PERIÓDICO TCHÊ QUÍMICA
ARTIGO ORIGINAL

CARACTERÍSTICAS DA DEFORMAÇÃO E DESTRUIÇÃO DE CERÂMICAS POROSAS À BASE DE DIATOMITO

THE FEATURES OF DEFORMATION AND DESTRUCTION OF POROUS DIATOMITE-BASED CERAMICS

ОСОБЕННОСТИ ДЕФОРМАЦИИ И РАЗРУШЕНИЯ ПОРИСТОЙ КЕРАМИКИ НА ОСНОВЕ ДИАТОМИТА

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RESUMO

Estudos experimentais e teóricos das propriedades mecânicas de materiais porosos são uma das áreas prioritárias para o desenvolvimento da física da matéria condensada. A cerâmica de diatomito pode servir como matéria-prima para os materiais estruturais de isolamento térmico e os materiais estruturais à prova de som, para os aditivos de certos tipos de cimento e para polimento dos metais e mármore. A cerâmica à base de diatomito também é usada para isolamento térmico na produção de alumínio. A cerâmica de espuma de diatomito é um material poroso promissor. Mas as propriedades da cerâmica de diatomito não são bem conhecidas, o que determina a relevância do estudo. O principal objetivo deste trabalho é estudar a porosidade e os módulos elásticos da cerâmica à base de diatomito, bem como o efeito do tratamento térmico sobre suas propriedades físicas e mecânicas. O trabalho é dedicado ao estudo das propriedades mecânicas de cerâmica porosa à base de diatomito – rocha sedimentar, consistindo principalmente de conchas com micro e nanoporos de 50 nm... 500 µm. Conforme os resultados do estudo da microestrutura de cerâmica porosa à base de diatomito, foi determinada a porosidade média das amostras (~ 50%) e os valores dos módulos elásticos estático (35... 45 GPa) e dinâmico (0,3... 0,8 GPa) foram medidos experimentalmente. Verificou-se que os módulos elásticos diminuem com o aumento da porosidade do material. O experimento mostrou que o módulo elástico do material altamente poroso em consideração era duas ordens de magnitude inferior ao do cristalino. O artigo pode servir como material para um estudo mais aprofundado das propriedades da cerâmica à base de diatomito. Os resultados do estudo também podem ser utilizados para aplicações práticas em isolamento térmico, produção de cimento, polidor de metais e mármore.

Palavras-chave: *material de espuma de diatomito, propriedades mecânicas, microestrutura, lei de Hooke.*

ABSTRACT

The experimental and theoretical investigations of mechanical properties of porous materials are one of the priority areas of development of condensed matter physics. Diatomite ceramics can serve as a raw material for structural heat and sound insulating materials and additives to some types of cement, as a polisher for metals and marble. Diatomite-based ceramics are also used for thermal insulation in aluminum production. The foam-diatomite ceramics is a promising porous material. But the properties of diatomite ceramics are not well studied, which determines the relevance of the study. The main task of the present work is the investigation of porosity and elastic moduli of diatomite ceramics, as well as the effect of thermal treatment on its physical-mechanical properties. The work deals with studying mechanical properties of porous ceramics based on diatomite – a sedimentary rock composed predominantly of shells with micro- and nanopores of 50 to 500 µm. From the results of studying the microstructure of porous diatomite-based ceramics, the average porosity of samples (~50%) was determined, and the values of static (35 to 45 GPa) and dynamic (0.3 to 0.8 GPa) elastic moduli were experimentally measured. It was found that the values of elastic moduli decrease as material porosity increases. The experiment showed that the elastic modulus of the considered high-porous material was two orders of magnitude less than that of the crystalline one.

Keywords: *foam-diatomite material, mechanical properties, microstructure, Hooke's law.*

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АННОТАЦИЯ

Экспериментальные и теоретические исследования механических свойств пористых материалов являются одним из приоритетных направлений развития физики конденсированных сред. Диатомитовая керамика может служить сырьем для конструкционных тепло- и звукоизоляционных материалов и добавок к некоторым типам цемента, а также полировкой для металлов и мрамора. Керамика на основе диатомита также используется для теплоизоляции при производстве алюминия. Пенодиатомитовая керамика является перспективным пористым материалом. Но свойства диатомитовой керамики изучены недостаточно, что определяет актуальность исследования. Основной задачей настоящей работы является исследование пористости и модулей упругости диатомитовой керамики, а также влияния термической обработки на ее физико-механические свойства. Работа посвящена изучению механических свойств пористой керамики на основе диатомита – осадочной породы, состоящей преимущественно из оболочек с микро- и нанопорами размером 50 нм… 500 мкм. По результатам изучения микроструктуры пористой керамики на основе диатомита была определена средняя пористость образцов (~ 50%) и экспериментально измерены значения статического (35… 45 ГПа) и динамического (0,3… 0,8 ГПа) модулей упругости. Было обнаружено, что значения модулей упругости уменьшаются с увеличением пористости материала. Эксперимент показал, что модуль упругости рассматриваемого высокопористого материала был на два порядка меньше, чем у кристаллического. Статья может служить материалом для дальнейшего изучения свойств диатомитовой керамики. Результаты исследования также могут быть использованы для практического применения в теплоизоляции, производстве цемента, полировщика для металлов и мрамора.

