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The Influence of Multifunctional Microalloyed Ceramics Microstructure on Its Capacity Properties

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Abstract: Modified porous alumo-silicate ceramics, alloyed with magnesium and microalloyed with aluminum, belongs to modern multifunctional ceramic materials. Microalloying has led to important changes in dielectric and electrical properties of ceramics, such as dielectric constant and electrical resistance. These changes are conditioned by the microstructural properties of modified porous ceramics. The obtained results have shown the unity of the influence of composition, structure, morphology and application of microalloyed multifunctional alumo-silicate ceramics on electrophysical properties. Microstructural investigations have shown that this type of ceramics has an amorphous-crystal structure, which causes important changes in its electrical properties and affects its activity. Therefore the ceramics can be considered as an active dielectric. A correlation between microstructural properties and structurally sensitive, i.e. electrophysical properties of microalloyed multifunctional alumo-silicate ceramics, was confirmed.

Keywords: Microalloying, Microstructure, Multifunctional Ceramics, Electrical Properties.

1 Introduction

Microalloying is most commonly used procedure in microelectronic technology, especially in thin film technologies, where microalloying is performed by ion implantation, chemical deposition from the gas phase and plasma chemical processes. Lately, microalloying takes a significant place in micro and nanostructured materials, in ceramic nano crystalline powders, metal-ceramics and hybrid composites, as well as nano biomaterials for biosensors, etc. Microalloying, as a well-known modern method of changing semiconductor properties of semiconductor and dielectric materials, is gaining in importance in

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the management of certain structurally sensitive properties of metals, alloys, ceramics and other materials such as electro conductivity, electrode potential, dielectric, magnetic, catalytic and mechanical properties [1 – 5]. Microalloyed and structurally modified multifunctional materials have a remarkable electrochemical and electrophysical activity. The surplus of microalloying and alloying metals, arranged in the form of a thin film along the grain boundaries, as well as a mixture of non-stoichiometric oxides with surplus of magnesium and aluminum, determines the electrical and electrochemical activity of ceramics in contact with water and the external environment. Thus, the oxide mixtures and metallized ceramics areas make the ceramics active. There is a primary modification of the microstructure, induced by synthesis and the sintering process, and secondary, due to the development of numerous physical-chemical interactions in a heterogeneous multiphase system solid-solid and heterogeneous system solid-liquid. Therefore, the changes in electrical conductivity, capacitance, dielectric constant, dielectric losses and impedance are an important indicator that significant primary and secondary changes in the microstructure of the active alumo-silicate microalloyed ceramics have occurred [6 – 12].

Alumo-silicate ceramics modified with magnesium and microalloyed with aluminum has such a microstructure that provides an amorphous-crystalline structure with two electrochemical active metals (Mg and Al) and a modified matrix, with respect to the non-stoichiometric composition of alumo-silicate and magnesium-silicate amorphous and crystalline layers. In terms of this type of ceramics, amorphous metal layers on the matrix are expressed, which provide high porosity, developed surface and non-equipotential surface. Therefore, the inevitable presence of macro and micro galvanic couples plays a crucial role in the spontaneous occurrence of physicochemical and electrochemical processes. Such composite multifunctional material has such a microstructure and morphology that supports changes in many structural-sensitive properties. Due to the presence of dissolved hydrogen in solid state and its molecularization, the entire composite is in a very mechanically stressed state of high potential energy, which can affect the occurrence and significant increase in dislocations and point defects. Thus, due to overcoming the limits of tension in certain areas and matrix grains, dislocations movement and spontaneous fragmentation of macro and micro grains into even smaller sub micro grains and mosaic blocks with fractal nature, can be activated [6 – 12].

The complex multiphase system, such as the active microalloyed multifunctional ceramics, has specific behavior under the influence of an external electric field, resulting in a change in the tangency of dielectric losses and impedance, depending on the frequency, temperature, applied voltage profile (sinusoidal or nonsinusoidal), humidity and other factors. Conduct current through the active dielectric, in this case, is not the same as through the passive dielectric, but it takes place through the dielectric barrier and through the conductive zones of thin metal films of aluminum and magnesium. Similarly, the dielectric constant (ε_r) has nonlinear distribution and complex functional dependencies, due to the pronounced non-homogeneity of the active micro-alloyed ceramics. Such addictions are expected in multiphase non-homogeneous dielectrics, as can be seen from papers in the field of dielectrics physics. Thin metal films and clusters of deposited metals, cause the channel conductivity of dielectric materials [12 – 14].

