Image Anal Stereol 2001;20:231-237
Original Research Paper

THE APPLICATION OF STEREOLOGY METHOD FOR ESTIMATING THE NUMBER OF 3D $BaTiO_3$ – CERAMIC GRAINS CONTACT SURFACES

VOJISLAV V MITIĆ[1,4], ZORAN S NIKOLIĆ[1], IVONA MITROVIĆ[1], BRANKA JORDOVIĆ[2] AND VLADIMIR BRANKOV[3]

[1]Faculty of Electronic Engineering, University of Niš, Beogradska 14, 18000 Niš, Yugoslavia, [2]Technical Faculty - Čačak, Sv. Save 65, 32000 Čačak, Yugoslavia, [3]Faculty of Philosophy, University of Niš, B. Krsmanovića bb, 18000 Niš, Yugoslavia, [4]Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Yugoslavia
(Accepted November 6, 2001)

ABSTRACT

Methods of stereological study are of great importance for structural research of electronic ceramic materials including $BaTiO_3$-ceramic materials. The broad application of ceramics, based on barium-titanate, in advanced electronics nowadays demands a constant research of its structure, that through the correlation structure-properties, a fundamental in the basic materials properties prognosis triad (technology-structure-properties), leads to further prognosis and properties design of these ceramics. Microstructure properties of $BaTiO_3$-ceramic material, expressed in grains' boundary contact, are of basic importance for electric properties of this material, particularly the capacity. In this paper, a significant step towards establishing control under capacitive properties of $BaTiO_3$-ceramics is being done by estimating the number of grains contact surfaces. Defining an efficient stereology method for estimating the number of $BaTiO_3$-ceramic grains contact surfaces, we have started from a mathematical model of mutual grains distribution in the prescribed volume of $BaTiO_3$-ceramic sample. Since the real microstructure morphology of $BaTiO_3$-ceramics is in some way disordered, spherical shaped grains, using computer-modelling methods, are approximated by polyhedra with a great number of small convex polygons. By dividing the volume of $BaTiO_3$-ceramic sample with the definite number of parallel planes, according to a given pace, into the intersection plane a certain number of grains contact surfaces are identified. According to quantitative estimation of 2D stereological parameters the modelled 3D internal microstructure is obtained. Experiments were made by using the scanning electronic microscopy (SEM) method with the ceramic samples prepared under pressing pressures up to 150 MPa and sintering temperature up to 1370°C while the obtained microphotographs were used as a base of confirming the validity of presented stereology method. This paper, by applying computer stereology method for estimating the number of grains contact surfaces, makes possible a further insight into the microstructure of $BaTiO_3$-ceramics with the final aim to design new properties of electronic materials based on barium - titanate ceramics.

Keywords: $BaTiO_3$-ceramics, computer stereology method, number of contact surfaces.

INTRODUCTION

Several thousands of devices and components in electronics today use electrical properties of $BaTiO_3$-ceramics. $BaTiO_3$-ceramics is one of the most important electronic ceramics for manufacturing small and multilayer capacitors of high capacity. It can be shown that the dielectric constant strictly depends on the size of grains and pores in the ferroelectric state, i.e. if the grain is smaller, the greater value of dielectric constant is achieved (Daniels *et al*., 1978; Kuwabara *et al*., 1995). The necessary step in designing $BaTiO_3$-ceramics is the research of its microstructure properties in the function of consolidation parameters (starting pressing pressure, sintering temperature and time). Structure research based on the application of basic methods of stereology technique provides better understanding of dielectric properties, especially in the sense of change the capacity of pure and doped $BaTiO_3$-ceramics. These properties show the importance of region near the grain boundary and in the grain contact. This is the reason for the great importance in modelling grain geometry, grain boundary surface and geometry of grain contacts. The stereology method which will be used for calculating the contact surfaces number in this paper demands an assumption of the model of $BaTiO_3$-ceramic grain structure by corresponding geometrical structure model for which a special

mathematical model is developed. By analyzing the grain distribution in the function of pressing pressure, and on the basis of the empirical density function, the grain size distribution density function of log-normal type is constructed. According to this distribution, the distribution of grains' radii inside the three-dimensional modelled $BaTiO_3$-ceramic sample is done. It is supposed that the grains are sphere-shaped at the beginning of iterative process, which simulates the beginning of consolidation, while later spherical grains deform with creating contacts in the process of materials densification. By the intercept plane method according to the given pace, in the intersection plane of specimen modelled microstructure, a certain number of contacts is identified. Calculation of the contact surface number on the level of the entire $BaTiO_3$-sample is a necessary step for establishing an effective procedure for calculating the integral contact surface of $BaTiO_3$-ceramic sample according to the fact that this surface directly determines the capacity.

