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Electrical Properties and Microstructure Fractal Analysis of Magnesium-Modified Aluminium-Silicate Ceramics

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Abstract:

The addition of $Mg_2(NO)_3$ and some active additives, composed of Al salts, to the mixtures of kaolinite and bentonite can provide clay compositions which, after sintering at high temperatures, produce very porous ceramics with microcrystalline and amorphous regions and highly developed metalized surfaces (mainly with magnesium surplus). Characterization of sintered samples was done before and after treatment in "synthetic water", i.e. in aqueous solution of arsenic-salt. Microstructure investigations have revealed non-uniform and highly porous structure with broad distribution of grain size, specifically shaped grains and high degree of agglomeration. Electrical characterization was estimated by determining dielectric constant and electrical resistivity in function of active additives amount and sintering temperature. Fractal analysis has included determination of grain contour fractal dimension.

Keywords: Aluminium-silicate ceramics; Active additives; Microstructure; Electrical properties; Fractals

1. Introduction

Ceramic materials are utilized for many different applications in a variety of fields. There are many types of ceramics, each with unique individual properties. Modified aluminium-silicate ceramics, alloyed with magnesium and microalloyed with aluminium, belongs to the group of advanced ceramics materials i.e. functional and ecological ceramics. The prognosis of electrical and electrochemical properties, which are structurally very sensitive characteristics, can be done with the change of microstructure, by the selection of synthesis parameters and by microalloying. Specific area of modified ceramics is highly developed, with very large number of pores ranging from micro to nano scale: macro, mezzo, micro and submicro pores. Porous ceramics have sponge like structures, with many pores like lacunae, or holes, that can make up from 25 to 70 percent of the volume. Because of the large number of pores, porous ceramics have enormous surface areas, and so can make excellent catalyzes [1-9].

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A solid state surface, depending on its chemical composition and morphology, can become a catalyst. Therefore, for the catalytic processes that take place on a solid surface, the density and physical-chemical character of surface states and active centers are of particular importance [3, 4]. Natural clays such as montmorillonite, kaolinite, bentonite and many other like them, have a considerable and important application in catalysts technology. An important application of hydrated aluminum silicates is in water treatment, where they are used as ion exchangers to remove different types of pollutants [5]. Bentonite and kaolinite are natural colloidal, hydrated aluminium silicates, which, depending on the chemical composition and purity, improve water quality and remove certain unwanted wastes from it [6]. Therefore, this particular type of clay was chosen to act, in its ceramic form, as the support substrate for magnesium aluminium silicate catalyst. Clay minerals generally have the ability to absorb heavy metal ions, due to high cationic exchange capacity [7]. Natural materials like clays and clay minerals, which are good and inexpensive sorbents and adsorbents, have shown to be some of the most useful heavy metal sorbents [8].

Porous ceramics made of mixture of natural kaolinite and bentonite clay exhibit crystalline areas, the most probably of zeolite structure, although the most of the ceramics bulk are made of amorphous oxides of Fe and alkaline metals [9]. Addition of Mg salts and some active components and additives, such as Al salts, to the mixture of kaolin and bentonite can provide clay mixtures which, after sintering at high temperatures, produce very porous ceramics with microcrystalline and amorphous regions of stoichiometric and nonstoichiometric new oxides. Some metalized surfaces with magnesium, being incorporated as an exchanging cation, form new structures in that way [10, 11]. The oxides mixtures and metalized amorphous ceramics regions show high electrochemical and chemical activities in contact with water, which make it "active" ceramics. The removal of heavy metal cations, and other ions and radicals, present in the treated water, can be done by a numerous of processes, such as adsorption, electrochemical reduction (electron exchange between surface and ions from "synthetic water"), partial ion exchange and other redox processes. Therefore, the modified ceramics is a very powerful tool for processing of drinking water and sewage disposal of waste waters [12].

In order to prognosis and design new ceramics structures, as well as to set up the control over ceramics properties, it is necessary to develop model for control of intergranular surfaces between different grains. Fractal nature of material structure and its recognizing is very helpful for control the way that grains contact, which imply possible control over ceramics structure. Considering the fractal nature of intergranular contacts, correlation between material electronic properties and corresponding microstructure has been established. Concept of fractal structure has great importance in physical characterization of materials. The fractals theory has been increasingly applied in the field of materials science and engineering. Models of fractal lines and surfaces have been generated to describe the microstructural features of materials [13-15].

