can be armed with special heating furnace of high temperature and they can be used for rheological test so complex materials like ceramic particles and ceramic fiber reinforced metal alloys and other hetero-module, hetero-viscous and hetero-plastic materials for safety and defend transport equipment and flying objects.

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Influence of raw materials composition on firing shrinkage, porosity, heat conductivity and microstructure of ceramic tiles

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Abstract. In this work some new raw material compositions from alumina, conventional brick-clays and sawdust were mixed, compacted and heat treated by the authors. Depending on raw material compositions and firing temperatures the specimens were examined on shrinkage, water absorption, heat conductivity and microstructures. The real raised experiments have shown the important role of firing temperature and raw material composition on color, heat conductivity and microstructure of the final product.

1. Introduction

In the last years in the convectional ceramic industry several works have shown the important roles of bio-original pore-forming additives both in technological processes and quality of final products [1-6].

The microstructure of the convectional brick-clays was examined and detailed described in the above works under paining the importance of the gaps between the solid particles of the used materials. To improved the thermal insulation of convectional brick-products waste materials were used by [7]. To predict the thermal performance of lightened fired clay-bricks organic additive materials were used by [8, 9]. Using sawdust and other bio-origin waste materials the relations between the microstructures and drying properties of ceramic-bricks and roof tiles were examined in [10, 11]. Their experiments have shown that the drying temperature i.e. intensity of drying influence essentially on dried and fired bricks and ceramic roof tiles.

The aims of this work are the development of porous ceramic tiles with increased thermal insulating properties using mixtures of convectional Hungarian brick-clays, alumina powders and sawdust.

2. Materials and experiments

For the laboratory experiments the basic materials was convectional grey brick-clay from Leier Mátraderecske in Hungary. The other ceramic raw material was MARTOXID KMS-
94 alumina powder from Martinswerk in 0, 20, 40, 60, 80, 100 m%. To alumina-clay mixtures sawdust pore-forming additives of fraction 0-2 mm were added in 0, 2, 4, 6, 8 m%. Before the experiments the ceramic raw materials were dried at 110 °C during 24 hours. After the drying the powders of brick-clays and alumina were measured in proportion as it is sown in Table 1 and mixed. Thereafter, 0, 3, 6, 9 and 12 grams of sawdust were added and mixed again. From the so prepared batches of 150, 153, 156, 159 and 162 grams powder mixes ceramic disc of 20 mm diameters were pressed at 220 MPa uniaxial compression equipment and method. Before firing each discs have 5 grams weights.

Table 1. The raw material mixtures

<table>
<thead>
<tr>
<th>Quantity [g]</th>
<th>Clay</th>
<th>Al₂O₃</th>
<th>Sawdust</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>120</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>60</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>120</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>150</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1. Influence of raw material composition and firing temperature on color of specimens

After compacting the ceramic disc specimens were divided to 3 groups by 10 pieces in each and heat treated (fired) at temperature of 1050 °C, 1150 °C and 1250 °C in laboratory chamber kiln. In Figure 1 are shown how the raw material composition and firing temperature are influenced on color of prepared for testing specimens. The diameters and weights of each specimen were measured before and after firing. The water absorption and firing shrinkage were also measured and determined on each specimen.

3. Results and Discussion

The firing shrinkages of specimens as function of alumina proportion and sawdust containments at different firing temperatures are shown in Figure 2, Figure 3 and Figure 4 and the water absorptions are shown in Figures 5-7. The water absorption of fired at different temperature specimens determined by Archimedes method.

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Generally the fired ceramics [12-14] convection brick clays have porous microstructures. These microstructures very strong depend on quality and quantity of the used pore forming additives light sawdust, rice husks, sunflower husks and others. From the works [1] and [15] it is well known that the thermal conductivity of fired ceramic bricks strong depends on the quantity and geometrical sizes of mixed in pore forming additives. The thermal conductivities of fired specimens were measured with instrument of C-THERM
TCi and are shown in Figures 4.