2 Materials and Methods

According to the basic physical properties of dielectric materials, the active microalloyed ceramic, which can be considered as a multiphase system solid-solid, belongs to a special type of active non-homogeneous dielectrics with multifunctional properties. The active microalloyed ceramics is not an active dielectric such as ferroelectrics, piezoelectrics and electrets etc., which are typical nonlinear dielectrics, but it is not a typical linear dielectric either. It probably possesses some transition properties between linear and non-dielectric dielectrics, and for this reason it is interesting to consider electrophysical properties.

The electrical characterization was done by measuring the electrical resistance using KEITHLEY 2400 SOURCEMETER instrument, whereby the active microalloyed ceramics samples were under voltage of 2V, while the capacitance was measured by the instrument Digital Multimeter DT-9207A. Measurements were performed on samples of active microalloyed ceramics with 2, 4, 6, 8 and 10 wt. % of additive. The dielectric constant results of all samples of microalloyed alumo-silicate ceramics of the primary microstructure, as active dielectric, were obtained based on the dependence of the capacitance on the temperature ($C = f(T)$). It should be expected that the dominant presence of magnesium, its silicates and oxides reduce the influence of microalloyed aluminum and the complete alumo-silicate matrix of microalloyed ceramics. Therefore, it follows that the quantities of magnesium as an additive in microalloyed and alloyed ceramics should not seriously disarrange the relationships in the alumo-silicate matrix, where the presence of alumo-silicate and non-stoichiometric aluminum oxides is dominant.

SEM microphotographs for samples of active microalloyed ceramics with 2, 4, 6, 8 and 10 wt. % of additives, sintered at 900°C, were recorded by a scanning electron microscope JEOL JSM-5300.

3 Results and Discussion

SEM microphotographs (Figs. 1 – 5), show a very complex, nonuniform and extremely porous structure.

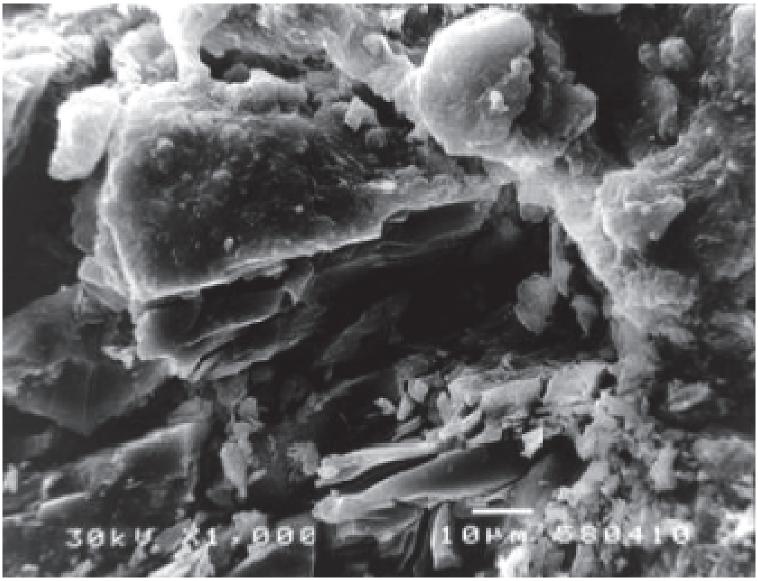

Fig. 1 – *SEM micrograph of sample* $2\cdot10^{-3}$ kg /900ºC.