The term "fractal" (for fractional dimension) was first used by Benoit Mandelbrot who proposed the concept as an approach to problems of scale in the real world. According to Mandelbrot, a fractal is a curve or a surface that is independent of scale. This phenomenon is referred to as self-similarity, which means that any portion of the curve or the surface, if blown up in scale, would appear identical to the whole curve or surface. In the area of materials science, fractals can be used to help analyze surfaces that were formed through some physical process. Fractal objects are characterized by their fractal dimension (D) that is the dimension in which the proper measurement of a fractal object is made. Fractals are objects whose dimensions are not whole numbers. In that sense, Mandelbrot has defined fractal dimension as a "degree of chaos". The fractal geometry is a mathematical concept that describes objects of irregular shape. Some natural geometrical shapes, that can be irregular, tortuous, rough or fragmented, can be described using concepts of fractal geometry as long as

the requirement of self-similarity is satisfied. The latter term implies that the geometrical features of an object are independent of the magnification or observation scale [16, 17].

Fractals are entities that display self-similarity in their geometry such that any portion of the system is a replica of the whole as seen at a larger scale. This scaling is quantified by the fractal dimension. In simplistic terms, the fractal dimension describes the manner in which a fractal entity fills up the available Euclidean space. More precisely, Mandelbrot (1983) defines a fractal as a set for which the Hausdorff-Besicovitch dimension (D) strictly exceeds the topological dimension. Every set with a noninteger D value is a fractal, but it is not necessary that all fractal dimensions be nonintegers. Since we are dealing with linear objects in two dimensions, noninteger fractal dimensions are expected within the range $1 < D < 2$ [18, 19].

The main goal of this work is to examine microstructure and electrical characteristics of Mg-enriched kaolinite-bentonite clay ceramics, prior and after treatment with aqueous solution of arsenic salt. The fractal analysis of microstructure is introduced as a new approach to understand and describe unarranged configuration of materials, by determining the fractal dimension of the ceramics grains surfaces.

2. Experimental

Microalloyed porous ceramics was obtained by chemical and thermal transformations of natural kaolinite and bentonite clay, taken from south of Serbia. The procedure included several steps: mechanical cleaning of natural clay by removing small stones and other unwanted ingredients; milling and drying; washing of the clay with water; centrifugation with the goal to remove remaining water in clay; homogenization with sodium silicate water solution to obtain a viscosity suitable for granulation; alloying with water solution of $Mg(NO_3)_2$ (2-10 wt%) and microalloying with water solution of $Al(NO_3)_3$; addition of $(NH_4)_2CO_3$ to achieve supplementary porosity during sintering. The plastic clay mass was reworked into pellets, 10-15 mm in diameter on average and 3-4 mm of thickness. The pellets were dried at 200°C for 3-4 hours and thermally treated for 30 min at 600°, 700°, 800°, 900° and 1100°C and subsequently cooled to room temperature. Cooled sintered pellets were kept in closed plastic container to avoid undesired adsorption of chemicals or water. All chemicals used were from Merck p.a. Sintered samples were treated in a glass beaker for 24 and 48 hours in 20 ml of "synthetic water", i.e. in aqueous solution of arsenic salt. Aqueous solution of arsenic (V), of concentration 500 mg l⁻¹, was prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ (Fluka AG, Buchs SG, Switzerland, p.a.) in distilled water. After the period of treatment, the ceramics samples were rinsed with distilled water, at first dried at room temperature on filter paper and then at 180°C for one hour. The as prepared samples were used for the characterization of the materials properties.

The microstructures and micro morphology of the as sintered samples were observed by scanning electron microscope (SEM-JEOL-JSM 5300). Prior to examination the specimens' surface was sputtered with gold. The qualitative analysis was performed using energy dispersive spectrometer with beam controller (EDS-LINK QX 2000 analytical). Mineralogical structural composition was determined by XRD analysis. X-ray diffraction patterns, for identification of crystalline phases, were collected on XRD SIEMENS D-500 type diffractometer, operating with Ni-filtered $CuK\alpha$ radiation. Peaks present in the diffractograms were identified with the aid of JCPDS cards. Capacitance was measured by digital multimeter model DT-9207A. Electrical resistance was measured by KEITHLEY 2400 sourcemeter. Prior to electrical measurement specimens' surface was coated with silver paste.