Figure 4. The heat conductivity of the test specimens burnt at 1050°C and 1150°C

4. Conclusions

The raw material composition and firing temperature are influencing very strong on microstructure, firing shrinkage, water absorption and heat conductivity of fired ceramic tiles. The realized experiments have shown that the water absorption, therefore the porosity are very strong depended on the volume of alumina in the raw materials mixtures. The thermal conductivities of prepared ceramic someplace have increased considerable with increasing the containment of alumina in the raw materials mixtures.

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Hydrothermal synthesis of TiO$_2$ nanotubes from concentrate of
titanium ore of pizhemske deposit (Russia)

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Abstract. A high cost of TiO$_2$ nanoparticles and their demand in industry determine the timeliness of the hydrothermal method of synthesis of titanium dioxide nanotubes from the low-cost natural mineral raw materials. The starting material- (non-magnetic fraction of gravity concentrate of titanium ore of Pizhemske deposit) and synthesized samples were characterized by scanning electron microscopy, X-ray diffraction and X-ray fluorescence methods.

Keywords: TiO$_2$ nanotubes, hydrothermal method, titanium ore, Pizhemske deposit

1. Introduction

Titanium is one of the strategic metals of modern industry. The demand for titanium has been steadily increasing, and this trend will obviously continue. In Russia there are mainly undeveloped deposits, titanium concentrate is not produced. On the territory of Komi Republic the prospects of mining industry are associated with the largest deposits of titanium (Yaregckoe and Pizhemske). New applications of titanium ore based on its mineralogical and processing characteristics have a real commercial interest: the list of commodity products is expanding (and consequently the prospects for production), energy costs are reducing, environmental risks are decreasing, efficiency of sustainable development of region is increasing. One of the promising directions of solution of this problem can be the synthesis of titanium dioxide nanotubes from mineral raw materials (for example from titanium ore of Pizhemske deposit).

In recent decades one-dimensional nanostructure materials, derived from titanium dioxide, have been widely used in photocatalysis, as a base for catalysts, implants, reagents enhancing blood coagulability, batteries, stb. [1-5].

Due to a high cost of commercially available TiO$_2$ nanoparticles their synthesis from cheap natural raw materials by hydrothermal method becomes very important.

The aim of this article: the development of scientific basics of synthesis of titanium dioxide nanotubes based on the mineral raw materials using a simple hydrothermal method.
2. Experimental Procedure

Titanium nanotubes can be obtained by several methods, such as sol-gel, electrospinning, template synthesis, chemical vapor deposition (CVD), etc. Each method has its advantages and disadvantages depending on the implementation. After the pioneer works by T. Kasuga et al. [6] the hydrothermal method became one of the most applied methods for the production of one-dimensional (1D) nanostructured TiO$_2$ products. The authors previously published a number of works on the synthesis of TiO$_2$ nanotubes from synthetic analogs of titanium minerals and their application [7-9].

TiO$_2$ nanotubes were produced by a simple hydrothermal method. The procedure for the preparation of nanostructures from synthetic TiO$_2$ is described elsewhere [7, 9]. In this work this procedure is adapted for the nonmagnetic fraction of gravity concentrate of titanium ore of Pizhemske deposit.

In a typical preparation 0.8 g of starting ore (reduced size) was placed in 100 ml autoclave, where 80 ml of 10 M NaOH solution were added. The autoclave was kept at 110°C during 24 h (temperature sensor was mounted on the stove, not inside the autoclave). After the hydrothermal reaction the autoclave was cooled to room temperature, and the resulting flaky precipitate was washed successively by distilled water and solution of hydrochloric acid (0.1 M) until neutral pH (6.5-7). The washed samples were dried in the oven at 90°C for 12 hours.

The shape and size of the starting ore and synthesized samples were obtained by scanning electron microscopy (TESCAN Vega 3). The crystalline structures of the initial ore and synthesized samples were analyzed by diffractometer (Shimadzu XRD-6000), the material composition was studied by X-ray fluorescence (XRF Shimadzu-1800).

3. Results and Discussion

Until recently the starting material for TiO$_2$ nanotubes synthesis was only high-purity synthetic analogs [1-5, 7]. In 2011 a group of scientists published a paper [10], which provided data on the production of titanium dioxide nanotubes by the hydrothermal method from Thai leucoxene. According to those data, Thai leucoxene was enriched. The starting material for nanotubes was a rutile concentrate with a TiO$_2$ content more than 93 %.