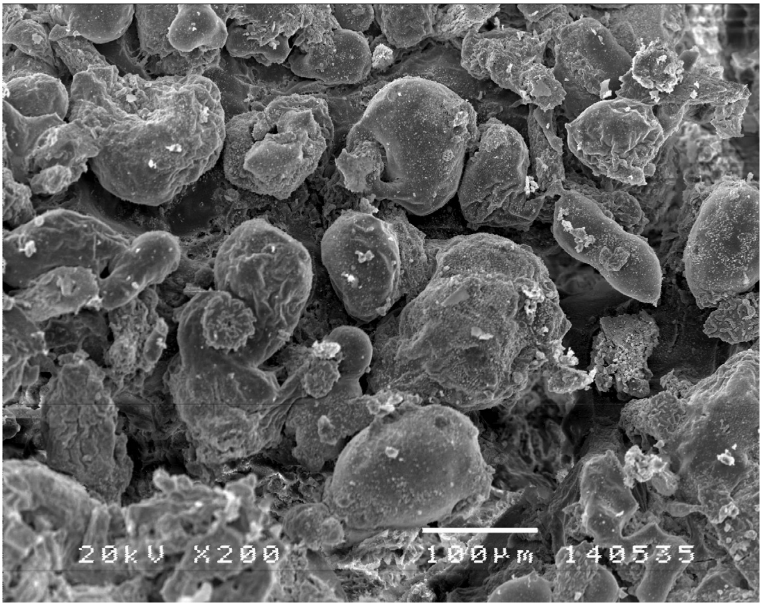

Fig. 2 – *SEM micrograph of sample* $4\cdot10^{-3}$ kg /900ºC.

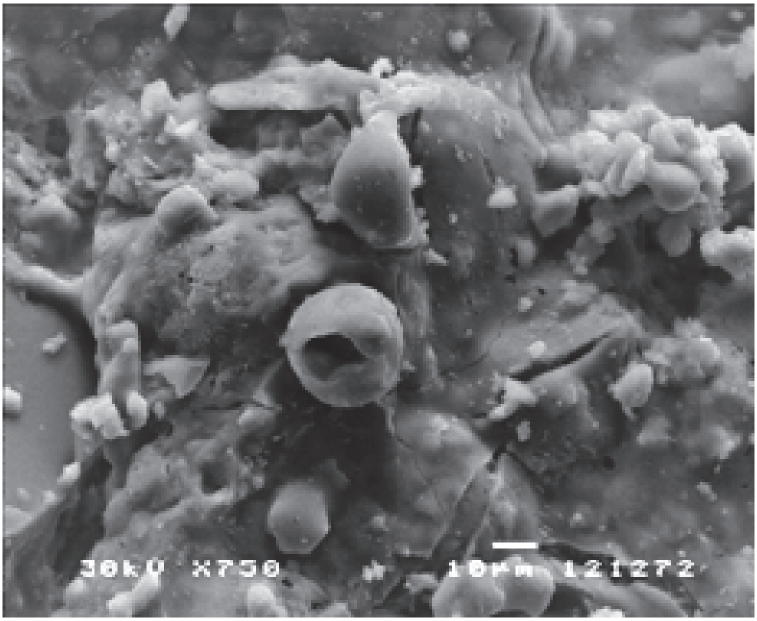

Fig. 3 – *SEM micrograph of sample* $6 \cdot 10^{-3}$ kg /900ºC.

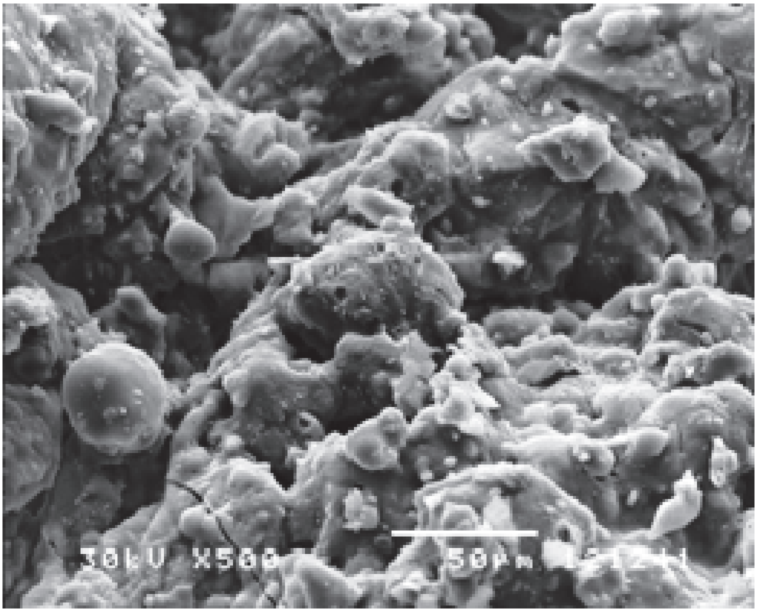

Fig. 4 – *SEM micrograph of sample* $8 \cdot 10^{-3}$ kg /900ºC.