Ключевые слова: *пено-диатомитовый материал, механические свойства, микроструктура, закон Гука.*

1. INTRODUCTION

Ceramics is the third most widely used industry material after metals and polymers. It is the most competitive class of materials compared to metals for use at high temperatures (Jones *et al.*, 2016; Rudnev *et al.*, 2016). Ceramics are artificial stone materials and products obtained in the processing of mineral raw materials and subsequent burning at high temperatures. The raw materials for the manufacture of ceramic materials are constituted by a variety of clay rocks (clays).

Most ceramic materials respond to machine processing with difficulty (Nikolaev, 2016; Sapronov *et al.*, 2017; Smelik *et al.*, 2019). Therefore, the main condition for ceramic technology is to obtain practically finished products upon consolidation. To finish the surfaces of ceramic products, abrasive treatment with diamond wheels, electrochemical, ultrasonic and laser processing are used (Yuan et al., 2015; Bilalov *et al.*, 2016; Dashko and Kotiukov, 2018; Soshko and Soshko, 2019). The use of protective coatings is effective as it heals the smallest surface defects – roughness, grooves, etc.

They are classified by a number of attributes:

– according to the purpose, ceramic products are divided into the following types: wall, decoration, roofing, for floors, for cover-ups, road, sanitary, acidproof, heat-insulating, fireproof, and filling aggregates for concrete;

– according to the structure, ceramic products with a porous and sintered (dense) shard are distinguished. Porous are products with water absorption by weight of more than 5%. These include products of both rough (ceramic wall bricks and stone, products for roofing and ceilings, drainage pipes), and fine (facing tiles, earthenware) ceramics. Products with water absorption by weight less than 5% are referred to as dense. They also include products of both rough (clinker bricks, large-sized cladding plates) and fine (earthenware, semi-porcelain, porcelain) ceramics;

– according to the melting temperature, ceramic materials and products are divided into low-melting (with a melting temperature below 1350°C), high-melting (with a melting point of 1350°C - 1580°C), refractory (1580°C - 2000°C), super-refractory (over 2000°C).

The experimental and theoretical investigations of mechanical properties of porous materials are one of the priority areas of development of condensed matter physics. Now porous ceramics are mostly applied in two areas (Vassileva *et al.,* 2013; Ilina and Shelekhova, 2014; Dong *et al.,* 2016): thermal insulation (Akhtar *et al.,* 2009; Jang *et al.,* 2013) and porosity (as well as related properties) (Van Garderen *et al.,* 2011; Dong *et al.,* 2014). Diatomite ceramics is a typical representative of such materials. Its basis is diatomite – amorphous material, mostly involving diatom shells (Vassileva *et al.,* 2013; Dong *et al.,* 2016; Wil'deman *et al.*, 2018). The chemical composition of diatomaceous material is presented in Table 1.

It has high porosity, ability to adsorption, low thermal conductivity and sound conductivity, infusibility, and acid resistance (Akhtar *et al.,* 2009). Now diatomite serves as a constructional material with low thermal conductivity (Galzerano *et al.*, 2018; Lyngsie *et al.,* 2019; Hao *et al.,* 2019) used to produce accumulators (Cheng *et al.,* 2019), supercapacitors (Liguori et al., 2017; Li *et al.,* 2019) and antibiotics (Wu and Zhang, 2019). It also serves as raw material for constructional heat-insulating and soundproof materials (Fraine *et al.,* 2019) and additives to some types of cement, as well as a polisher (in the paste composition) for metals and marbles (Ho *et al.,* 2019; Jiang *et al.,* 2019). The diatomite-based ceramics is also used for heat insulation when producing aluminum (Li and Shi, 2019). The foam-diatomite ceramics is a promising porous material. However, its physical-chemical properties (elastic moduli, porosity, etc.) are not sufficiently investigated yet. Therefore, the main task of the present work is the investigation of porosity and elastic moduli of diatomite ceramics, as well as the effect of thermal treatment on its physical-mechanical properties.