MATERIALS AND METHODS

As the basic powder for the experimental research it is used the pure $BaTiO_3$. The blend of $BaTiO_3$ starting powder is mixed in the water suspension with connective device. Then, the homogenization is carried out, and after that the dehydration by dispersing method. Granulation and process control preceded the sample pressing. Sample pressing was done on hydraulic press JAPAN-KYOTO MURATA B1 of 37 tons with the possibility of the minimum working pressure of about 3 MPa, where there was a possibility of changing pressures from 86 to 150 MPa. After the repeated process control and preparation of samples, sintering of samples is done. Sintering was carried out in the electric tunnel furnace type "CT-10 MURATA" at the temperatures of 1190-1370°C for 2 hours. Powder morphology, as well as microstructure morphology of pressed and sintered $BaTiO_3$-ceramics were observed by the method of scanning electronic microscopy (electronic microscope type JEOL-JSM-T20, magnification of 35000 times, resolution of 4.5 nm).

In Fig. 1a and b, SEM microphotographs of pressed and sintered $BaTiO_3$-samples are presented, respectively, and conditions of consolidation were as follows: p = 86-150 MPa, T_{sint} = 1370°C and τ_{sint} = 2h (×7500).

On SEM micrographs of pressed samples (Fig. 1a), it can be seen that pressed samples are created by uniform particles, mostly sphere-shaped, of the size 1-3 μm; obviously, during the pressing, the powder deaglomerization was happened, because the starting powder consisted of agglomerates of 10-120 μm, too. During the research of sintered $BaTiO_3$ without additives (Fig. 1b), grain size distribution showed that it was about an abnormal grain growth. Grain size is in the range of 10-50 μm, and by increasing the pressing pressure; the uniformity of grain size increases too. By further analysis of microstructures, it can be concluded that the grain size increases till the pressure of 105 MPa, and after that it remains constant. This pressure represents the critical value of pressing pressure of pure $BaTiO_3$ above which it does not influence the grain size during the sintering in given conditions.

Let $\{l_1, l_2, ..., l_n\}$ be the set of measured grain size values (the sample), and let (C_{i-1}, C_i) $(i = 1,2,...,m)$ be the cells of equal length, where C_o and C_m are near to the smallest and largest sample elements l_1 and l_n, respectively. Now, if f_i are the cell frequencies, the number of values l_i inside cell (C_{i-1}, C_i), then the empirical density function $f_n(l)$ can be defined as $f_{ri}/(C_i - C_{i-1})$ on the i-th cell (Sarkadi *et al.*, 1974), *i.e.*,

$$f_n(l) = \begin{cases} 0 & l < C_o \\ \dfrac{f_{ri}}{C_i - C_{i-1}} & C_{i-1} \le l < C_i, \quad i = 1,2,...,m \\ 0 & l \ge C_m \end{cases}, \quad (1)$$

where f_{ri} $(\equiv f_i/n)$ denotes the relative frequency of the i-th cell. It can be seen that

$$\int_{-\infty}^{\infty} f_n(l) \cdot dl = \sum_{i=1}^{m} \frac{f_{ri}}{C_i - C_{i-1}} \cdot (C_i - C_{i-1}) = \sum_{i=1}^{m} f_{ri} = 1.$$

For the analysis of grain size distribution as a function of pressing pressure, the intercept method of measuring (Mitić *et al.*, 1995; 1997) has been used, where samples grain size range was 0-3 μm. Grouping of the sample data was done by 0.2 μm length of cell. For description of the empirical density Eq. 1 we will use log-normal distribution in which the logarithm of the grain size will be normally distributed (Jensen, 1995), *i.e.*,

$$f(l) = \frac{1}{\sigma \cdot l\sqrt{2\pi}} \cdot e^{-\frac{(\ln l - \ln \bar{l})^2}{2 \cdot \sigma^2}}, \quad (2)$$

where σ is dispersion of the log-normal distribution and $\bar{l}$ is an average grain size. The values of parameters σ and $\bar{l}$ obtained by fitting the Eq. 2, are given in Table 1. As it can be seen, by approximately

same values of dispersion σ, the average grain size depends directly on the pressing pressure. These results are the basis for establishing 3D mathematical model of the $BaTiO_3$-ceramic sample microstructure as the basis for stereological calculation of the contact surfaces number.