3. Results and discussion

3.1. Microstructure characteristics

The morphology of the samples, before and after treatment in “synthetic water”, is clearly revealed in SEM microphotographs, which indicate rather high porosity, inhomogeneous surface and particles varying in shape. SEM images of untreated samples (Fig. 1) show that particles exhibit the high degree of agglomeration. Amorphous regions, coarse grained microstructures and well defined crystalline grains are visible. Broad distribution of grain size ranged from 1-20 μm or more was noticed. They also show non-uniform ceramics structure with high percentage of porosity, polygonal shape of grains and well developed surface. There is a significant concentration of irregularly shaped large agglomerates, consisting of smaller particles, and also a large quantity of particles with different shapes and dimensions. That leads to the conclusion that this kind of ceramics has bimodal structure. The qualitative chemical composition of samples was estimated from EDS spectra. The intensity of Mg, Al and Si X-ray peaks pointed out that the oxides of these elements are dominant in ceramics structure, while the oxides of other present elements are in traces.

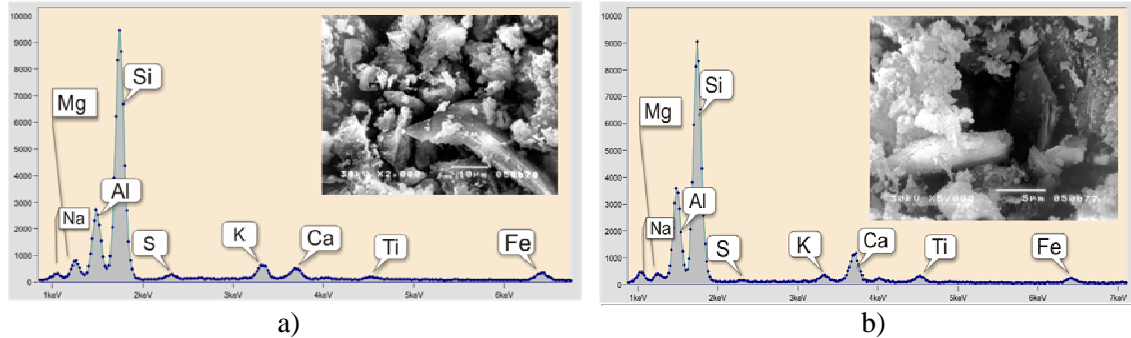


Fig. 1. SEM/EDS images of untreated samples with 6 wt% $\text{Mg}(\text{NO}_3)_2$ sintered at: a) 600°C and b) 800°C.

SEM and EDS results, obtained from the ceramics being into the contact for 24 or 48h with “synthetic water”, showed a very convincing visible difference in comparison with the results for the ceramics before the water treatment. SEM images of samples treated for 48 hours in “synthetic water” (Fig. 2) reveal very interesting crystalline form of grains. Since the $\text{La}1$ X-ray peak of arsenic was detected in EDS spectra (Fig 2b), it can be concluded that during the interaction of ceramics with “synthetic water” the arsenic was adsorbed and incorporated in its structure. EDS beam controller (cross section area of 5 μm^2) for specifically shaped grains, (flower like), confirmed that they were entities, i.e. new phases or clusters with a very high concentration of deposited arsenic. It can be seen that the arsenic peak is dominant in EDS spectra.

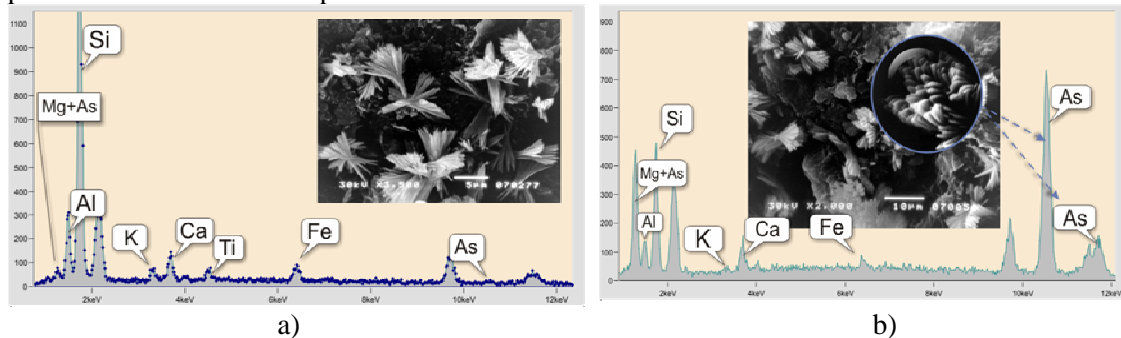


Fig. 2. SEM/EDS images of samples with 6 wt% $\text{Mg}(\text{NO}_3)_2$, treated for 48h in “synthetic water” sintered at: a) 600°C and b) 800°C.