Mineral and chemical composition of bulk concentrates of titanium ore of Pizhemske deposit is given in [11]. Beside leucoxene pseudorutile, Fe-ilmenite, ilmenite and siderite were found. Chemical composition (wt. %): TiO$_2$ — 50.07, SiO$_2$ - 30.52, Fe$_2$O$_3$ - 13.37, MnO - 0.26, CaO - 0.04, MgO - 0.17, Al$_2$O$_3$ - 2.16, K$_2$O - 0.77, Na$_2$O - 0.02, P$_2$O$_5$ - 0.16, ZrO$_2$ - 0.10, S - 0.09, CO$_2$ - 1.90, H$_2$O$^+$ - 0.39.

In comparison with bulk concentrates of titanium ore of Pizhemske deposit characterized in [11] the used starting material - non-magnetic fraction of gravity concentrate of titanium ore of Pizhemske deposit - the content of Fe$_2$O$_3$ and TiO$_2$ is lower, while content of SiO$_2$ and Al$_2$O$_3$ - higher. Chemical composition (wt. %): TiO$_2$ -
42.12, SiO₂ -46.57, Fe₂O₃ - 1.04, Al₂O₃ - 7.57, K₂O - 1.61, MnO - 0.06, CaO - 0.13, MgO - 0.37, SO₃ - 0.06, P₂O₅ - 0.17, ZrO₂ - 0.05, NbO - 0.11. The average particle size after grinding - 20-40 pm.

The X-ray diffraction pattern (Fig. 1) indicates that the starting ore is mainly a mixture of two phases: rutile and quartz. The peaks are clear, that testifies to a high crystalinity of these phases. The weak reflections of clay minerals, ilmenite and anatase are present.

The synthesized sample (Fig. 2) is a mixture of two phases: quartz and hydrogenteritane (NaₓH₂₋ₓTi₇O₁₇), which is consistent with the results of [1-3]. Chemical composition (wt. %): TiO₂ - 74.68, SiO₂ - 12.64, Fe₂O₃ - 5.44, Al₂O₃ - 4.71, Na₂O - 0.14, K₂O - 0.93, MnO - 0.64, CaO - 0.12, MgO - 0.25, P₂O₅ - 0.09, ZrO₂ - 0.08, NbO - 0.14.

The formation of titanium dioxide nanotubes takes place in several stages: the slow dissolution of raw is accompanied by the epitaxial growth of layered sodium titanate nanosheets → exfoliation of nanosheets → folding of nanosheets into tubes → growth of nanotubes along X axis → exchange of sodium ions by protons during washing and separating of nanotubes from each other. The crystalline lattice of initial rutile is
converted into amorphous product at alkali processing, after treatment with distilled water and solution of hydrochloric acid the titanium dioxide nanotubes are formed. According to [7], the nanotubes consist of layers of titanate, which composition depends on such synthesis conditions as temperature and duration of treatment, ratio of solid and liquid phases.

Fig. 3 shows SEM image of synthesized TiO$_2$ nanotubes. The channels inside the produced nanotubes are clearly visible. The resolution of scanning electron microscope allows evaluating their outside diameter (70-100 nm) and length (up to 4500 nm). The synthesized TiO$_2$ nanotubes have a large surface area, which is, according to [7], by orders higher than the specific surface of the starting raw, which provides high sorption properties.

**Fig. 3. Titanium dioxide nanotubes**

4. **Conclusion**

The TiO$_2$ nanotubes were obtained using simple hydrothermal method in Laboratory of mineral raw technology in Institute of Geology Komi SC UB RAS. An inexpensive natural raw material - non-magnetic fraction of gravity concentrate oftitanium ore ofPizhemskoe deposit - was used as a starting material. The synthesized titanium dioxide nanotubes have outer diameter 70-100 nm and length up to 4500 nm. The synthesized TiO$_2$ nanotubes have a large surface area that results in a good sorbent material.

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