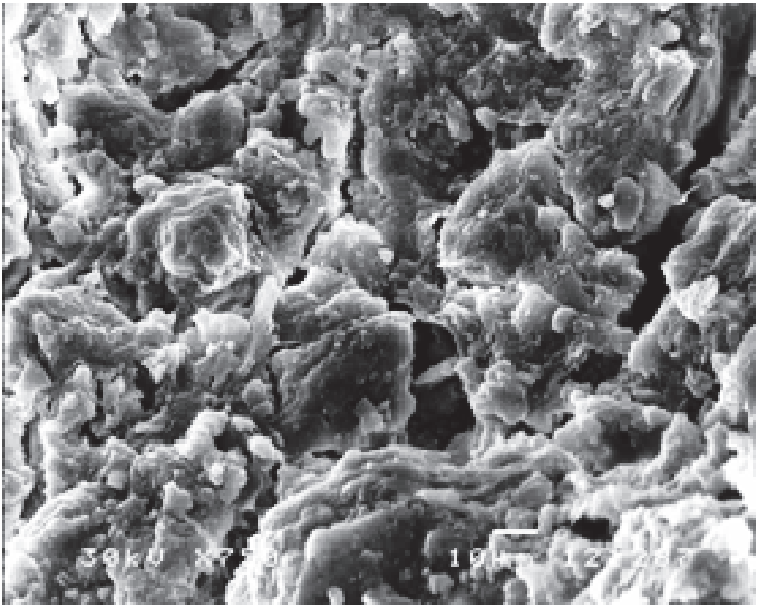

Fig. 5 – *SEM micrograph of sample* $10\cdot10^{-3}$ kg /900ºC.

Nonuniformity is reflected in differences in grain size (1 – 20) μm, porosity and amorphous-crystalline micromorphology. From the microphotography, a layered structure with aggregates in the form of plate particles of different dimensions, originating from montmorillonite, can be observed. In addition to amorphous regions and coarse grain microstructure, pronounced crystalline grains are also present. A layered structure with polygonal grain shapes and some grains with planar surface defects are also present. Generally speaking, active ceramics is characterized by multiphase amorphous crystal structure and morphology, with inevitable non-stoichiometry of certain phases in the complex multiphase microalloyed ceramics system. Most likely the crystalline phases are imprinted in the porous amorphous mass of the alumo-silicate matrix and the microalloying and alloying additives, i.e. crystalline phases are masked by an amorphous phase that surrounds each grain. The existing multiphase, with highly developed crystalline blocks placed in the amorphous silicate matrix, Mg and Al, is reflected in surface textures and complex interphase boundaries. Some areas have a large volume of small leafs formed by layering, which are very close to each other and thus create compact layers of microstructure, while others have leafs with very open pores. Thus, after the modification of the matrix, the fragmentation of crystalline grains, partial occurrence of dendrites with fractal nature and the amorphization of alumo-silicate occur. On the other hand, particles of microalloying and alloying additives are located on the surface of the matrix in the form of clusters of thin micro and nano-metal films, or are present as special phases stacked on an alumo-silicate matrix in the form of silicates or oxides.

The results given in **Table 1** and the diagram in Fig. 6 shows a significant deviation and poorly defined functional dependencies of the dielectric constant on the sintering temperature.