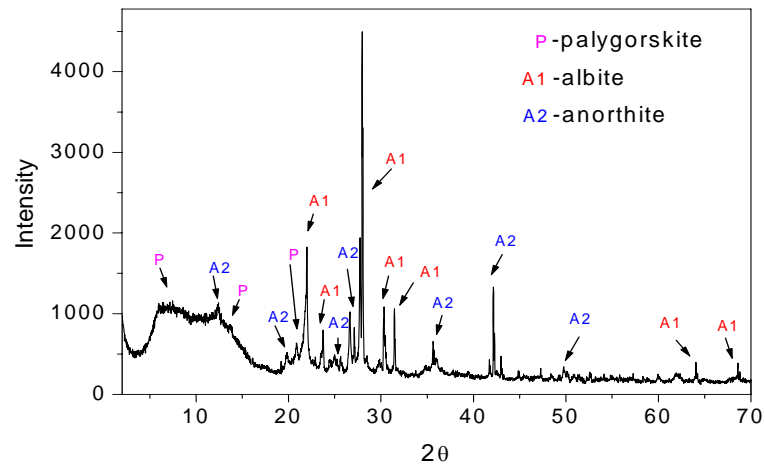


Fig. 3. XRD patterns of clay mixed with active additive.

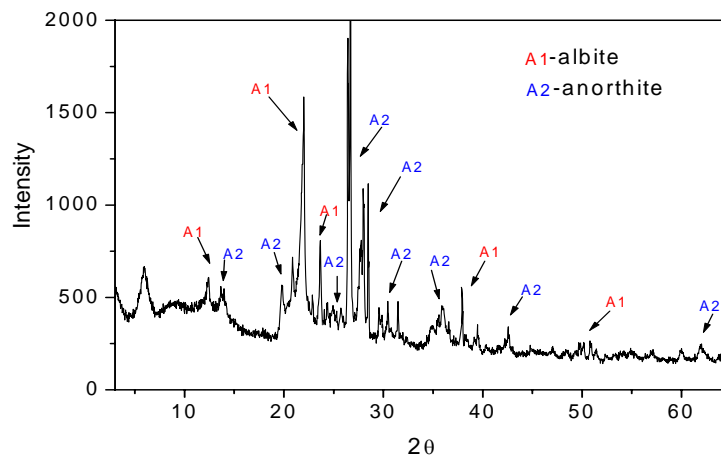


Fig. 4. XRD patterns of ceramics samples with 6 wt% of active additive sintered at 800°C.

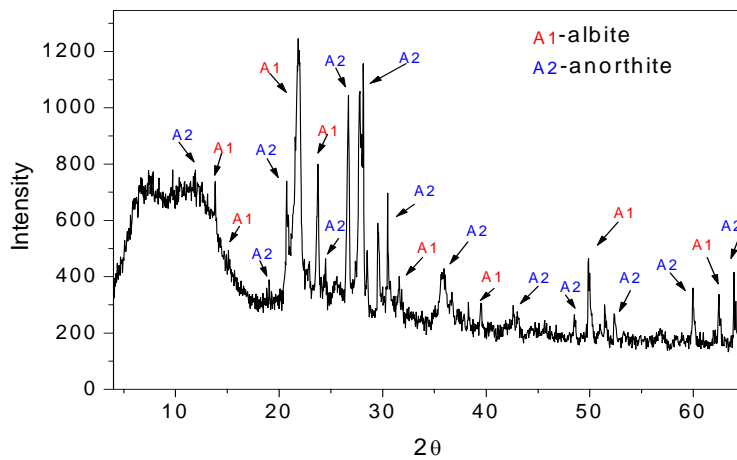


Fig. 5. XRD patterns of ceramics samples with 6 wt% of active additive sintered at 800°C and treated for 24h in "synthetic water".

XRD analysis of clay powders mixed with active components (Fig. 3) revealed more about phase composition of the ceramics, i.e. the presence of anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (JCPDS 20-0020), albite $\text{NaAlSi}_3\text{O}_8$ (JCPDS 20-0572) and palygorskite (hydrated magnesium aluminium-silicate) $\text{Mg, Al}_5(\text{Si, Al})_8\text{O}_{20}(\text{OH})_{28}\text{H}_2\text{O}$ (JCPDS 21-0957), as major minerals. Anorthite is the most dominant mineral phase, while albite and palygorskite are in the less percent present. Crystalline composition of powders of sintered ceramics sample, before and after treatment in “synthetic water” (Figs. 4 and 5) show dominant presence of crystalline phases of anorthite and albite. The existence of crystal modifications in, predominantly, amorphous structure of porous modified aluminium-silicate ceramics is confirmed by this analysis.

