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Intergranular Area Microalloyed Aluminium-silicate Ceramics Fractal Analysis

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Abstract:

Porous aluminium-silicate ceramics, modified by alloying with magnesium and microalloying with aluminium belongs to a group of advanced multifunctional ceramics materials. This multiphase solid-solid system has predominantly amorphous microstructure and micro morphology. Intergranular and interphase areas are very complex, because they represent areas, where numbered processes and interactions take place, making new boundaries and regions with fractal nature. Fractal analysis of intergranular microstructure has included determination of ceramic grain fractal dimension by using Richardson method. Considering the fractal nature of intergranular contacts, it is possible to establish correlation between material electrical properties and fractal analysis, as a tool for future correlation with microstructure characterization.

Keywords: *Aluminium-silicate ceramics, Microalloying, Intergranular area, Fractals*

1. Introduction

The ceramic tools use in different fields of materials science is beginning to increase with the advent of alloyed ceramics and ceramic-matrix composites, as well as with the advances in ceramic processing technology [1, 2].

Microalloying is a very significant process for the control of some structurally sensitive properties of metals, alloys, ceramics and other materials. Microalloying involves the addition of some elements in small (ppm) amounts, which leads to the modified structure and further to changing of electroconductivity and dielectric properties [3-6].

Microalloyed and structurally modified multifunctional materials have marked electrochemical and electrophysical activity [7-11]. Modified aluminium-silicate ceramics, alloyed with magnesium and microalloyed with aluminium, has highly developed specific area, with very large number of macro, mezzo, micro and submicro pores. [12].

Microalloying implies generation of microgalvanic couples and unstable phases which make ceramics active. Magnesium and aluminium are distributed in intergranular areas, forming in that way clusters and metal films. Cluster nanostructures, layered on porous alumo-silicate matrix, and thin metal films on grains boundaries make dielectric insulator

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material an active dielectric. Additives, dislocations and defects in crystal grains, move dislocations from grains boundaries and fragmentation on large number of subgrains-mosaic blocks with regular symmetry and shape occurs. Amorphous nanostructure metal and oxide films on grains boundaries are formed. Contact between subgrains-mosaic blocks with amorphous layer is responsible for electron exchange processes. Contact potential difference causes appearance of microgalvanic couples and ion-electron processes through solid phase, which implies additional porosity, i.e. micromorphology secondary changes.

Pronounced amorphisation and phases interactions determine multifunctional microalloyed alumo-silicate ceramics fractal properties. On micrograins boundaries, formed by alumo-silicate matrix grains fragmentation, subthin metal, oxide and silicate layers are deposited during sintering process. Amorphous phase with fractals crystal substructure is dominant. Therefore, it is very important to accomplish intergranular area fractal analysis. Intergranular area involves additives, dislocations and new phases which can interact. It is nonhomogeneous, disordered dimensional range, which implies new pores and new boundaries formation and more delicate intergranular areas between nanostructure phases. Stable substructure has regular crystal symmetry, i.e. fractal nature [13-16].

Knowledge of the fractal nature of material structure is very helpful for the control of the way in which grains contact, which implies possible control over ceramics structure. Fractal objects are characterized by their fractal dimension (D), that is, the dimension in which, the proper measurement of a fractal object, is made. Since we are dealing with linear objects in two dimensions, noninteger fractal dimensions are expected within the range $1 < D < 2$ [17-19].

Since sintered materials properties depend on grains configuration, package density and porosity, very important starting parameter is grains morphology [20]. In this paper the fractal analysis of microstructure, taken from scanning electron microscopy microphotographs, is introduced as a new approach for understanding and describing unarranged configuration of materials. It is achieved, by determining, the ceramics grains surfaces fractal dimension by using Richardson method, as a continuation of previously determined fractal dimension of grain contour using the method of iterative functional systems (IFS), in the form of fractal interpolation [21].

2. Experimental

Microalloyed porous ceramics was obtained by chemical and thermal transformations of natural kaolinite and bentonite clay. Alloying was accomplished with water solution of $Mg(NO_3)_2$ (2-10 wt%) and microalloying with water solution of $Al(NO_3)_3$. In order to achieve supplementary porosity during sintering, $(NH_4)_2CO_3$ was added to starting powders. 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. 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. Fractal analysis was done using software programs Mathematica 7.0.