2. MATERIALS AND METHODS

Diatomite as a raw material to make foam-diatomite products, is a light porous rock composed of amorphous silica (70-80%) and clay material (30-20%). Amorphous silica is presented by the microscopic leaves of dead ancient water plants – diatoms (Vassileva *et al.,* 2013) whose microphotographs are presented in Figure 1. The apparent density of raw material is usually in the 250-550 kg/m^3 range. The materials for investigations were formed products of diatomite ceramics (with porosity over 30% and working temperature range up to 900 ^{0}C). It was made from the SiO_2 – and Al_2O_3-based raw material using the standard technology that involved (i) rock drying and crushing, (ii) flask formation with adding a foaming agent, and (iii) burning (Skvortsov *et al.,* 2017; Li and Shi, 2019). The samples (15×15×100 mm parallelepipeds) were made of the material obtained.

Originally, the mass of the samples was measured, and their density was calculated. An analysis of the composition and structure of the sample was performed using a high-resolution field-emission scanning electron microscope (SEM) JSM 7500F (JEOL) equipped with an EMF detector. Silicon served as an element of optimization. The instrument sensitivity was 0.2-1 at %, depending on the element. The spatial resolution was no less than 1 nm. During shooting, the pressure in the chamber with samples was no more than 9.6×10^{-5} Pa. The compression-test diagrams were registered using a testing machine. The resonance method was used to measure the dynamic elastic moduli (Van Garderen *et al.,* 2011; Dong *et al.,* 2014).

3. RESULTS AND DISCUSSION:

At room temperature, the diatomite ceramics (as most of other ceramics) is a brittle material for which Hooke's law is satisfied. Its elastic modulus E_0 is 71 GPa at zero porosity (Lyngsie *et al.,* 2019; Hao *et al.,* 2019) and may decrease as porosity increases. The typical results of the mechanical tests of the samples are presented in Figure 2. Young's modulus for the given sample is 35 GPa. A microphotograph of its surface is given in Figure 3. It is easy to see a wide range of pore sizes in the material under investigation. Therefore, to estimate ceramics porosity, a morphological analysis of the ceramics studied was performed (Figure 4). The results of the sample studying before and after its deformation are given in Figure 5 and are combined in Table 2.

As expected, deformation promotes the reduction of material porosity. Then dynamic elastic moduli of the samples were measured by applying the resonance method (Dong *et al.,* 2014; Skvortsov *et al.,* 2017). The essence of the method using bending vibrations is as follows. The bending vibrations of variable frequency are excited by an electronic generator and an electro-acoustic transducer in a sample (lying on bearings). These vibrations are taken by another transducer (receiver) and are delivered to an indicator. The generator frequency changes. When the frequency of the natural fundamental oscillations of a sample coincides with the frequency of exciting oscillations, an abrupt increase of oscillation amplitude (resonance) occurs. One can quantify the value of elastic modulus of the given sample by measuring the natural resonant frequency of steady-state vibrations of a solid sample with undisturbed structure: $E=4\cdot\pi\cdot10^{-3}\cdot L^2\cdot\rho_k\cdot f^2$. Here L is sample length; ρ_k is sample density, and f is the resonant frequency.

The dependence of elastic modulus on

porosity (0-20%) is known (Lou and Stevents, 1999; Akhtar *et al.,* 2010). For high-porous diatomite ceramics, investigations of dynamic elastic modulus dependence on porosity (30-80%) were performed. The obtained results are presented in Figure 5. One can see that elastic modulus of the considered high-porous material is two orders of magnitude less than that of the crystalline one (Lou and Stevents, 1999; Romashin *et al.,* 2004). Similar results were also obtained by measuring the dependence of dynamic elastic modulus on sample density. The results of this set of experiments are shown at the insert of Figure 5. The numerical *E* values agree with the known literature data on high-porous quartz ceramics (Pivinsky and Romashin, 1974; Lou and Stevents, 1999; Romashin *et al.,* 2004).

4. CONCLUSIONS:

The properties of solids, in contrast to the properties of liquids and gases, are determined not only by the chemical composition but also by the structural features. In this work, the mechanical properties of porous diatomite-based ceramics were experimentally investigated. The values of static (35 to 45 GPa) and dynamic (0.3 to 0.8 GPa) elastic moduli of samples are obtained. Ceramics structure and pore morphology (general, minimum, and maximum area and average pore diameter) were studied, and the values of sample porosity in the 30 to 80% range were determined. The dependences of dynamic elastic modulus of diatomite ceramics on porosity were also studied. It was fixed that (i) the elastic moduli decrease as material porosity increases and (ii) after deformation material porosity decreases. It is found experimentally that the elastic modulus of the considered high-porous material is two orders of magnitude less than that of the crystalline one.