3.2. Determination of fractal dimension of ceramics grain contour

Irregularity of the ceramics grains surfaces can be expressed using the term called fractal dimension. The determination of grain contour fractal dimension includes several steps. First of all, coordinates of chosen points from the contour must be determined in relation to some rectangular coordinate system. Then, the method of iterative functional systems (IFS) is applied [20], in the form of fractal interpolation, modified to parameter level. The method of fractal interpolation can be improved by taking contour points coordinates (sampling) in few different positions of the same contour. The contour is rotated for $+\pi/4$, and then for $-\pi/4$, together with chosen interpolation points. After that, the coordinates of points are scanned in rotated coordinate systems.

The contour of big grain observed on SEM micrograph of sample with 6 wt% of $\text{Mg}(\text{NO}_3)_2$, sintered at 900°C , treated for 24h in “synthetic water” (Fig. 6) is taken as an example for this estimation.

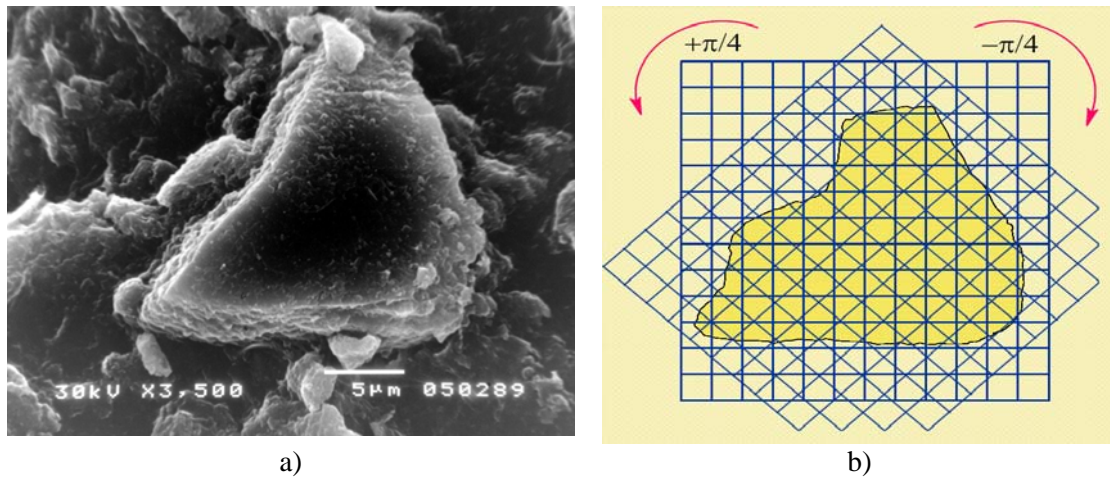


Fig. 6. Grain contour: a) SEM image and b) sampling in three rectangular coordinate systems.

The coordinates of chosen points from the contour, (X_i, Y_i) , $i = 1, \dots, 55$, are represented in starting position of coordinate system (0 degree) and in rotated positions ($\pm \pi/4$) (Fig. 7). Interpolation data, taken from the contour of observed ceramics grain are represented in Fig. 8 and Tab. I. In this way, the calculation of average fractal dimension is possible [21, 22].

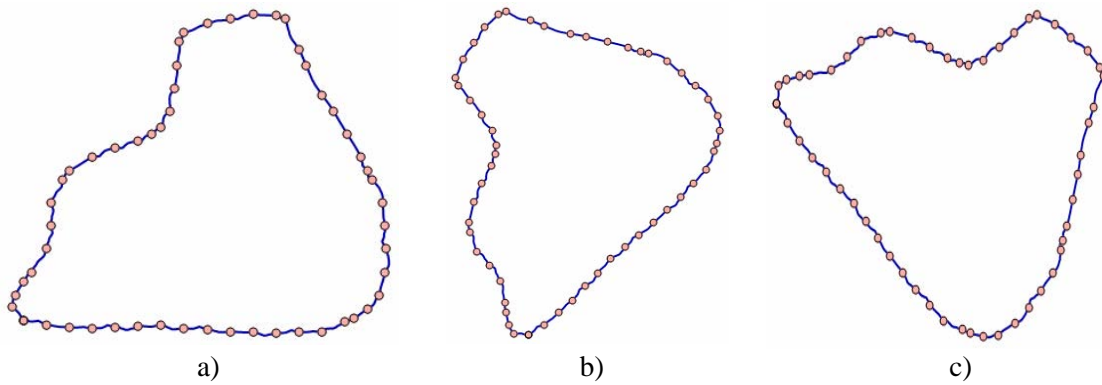


Fig. 7. Chosen points from the contour in positions: a) 0 degree, b) $+\pi / 4$ and c) $-\pi / 4$.