3. Results and discussion

Microstructure characteristics

The morphology of the sintered samples is clearly revealed in SEM microphotographs (Fig. 1), which indicate high porosity, inhomogeneous surface and particles varying in shape and exhibiting the high degree of agglomeration. They also show non-uniform ceramics structure 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.

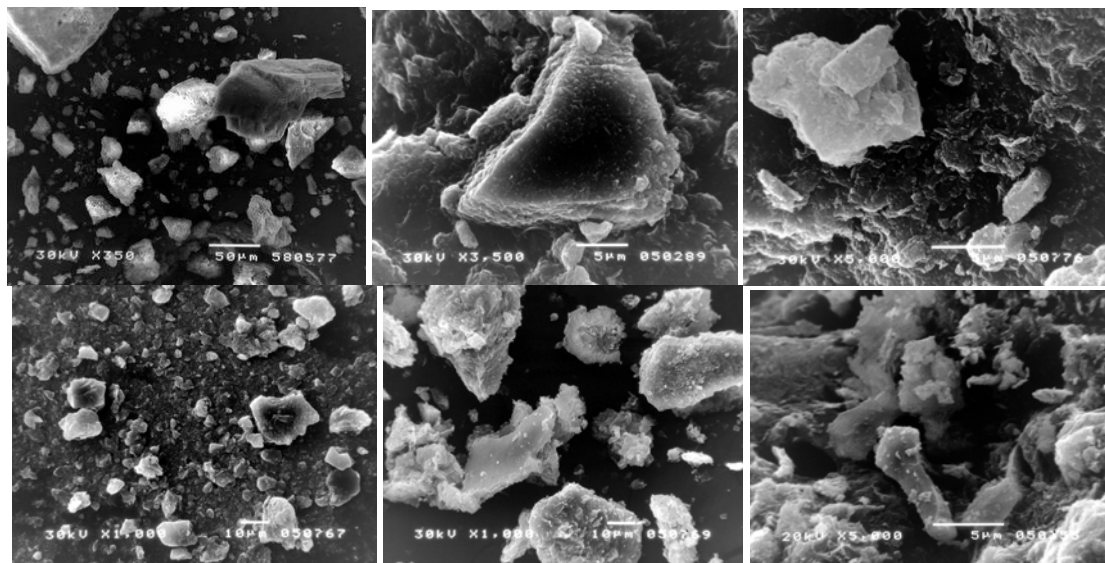


Fig. 1. SEM microphotographs of microalloyed aluminium-silicate ceramics.

Determination ceramics grain contour fractal dimension

Fractal analysis enables surface irregularity parameters characterization and surface morphology examination. Sintered materials grains shape, their arrangement and contact nature are subject to fractal analysis. Grains arrangement before and during sintering process can form fractal configurations. Irregular grains shape could be better described using rather fractal than Euclidian geometric structure. Grains contact zone, which form complex pores system inside material, also exhibits fractal structure [22-24].

Irregularity of the ceramics grains surfaces can be expressed by using the term called fractal dimension. Fractal dimension is coherent with the degree of particles complexity. Larger fractal dimension means more complex grain contour and more compact grains contact. Cognition of grain surface fractal dimension is useful for understanding physico-chemical properties of aluminium-silicate ceramics [25-27].

The contours of some characteristic grains observed on SEM microphotographs are taken as an example for this estimation. The determination of grain contour fractal dimension includes several steps. Grain contour can be taken from SEM microphotographs (Fig. 2). The number of characteristic points from contour varies from 30 to 80. Then formula for parameter fractal interpolation, which approximates contour shape, is applied [28].