Table 1

Measured values of dielectric constant ε_r *for samples of different composition, sintered at different temperatures.*

	600ºC	**700ºC**	**800ºC**	**900ºC**	**1100ºC**
2 wt%			115.43		
4 wt%	81.93	92.34	66.87	53.25	91.71
6 wt%	85.3	44.74	40.73	39.25	38.98
8 wt%			56.73		
10 wt%	177.24	74.25	46.06	100.95	139.85

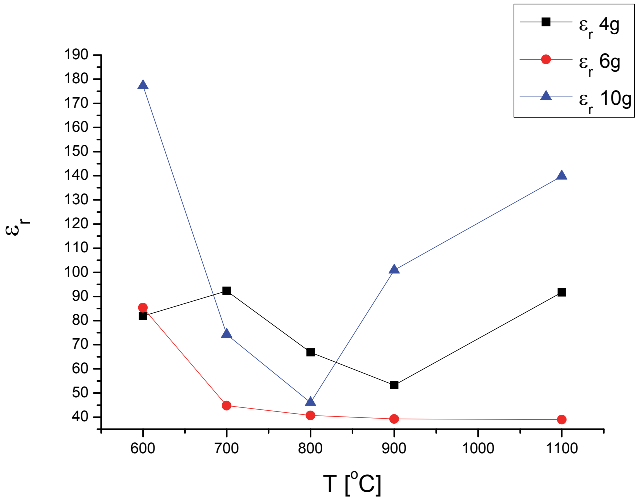

Fig. 6 – *The dependence of the dielectric constant on the sintering temperature.*

A high value of the dielectric constant for the samples sintered at 600ºC is observed, and the minimum dielectric constant for the samples sintered at 800ºC. Also, significant dielectric constant values are observed at the highest sintering temperature of 1100°C.

The dependences of capacitance on temperature for the samples with $6\cdot10^{-3}$ kg of additives at all sintering temperatures were determined. The temperature range is (30 – 150)ºC, with a step of 5ºC. Based on the dependence $C = f(T)$, the dielectric constant was calculated.

Table 2

The results for sample with $6\cdot10^{-3}$ kg *of additive sintered at* 600ºC.

***T* (ºC)**	30	35	40	45	50	55	60	65	70	75	80	85	90
***C* (pF)**	22	22	21	21	20	19	17	15	13	10	9	8	7
***T* (ºC)**	95	100	105	110	115	120	125	130	135	140	145	150	
***C* (pF)**	7	8	6	6	6	9	8	7	7	5	5	4	

Table 3

The results for sample with $6\cdot10^{-3}$ kg *of additive sintered at* 700ºC.

***T* (ºC)**	30	35	40	45	50	55	60	65	70	75	80	85	90
***C* (pF)**	9	8	8	8	7	7	6	6	5	6	6	5	6
***T* (ºC)**	95	100	105	110	115	120	125	130	135	140	145	150	
***C* (pF)**	5	4	5	5	4	5	6	4	5	5	4	6	

Table 4

The results for sample with $6\cdot10^{-3}$ kg *of additive sintered at* 800ºC.

***T* (ºC)**	30	35	40	45	50	55	60	65	70	75	80	85	90
***C* (pF)**	4	4	8	8	7	7	7	6	7	5	7	8	7
***T* (ºC)**	95	100	105	110	115	120	125	130	135	140	145	150	
***C* (pF)**	7	8	7	7	6	7	7	7	8	7	7	6	

Table 5

The results for sample with $6\cdot10^{-3}$ kg *of additive sintered at* 900ºC.

***T* (ºC)**	30	35	40	45	50	55	60	65	70	75	80	85	90
***C* (pF)**	7	7	6	6	5	6	7	6	5	6	7	6	6
***T* (ºC)**	95	100	105	110	115	120	125	130	135	140	145	150	
***C* (pF)**	5	8	6	5	6	5	5	6	5	6	7	6	

Table 6

The results for sample with $6\cdot10^{-3}$ kg *of additive sintered at* 1100ºC.

***T* (ºC)**	30	35	40	45	50	55	60	65	70	75	80	85	90
***C* (pF)**	8	7	6	6	5	5	5	4	5	5	5	4	6
***T* (ºC)**	95	100	105	110	115	120	125	130	135	140	145	150	
***C* (pF)**	5	5	4	4	6	5	5	5	6	6	5	5	

The mean dielectric constant values were obtained:

Sample with $6\cdot10^{-3}$ kg of additives sintered at: 600ºC / $\varepsilon_r = 119.15$, 700ºC / $\varepsilon_r = 58.16$, 800ºC / $\varepsilon_r = 45.74$, 900ºC / $\varepsilon_r = 63.78$, 1100ºC / $\varepsilon_r = 116.94$.