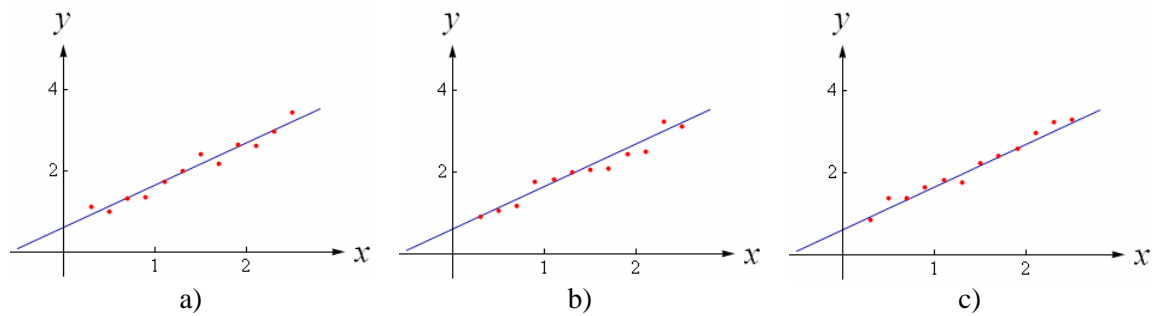


Fig. 8. Fitting diagrams for the contour in positions: a) 0 degree, b) $+\pi / 4$ and c) $-\pi / 4$.

Tab. I. Data summarization for fractal dimensions in three rectangular coordinate systems

Rotation angle	Hausdorff dimension of grain contour (root of equation $\sum_{n=1}^N s_n ^{D(A)} = 1$) s_n -Lipschitz constant
0 degree	$D_0 = 1.04467649987727$
+45 degree	$D_{+\pi/4} = 1.04665207610862$
-45 degree	$D_{-\pi/4} = 1.05159734310688$

Approximate average value of fractal (therefore Hausdorff) dimension of grain contour can be calculated and introduced as $D \approx 1.0476419730309232126$. It was for expected that fractal dimension should have value between 1 and 2, since the grain is represents as object in two dimensional system.

Software Mathematica 6.0 was used for all above quoted computations.

3.3. Electrical characteristics

Electrical characterization of microalloyed ceramics, prior and after treatment in “synthetic water”, was accomplished by determining the dependence of dielectric constant and specific electrical resistivity on the amount of active additives and sintering temperature.

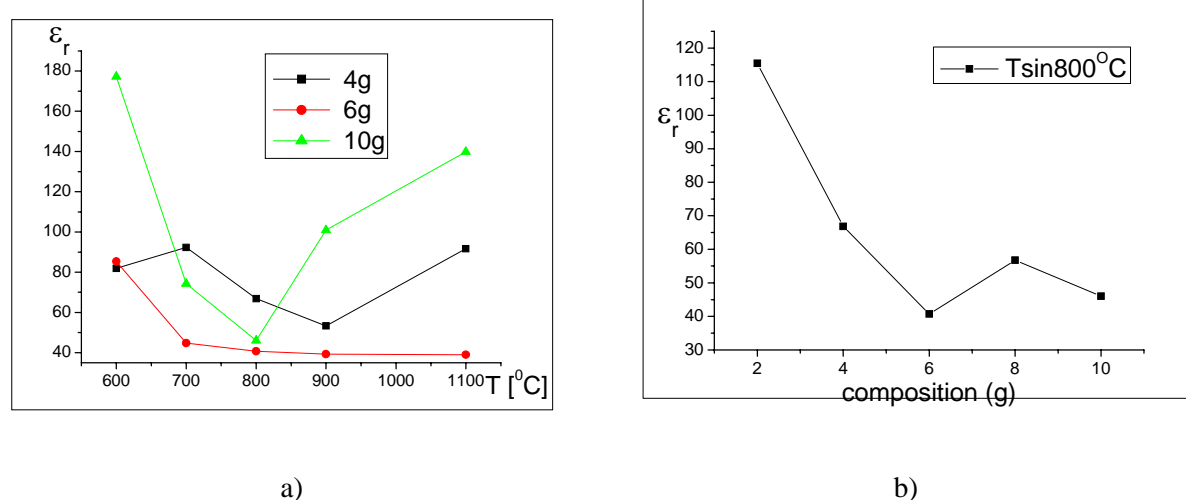


Fig. 9. Dielectric constant for untreated samples with 6 wt% $\text{Mg}(\text{NO}_3)_2$ in function of: a) sintering temperature and b) amount of active additives.