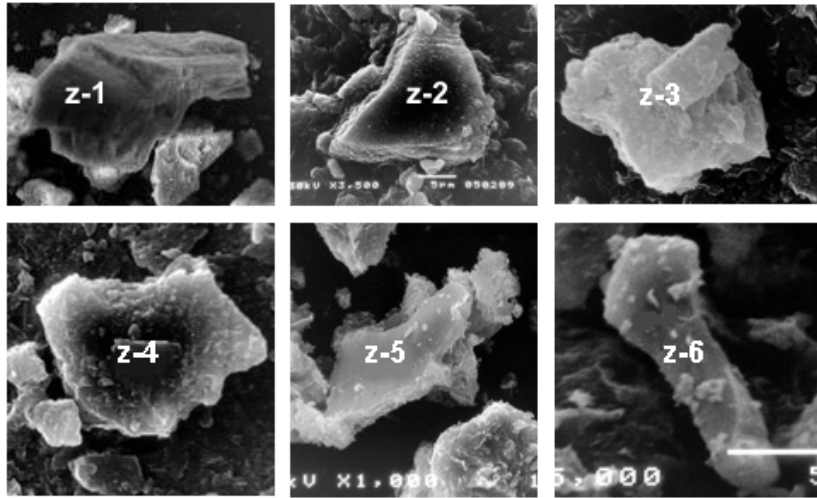


Fig. 2. SEM images of aluminium-silicate ceramics grains used for fractal analysis.

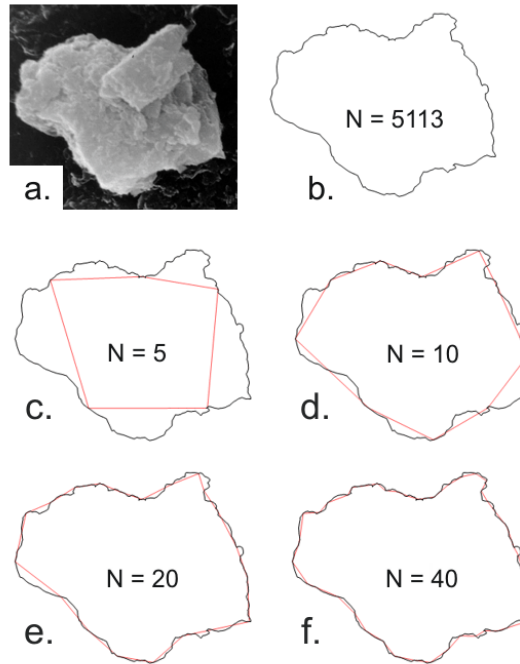


Fig. 3. Modified Richardson method for contour of grain z-3.

First example of fractal analysis is given for grain denoted as z-3 (Fig. 3-a). 72 points from contour are segregated by sampling method. Perpendicular scaling vector is chosen in the manner that contour does not have singular points. Only one fractal interpolation process iteration is enough to acquire contour in $m = 5113$ points (Fig. 3-b). Next step is contour points number modular dividing, with modul equal to degrees of number two.

On the basis of relation

$$\max_N \left\{ \left\{ \frac{m}{2^N} \right\} \bmod 2 \right\} = \max_N \left\{ \left\{ \frac{5113}{2^N} \right\} \bmod 2 \right\} = 11,$$

could be seen that by dividing of point number $m = 5113$ with 2^{11} three points on contour exist and they form triangle. If m is divided with next lower number, $2^{\max N - 1} = 2^{10}$, five points which can form irregular pentagon are obtained (Fig. 3-c). By continuing this procedure, irregular polygons with 10, 20, 40 etc. sides are derived from interpolation

contour. Further procedure is calculation of polygons succession perimeter. By using logarithm of both sides of equation $L(r) = K r^{1-D}$, it is obtained

$$\log L(r) = (1 - D) \log r + \log K,$$

which make linear dependence of $\log L(r)$ from $\log r$, given by formula

$$\log L(r) = a \log r + b. \tag{1}$$

When value \square is determined, than fractal dimension could be obtained from simple expression $D = 1 - \square$. In case of fractal curve equation (1) is approximative, so succession of measured values logarithms represents succession of points

$$p_i = (\log r_i, \log L(r_i)), i = 1, 2, \dots, N,$$

in $(\log r, \log L(r))$ -plane, and thereby digression

$$e = \max_i \{ \text{dist} (p_i, (\log r_i, \log L(r_i))) \},$$

is a small number comparing with measured values codomen and domen size.

All the above quoted present definition of procedure for approximate determination of alumo-silicate ceramics grain contour.