The dielectric constant has a nonlinear distribution. As it can be seen in Fig. 6, the highest values were measured for the highest content of the active additive of $10 \cdot 10^{-3}$ kg at the lowest temperature of 600ºC. For the content of the additive of $6 \cdot 10^{-3}$ kg, the smallest variation is observed, i.e. the dielectric constant values are approximately in the uniform range, or in a slight decrease.

Measurement results of the dielectric constant on the modified porous ceramics of different levels of alloying and at different sintering temperatures, point that the dielectric constant has complex functional dependences, with minimum and maximum values. The high dielectric constant value at the sintering temperature of 600°C is the result of the dominant influence of the dielectric constant of bound water molecules in the form of crystallohydrate or structural water. The lowest value was observed at the sintering temperature of 800ºC, because at that temperature decomposition and traces of the water molecule occurred, at one side, but also alloying and microalloying of the ceramics, without significant phase changes in the transformation of the starting kaolinite-bentonite clay into the corresponding magnesium and aluminum silicate, of stoichiometric and non-stoichiometric compositions. The best results were obtained with modified ceramics with $6 \cdot 10^{-3}$ kg of additives. It seems that this quantity of additives is a critical boundary, above and below which one the dielectric constant is drastically changed.

The obtained results for the specific electrical resistance given in **Table 7** and diagrams in Fig. 7 show that the electrical resistance is the smallest at the lowest sintering temperature of 600°C, for all samples ranging from $2 \cdot 10^{-3}$ kg to $10 \cdot 10^{-3}$ kg of additive and it's in range $(1 - 4 \cdot 10^{6})$ Ωm.

Table 7

Measured values of specific electrical resistance ρ [Ωm]
for samples of different composition, sintered at different temperatures.

	600ºC	**700ºC**	**800ºC**	**900ºC**	**1100ºC**
2 wt%	$1.05 \cdot 10^{6}$	$6.12 \cdot 10^{6}$	$33.93 \cdot 10^{6}$	$8.08 \cdot 10^{6}$	$7.96 \cdot 10^{6}$
4 wt%	$4.33 \cdot 10^{6}$	$12.09 \cdot 10^{6}$	$24.36 \cdot 10^{6}$	$2.35 \cdot 10^{6}$	$12.01 \cdot 10^{6}$
6 wt%	$2.33 \cdot 10^{6}$	$6.23 \cdot 10^{6}$	$10.37 \cdot 10^{6}$	$6.36 \cdot 10^{6}$	$6.45 \cdot 10^{6}$
8 wt%	$4.31 \cdot 10^{6}$	$3.56 \cdot 10^{6}$	$17.21 \cdot 10^{6}$	$3.58 \cdot 10^{6}$	$4.83 \cdot 10^{6}$
10 wt%	$1.12 \cdot 10^{6}$	$8.01 \cdot 10^{6}$	$18.95 \cdot 10^{6}$	$10.02 \cdot 10^{6}$	$5.1 \cdot 10^{6}$

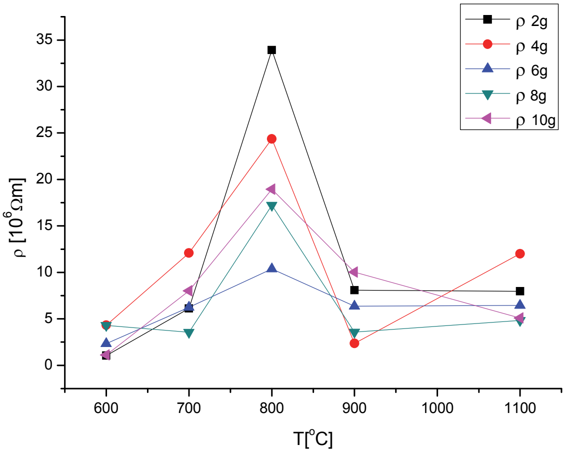

Fig. 7 – *The dependence of specific electrical resistance on the sintering temperature.*

The defined maximum for a sintering temperature of 800ºC is observed at all curved lines, but the maximum values are reduced, so that the minimum value of the maximum is observed for the content of $6\cdot10^{-3}$ kg of additive. The highest resistance value is for the ceramic sample with the addition of $2\cdot10^{-3}$ kg of additive. For samples sintered at temperatures higher than 800ºC, all resistance values are approximately equal.