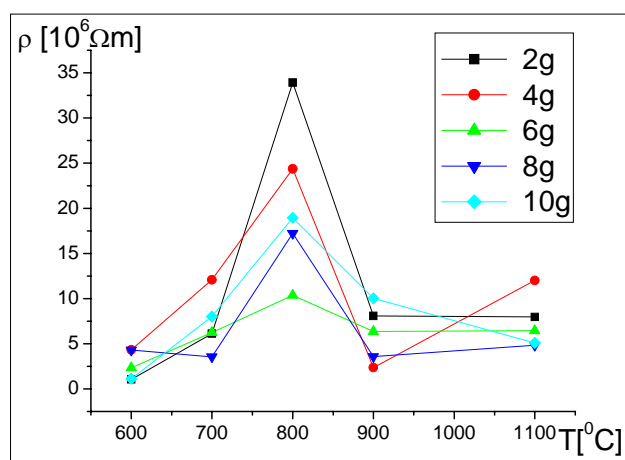


Fig. 10. Electrical resistivity for untreated samples with 6 wt% of $\text{Mg}(\text{NO}_3)_2$ in function of sintering temperature.

The results of electrical properties for untreated samples are represented in Fig. 9 and Fig. 10, while for samples with 6 wt% of $\text{Mg}(\text{NO}_3)_2$ after 24h treatment in “synthetic water” are shown in Fig. 11 and Fig. 12.

As it can be seen from Fig. 9a, dielectric constant has non-linear dependence, regarding the sintering temperature, although for samples with 6 wt% $\text{Mg}(\text{NO}_3)_2$ certain regularity can be distinguished. In this case, it can be seen that the dielectric constant is nearly independent for sintering temperature higher than 700°C. It seems that high value of dielectric constant for samples sintered at 600°C is the result of dominant influence of bonded water molecules, while the minimum value at 800°C is the consequence of water molecules

decomposition and microalloying of ceramics. The results presented in Fig. 9b show that minimum values of dielectric constant are measured for samples with 6 wt% of $\text{Mg}(\text{NO}_3)_2$. The results shown in Fig. 11 reveal that samples with 6 wt% $\text{Mg}(\text{NO}_3)_2$, treated for 24h in “synthetic water” have higher values of dielectric constant. It occurs as the result of the appearance of new phases of deposited arsenic. As-colloidal particle is deposited as thin layer in the pores.

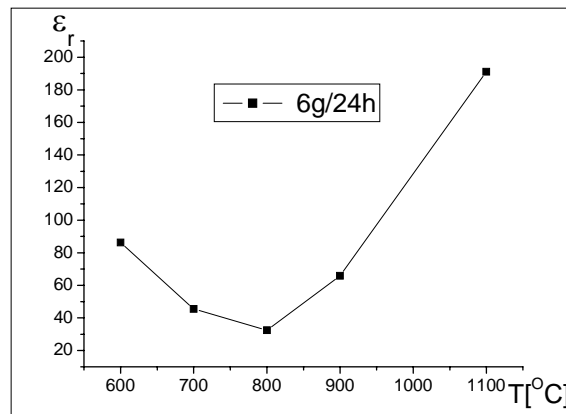


Fig. 11. Dielectric constant for samples with 6 wt% $\text{Mg}(\text{NO}_3)_2$ after 24h treatment in “synthetic water” in function of sintering temperature.

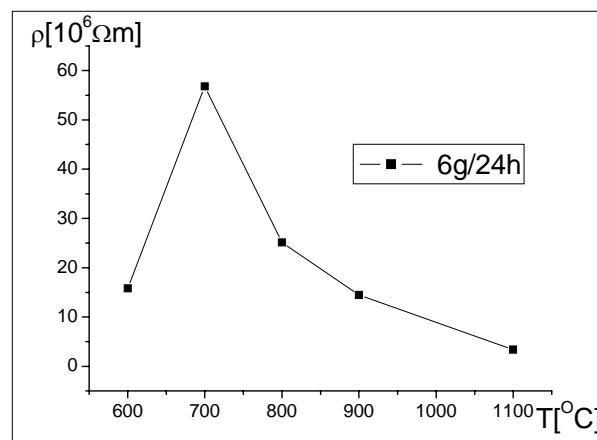


Fig. 12. Electrical resistivity for samples with 6 wt% $\text{Mg}(\text{NO}_3)_2$ after 24h treatment in “synthetic water” in function of sintering temperature.