The materials of the paper are of practical importance since industrial ceramics has been used in mechanical engineering, in metallurgy, in the chemical industry, in the woodworking, and in the aviation industry for many decades. The development of this industry has high prospects, which entails an increase in the quality of processing of materials, service life, productivity, wear-resistance, and many other factors. The most important task in the field of production of ceramic products is the establishment of patterns between the structure of the material and its operational properties.

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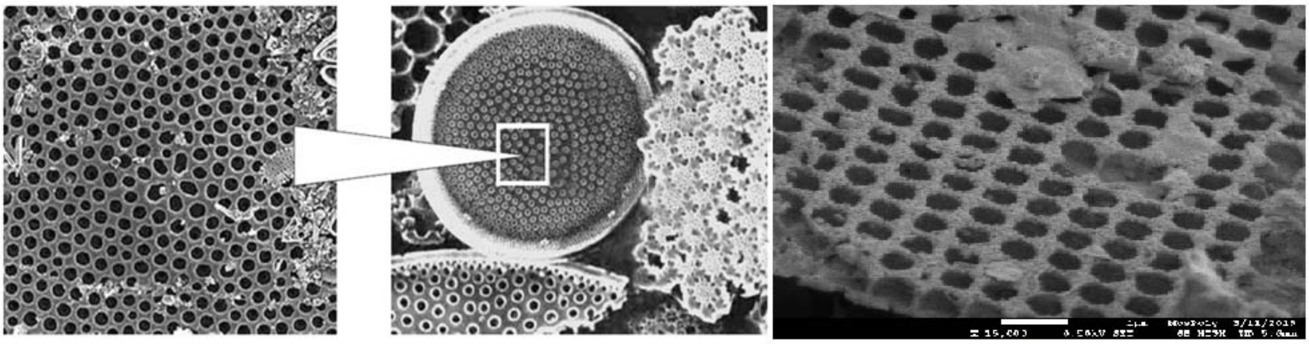

a) b)

Figure 1. *a) Microstructure of a diatoms leaf: right – diatoms leaf (diameter of 0.2 mm); left – leaf porous structure (Vassileva et al., 2013); b) microstructure of a diatoms leaf at the samples.*

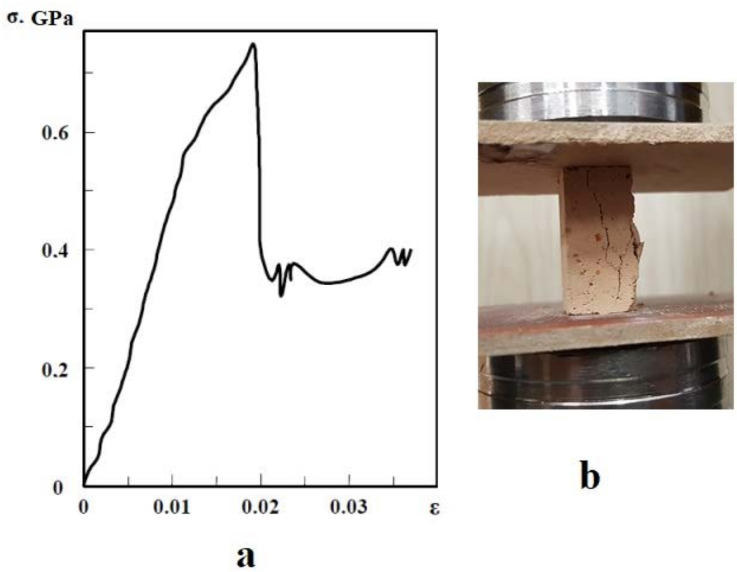

Figure 2. *A typical compression-test diagram of diatomite ceramics (a) and a photograph taken at the moment of crack formation at sample compression (b).*