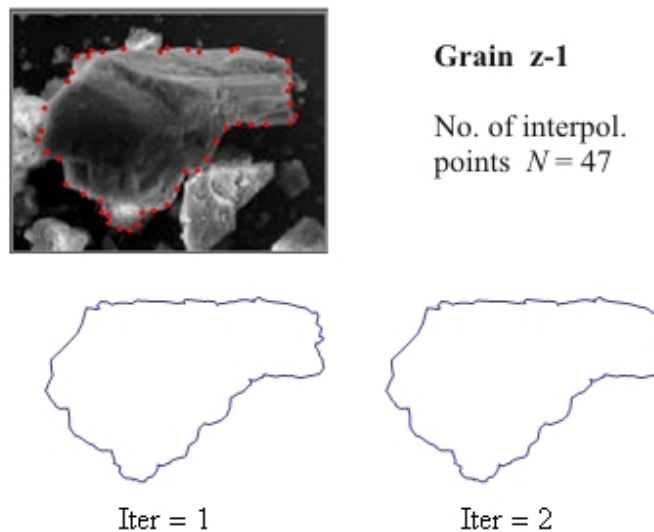


Fig. 4. Sampling of grain z-1 contour.

This theory applied on grain z-1, taken from Fig. 2 is represented in Figures 4, 5 and 6. Firstly, points from SEM microphotographs are chosen in interactive graphic editor (Fig. 4, left above). Fractal parameter interpolant is formed on the base of chosen $N = 47$ points, using deterministic method [25] which enables orientation of numerically obtained grain contour. Calculation in one iteration provides $m = 2163$ points on fractal contour named first iteration contour (Fig. 4-left). Second iteration contour is made of 99453 points (Fig. 4-right). Next is inscription of polygons succession in first iteration contour. These polygons could be in the form from triangle to polygons with $\frac{m}{\xi} \bmod 2^9 \frac{0}{\xi} = 541$ sides. Contour with polygons is represented in Fig. 5 left above, while $(\log r, \log L(r))$ -diagram is represented right above. Points $(\log r_i, \log L(r_i))$ are calculated in apparent way, while lengths r_i are

calculated by formula $r_i = \frac{1}{m} \sum_{j=1}^m r_j$, which represents average value of side length for each polygon. Regression line, obtained by fitting with smallest square method has slope value $\alpha = -0.0607403$, so that $D = 1.06074$. It is recommendable to determine two additional values obtained by separate fitting two disjoint parts of data, which can be obtained by partition of points group $(\log r_i, \log L(r_i))$. In our case there are nine points, so division can be as four plus five points. Separate diagrams are given in Fig. 5-left below. These are two separate lines which fit two data groups by the smallest square method, with slopes which determine two values for fractal dimension $D_1 = 1.03814$ and $D_2 = 1.09381$. Calculated arithmetic average value is $D_s = 1.06598$. The difference between, firstly obtained value $D = 1.06074$ and the other one $D_s = 1.06598$ is

$$DD = |1.06074 - 1.06598| = 0.00523571,$$

which is about 0.5%.

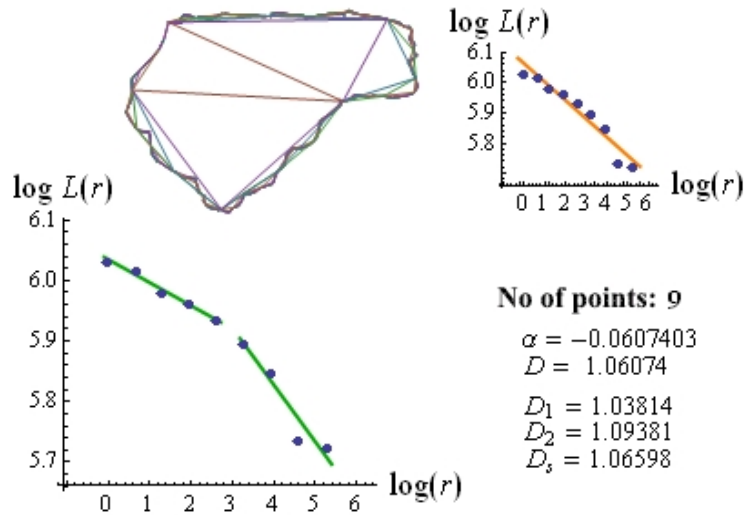


Fig. 5. Richardson method for first iteration of grain z-1 contour.