The specific electrical resistance, shown in Fig. 7, first increases for all quantities of additive up to the temperature 800°C, and then decreases and a sample of $2\cdot10^{-3}$ kg of active additive has the highest measured value.

Since electrical conductivity and resistance are structurally very sensitive properties, as expected, there has been a significant change in resistance. Modified ceramics with different content of additives shows approximately normal distribution of values, minimum values for sintering temperatures between 600ºC and 700ºC to 900ºC and 1100ºC, and pronounced maximum for samples sintered at 800ºC. The reason for this behavior is the presence of mobile ions at sintering temperatures of (600 – 700)ºC, and at temperatures of (900 – 1100)ºC, in addition to the appearance of mobile ions, there is a different redistribution of the present and newly formed phases by recrystallization and finer distribution of phases along the grain boundaries and submicron grains, and their amorphization. The maximum value is related to the phase transformations that followed during the sintering process, by upgrade of magnesium and aluminum silicate structures with surplus of additives for alloying and microalloying. Thus, the immobilization of the mobile ions of sodium and potassium, calcium and metal hydride was caused by decomposition of water at temperatures above 500°C.

4 Conclusion

Micro-activated active ceramics with active additives does not essentially change macromorphology and structure, but the micro-amorphous surface of the crystal grains results in the formation of a thin layer of amorphous metal and silicate magnesium and aluminum films on the surface of the grain. In this heterogeneous ceramics material, there is a direct connection between porosity and structure. The dominance of the amorphous state with fractal nature is interesting, where the natural genetic crystal structure is retained in amorphous matter. Porous ceramics with pronounced structural-sensitive properties and high surface activity, which change with the changes in the microstructure, were obtained. Additionally, the amorphization of the crystalline ceramic structure was observed, and such amorphous-crystalline ceramics drastically changed the structurally sensitive properties. The used microalloying elements have caused drastic structural changes and increased activity of microalloyed ceramics.

The results unambiguously provided the answer to the object and goals of the paper. High surface activity, with surface states of different energy levels, reflected on the measurement results of dielectric constant, resistance, as well as other structurally sensitive properties. Magnesium and aluminum, in effect with other present mixtures, affect observable changes in structurally sensitive properties. Mg and Al surplus during sintering leads to the amorphization of the grain boundary and the effect of metallization of ceramics. Such metallization provides much greater mobility to the present ions and conductivity. Al in the ceramic serves as the main receiver for mobile oxygen ions because it builds the most stable oxides of all metals present. The electrons created on the surface of the ceramics during mutual contact of certain phases, cause the reduction processes, where the electrons are exchanged.

Starting from the multiphase structure, micro and macro morphology, the content of metal films of microalloying and alloying metals, non-stoichiometric silicates and oxides of magnesium and aluminum, this non-homogeneous solid material belongs to a group of non-homogeneous active dielectrics. This is the reason that this modern multifunctional material has complex dielectric and conductive properties, which are the result of pronounced changes in the microstructure and the presence of certain additives and other added ingredients. Microalloying additives and ingredients in this dielectric material cause certain energy levels in dielectric.

It is worth pointing out that the dielectric constant has a nonlinear distribution. Therefore, it has been founded that the dielectric constant has complex functional dependencies, with minimum and maximum values, depending on the level of microalloying and alloying and the sintering temperature. The high dielectric constant value at the sintering temperature 600°C is the result of the dominant influence of the dielectric constant of bound water molecules in the form of crystallohydrate or structural water. On the other hand, the maximum value is related to the phase transformations that followed during the sintering process, by the upgrade of magnesium and aluminum silicate structures with surplus of additives for alloying and microalloying. Under those conditions, immobilization of Na, K, Ca and metal hydride occurs by water decomposing at temperatures above 500°C.

Therefore, microalloying has led to significant changes in dielectric and electrical properties of ceramics, such as dielectric constant and specific electrical resistance. Those changes are conditioned by the microstructural properties of modified porous ceramics. The obtained results showed the unity of the influence of composition, structure, morphology and the application of microalloyed multifunctional alumo-silicate ceramics on its electrophysical properties.

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