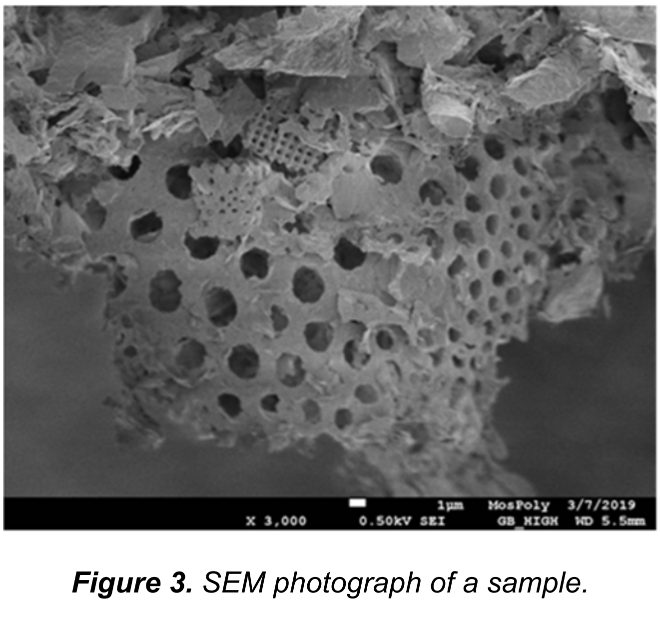

Figure 3. *SEM photograph of a sample.*

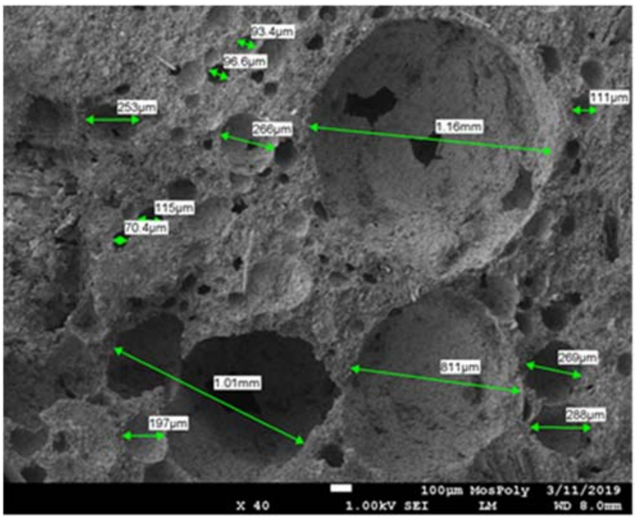

Figure 4. *SEM photograph of the sample under consideration with characteristic pore sizes.*

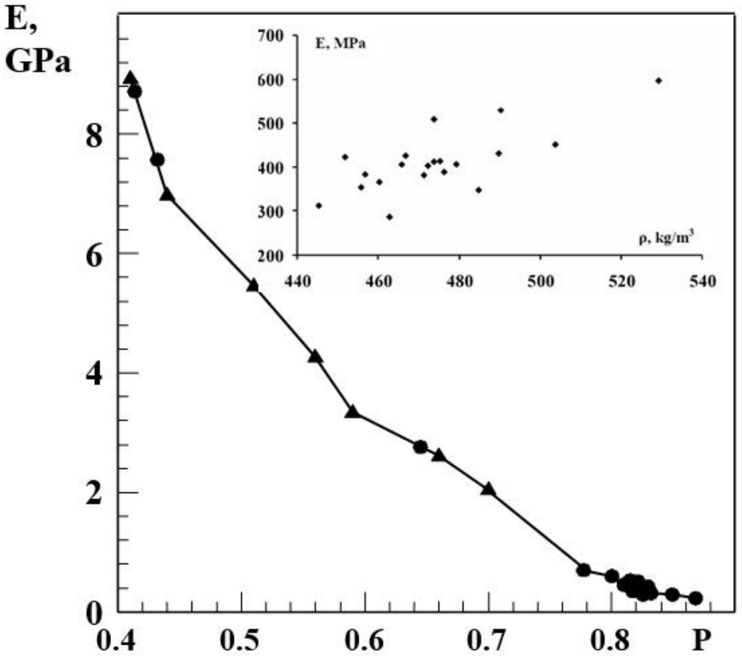

Figure 5. *Elastic modulus vs quartz ceramics porosity: ▲ – data from (Cheng et al., 2019), ● – data from this investigation. Insert: (for initial 25×30×120 mm samples of foam-diatomite ceramics) dynamic elastic modulus vs material density.*

Table 1. *Chemical composition of foam-diatomite ceramics*

Compound	Content, %	Compound	Content, %
SiO_2	86.00	MgO	0.84
Al_2O_3	6.10	CaO	0.32
Fe_2O_3	2.80	TiO_2	0.29
K_2O	1.34	Na_2O	0.20

Table 2. *General indicators of ceramics pore space.*

	Initial	After deformation
Porosity, %	26±5	21±4
Total pore area, μm^2	972 323	1 120 520
Total pore perimeter, μm	7 592 290	3 959 696
Average pore diameter, nm	84	55
Average area, μm^2	0.12	0.10
Average perimeter, μm	0.90	0.34
Minimum pore area, μm^2	0.003	0.001
Maximum pore area, μm^2	88 988	22 784
Permeability coefficient, mm/min	6.3±0.5	7.6±0.5