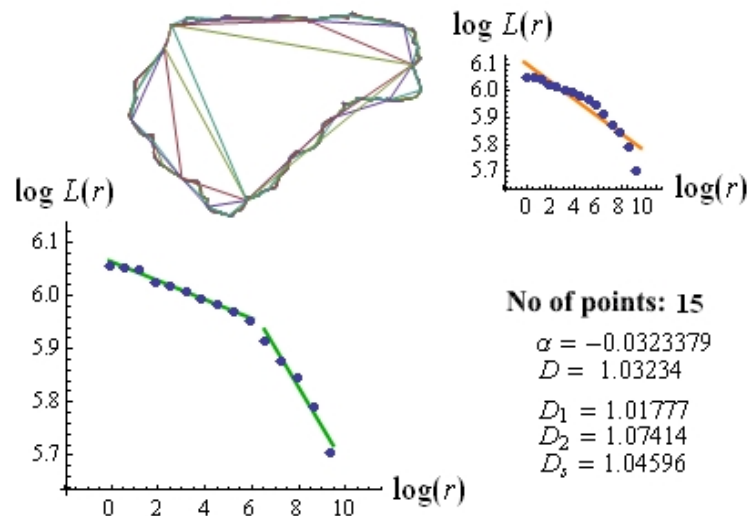


Fig. 6. Richardson method for second iteration of grain z-1 contour.

Grain z-3 contour taken from Fig. 2 is sampled in 53 points (Fig. 7).

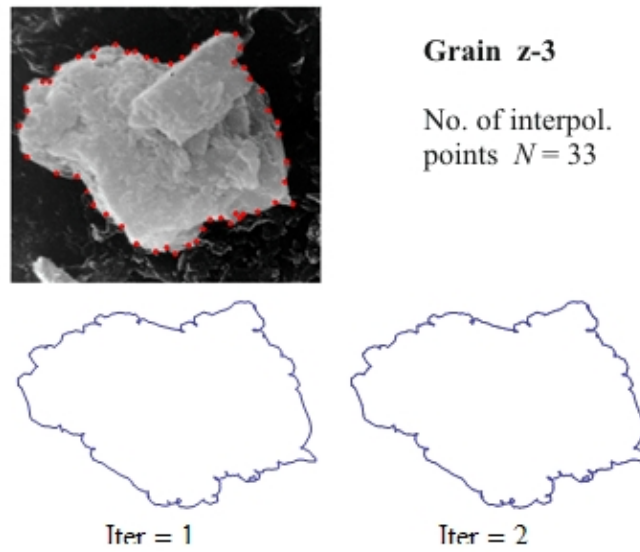


Fig. 7. Sampling of grain z-3 contour.

Parameter interpolation with perpendicular scaling vector $d = [d_1, \dots, d_N]^T$ is applied, with dimension $|d_i| \in [0, 0.04]$. First and second iteration are represented in Fig. 8 and Fig. 9, with calculated fractal dimensions.

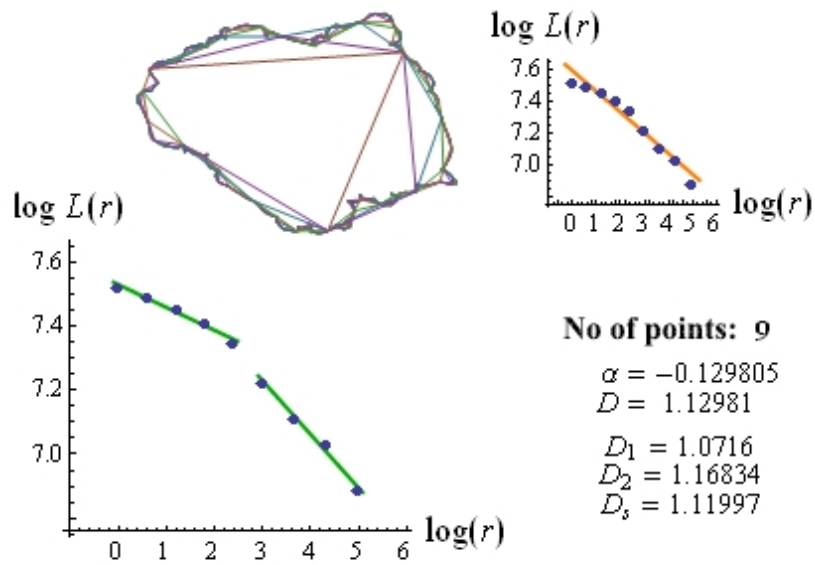


Fig. 8. Richardson method for first iteration of grain z-3 contour.