The dependence of electrical resistivity on sintering temperature (Fig. 10) is also specific, with explicit maximum values at 800°C, which, it is for believed, is the result of creation of new phases in ceramics structure and phase transformations during sintering process. The lowest maximum value can be seen for concentration 6 wt% of $\text{Mg}(\text{NO}_3)_2$. The values of electrical resistivity for samples with 6 wt% of $\text{Mg}(\text{NO}_3)_2$, treated for 24h in “synthetic water”, presented in Fig. 12, are significantly higher in relation to those for untreated samples. Assumption is that this happens because thin layers of adsorbed arsenic cause change in structure and appearance of phase transformations in ceramics. Arsenic, as metalloid, forms inter-metallic compounds with Mg, as Mg_3As_2 . It is supposed that the

shifting of electrical resistivity maximum from 800°C to 700°C, comparison of Fig. 10 and Fig. 12, is the result of changes in ceramics structure after arsenic deposition.

4. Conclusions

Aluminium-silicate ceramics modified with magnesium exhibits very porous amorphous structure, with appreciate portion of crystalline grains sited in magnesium and aluminium silicates matrix. Microalloying additives cause the formation of thin layers of magnesium and aluminium silicates on grains surface. Al and Mg metals surplus make this ceramics unstable in contact with other medium. Therefore, this ceramics is active and enables deposition of heavy metals ions from water solution into ceramics structure. Most probably, this deposition takes place on the surface of nonstoichiometric phases and amorphous structures, which cover almost every grain of the ceramics exposed to the aqueous solution of heavy metal. In this case, electrochemically deposited arsenic is in the form of very thin adsorbed layers, although electrophoretic deposition of As-colloidal particle into the macro, mezzo, micro and submicro pores of the ceramics is very probable.

Magnesium enriched aluminium silicate ceramics exhibited highly developed surface area and porosity, zones of crystalline and amorphous structure and individual metal clusters scattered over the ceramics surface. Observed porosity is most probably a result of gas evolution from decomposition of the active components during the high temperature sintering. The pores themselves increased surface density of active centers for adsorption/desorption when in contact with water. Crystalline stoichiometric, as well as amorphous nonstoichiometric structures, substantially contributed to ceramics surface development. It is possible that crystalline structures were mainly aluminium silicates and amorphous structures, most probably, nonstoichiometric oxides. The sintering process conditions don't permit full transformation of added magnesium and aluminium surplus into oxides or silicates on the surface of the sintered ceramics. Thus obtained metal clusters on the ceramics surfaces dissolve when in contact with water.

Since microalloying additives are metals, metallization of ceramics grains occur and also appreciable changes of electrical properties. Synthesis, structure and morphology of ceramics affect on its properties, both microstructure and electric. Due to inhomogeneity of microalloyed porous ceramics, dielectric constant and electrical resistivity have nonlinear distribution.

Fractal analysis represents a new approach for deeper examination of microstructure of ceramics materials, and further, for prognosis of materials properties. Fractal method provides a new approach for describing, predicting and modeling the grains shape and relations between ceramics structure and its electrical properties.

General conclusion is that magnesium-modified aluminium-silicate ceramics can be used in water filtration systems, for removal of arsenic ions from water solution via redox and ion exchange processes, by incorporating them in its structure.

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Садржај: Додатак $Mg_2(NO)_3$ и неких активних адитива, сачињених од соли Al , смеши каолинита и бентонита може створити смеше глине које, након синтеровања на високим температурама, производе веома порозну керамику са микрокристалним и аморфним областима и врло развијеним метализираним површинама (углавном са вишком магнезијума). Карактеризација синтерованих узорака извршена је пре и након третмана у “синтетичкој води”, у воденом раствору соли арсена. Микроструктурна испитивања су показала неуниформну и високопорозну структуру са широком расподелом величине зрна, специфично обликованим зрнима и великим степеном агрегације. Електрична карактеризација урађена је одређивањем зависности диелектричне константе и електричне отпорности од количине активних додатака и

температуре синтеровања. Фрактална анализа обухватила је одређивање фракталне димензије контуре зрна.

Кључне речи: *Алуминијум-силикатна керамика; активни адитиви; микроструктура; електрична својства; фрактали*