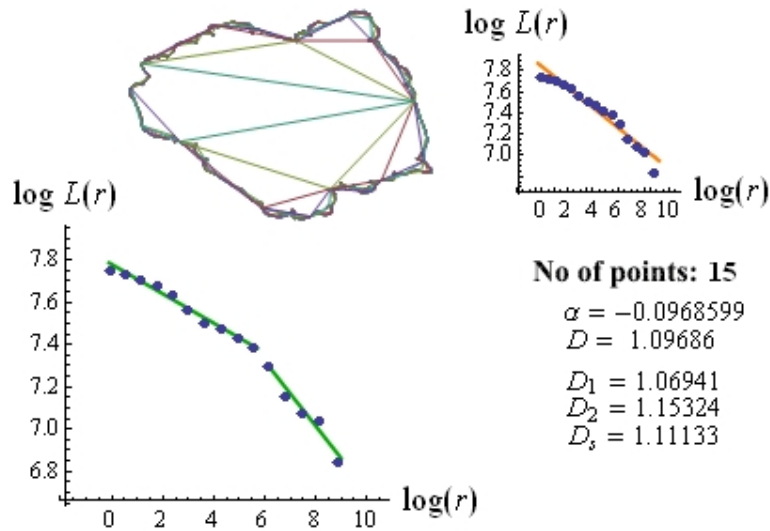


Fig. 9. Richardson method for second iteration of grain z-1 contour.

The same analyses were done for all other grains represented in Fig.2. It could be expected that fractal dimension should have value between 1 and 2, since the grain is represented as object in two-dimensional system.

4. Conclusions

Aluminium-silicate ceramics, modified with magnesium, exhibits very porous amorphous structure, with highly developed surface and significant 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. Microalloying enables forming of nonhomogeneous and cluster nanostructures with pronounced fractal nature.

Very complex intergranular and interphases area is location, where interaction between phases takes place, microporosity is formed and new boundaries and more complex interphases areas are created. Intergranular and interphase areas are responsible for the change of structurally sensitive properties.

Deposited magnesium and aluminium phases (metal, oxide and silicate films) form multiphase solid-solid system which has intergranular area with micromorphology of fractal nature. The more microamorphisation is emanated, fractal nature is more enounced.

Primary porosity, caused by grains fragmentation and intergranular area densification, is decreased by synthesis, microalloying and sintering processes. Grains shape, which is mostly irregular, can affect the porosity of sintered materials. Cognition of grain surface fractal dimension is useful for understanding physical-chemical properties of aluminium-silicate ceramics

Fractals could be used for characterization of surface irregularity parameters and for surface morphology research. Fractal analysis represents a new approach for deeper examination of microstructure of ceramics materials, and further, for the prognosis of materials properties. Grains shape, grains arrangement and contact nature for sintered ceramics materials could be elaborated with fractal analysis. Fractal dimension, as a degree of

complexity, is more expressed if the scale for its measurement is smaller. Fractal dimensions of aluminum-silicate ceramics grains have values between 1 and 2, which was to be expected, since the grain is represented as object in two-dimensional system.

Each point of micro contact of ceramics grains could be presented as electrical parameter-resistivity, capacitance or inductivity [29]. Therefore, fractal method could provide a new approach for describing, predicting and modeling the grains shape and correlations between ceramics microstructure and its electrical properties, as a further phase in research.

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5. References

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Садржај: Порозна алумо-силикатна керамика, модификована легирањем са магнезијумом и микролегирањем са алуминијумом спада у групу свремених мултифункционалних керамичких материјала. Овај вишефазни систем чврсто-чврсто има доминантну аморфну микроструктуру и микроморфологију. Међузрни и међуфазни простори су веома сложени, јер су то области где се одигравају бројни процеси и интеракције, стварајући нове границе и просторе са фракталном природом. Фрактална анализа интергрануларне микроструктуре је обухватила одређивање фракталне димензије керамичког зрна користећи Ричардсонов метод. Разматрајући фракталну природу међузрних контаката могуће је успоставити корелацију између електричних особина и фракталне анализе, као средства за будућу повезаност са микроструктурном карактеризацијом.

Кључне речи: Алуминијум-силикатна керамика, микролегирање, интергрануларни простор, фрактали