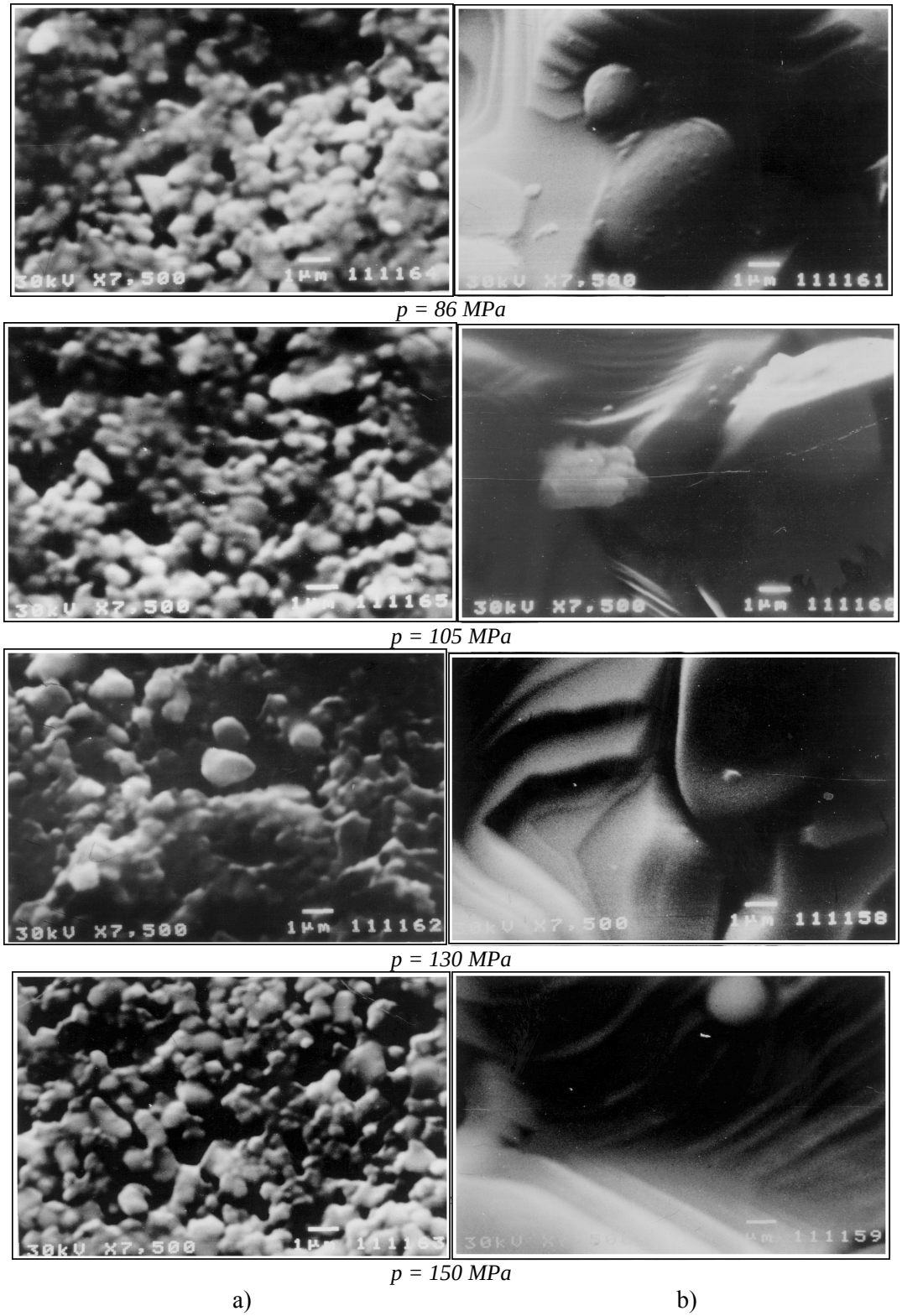


Fig. 1. *SEM microphotographs of $BaTiO_3$-ceramic samples: a) pressed samples; b) sintered samples (T_{sint} = 1370°C, τ_{sint} = 2h) (×7500).*

Table 1. *Calculated values of grain size $\bar{l}$ and dispersion σ as a function of pressing pressure.*

Pressing pressure [MPa]	$\bar{l}$ [μm]	σ
86	0.73	0.46
105	0.65	0.43
130	0.54	0.41
150	0.50	0.39

$BaTiO_3$-ceramic sample is presented by the cube in which grains of approximated system are distributed. Lateral sides of the cube are connected, i.e. the cube is modelled in such way that a part of grain, which "sticks out" of one of lateral sides of the cube, goes into the opposite lateral side. The problem of system anomalies on the edge of the cube is eliminated in this way. Grains are approximated by spheres which radii distribution inside 3D-modelled sample is done according to the Eq. 2. In the first phase of consolidation process, grains contact each other only in one point, or they do not contact at all, so the porosity percentage is high. In further consolidation process, the contact surfaces are being formed, densification and the shrinkage of the specimen are happened, so the percentage of porosity decreases. Starting from the assumption that the grains' penetration depth does not exceed the value of 10-15% of the grain size (Mitić *et al*., 1994; 1995), the grain system is condensed according to the iterative procedure being constructed. Spherical grains are, at the beginning, distributed randomly. After defining forms of initial and final stage of the system, the transfer function is constructed. Essentially, this function is an iterative procedure and it makes arrangement of grains inside the cube. Each two spherical grains gravitate to the mutual position that have the penetration coefficient less or equal to 0.92% of grain's radius being an assumption of the entire model. The accuracy of the iterative procedure is high confirmed by the fact that after 200 iterations the system is in approximately stable state. In Fig. 2 the model of three sphere-shaped grains is presented: a. grains contact only in one point and b. penetrate each other to a certain degree. Essentially, these spheres are polyhedra with great number of small convex polygons N, thus when $N \to \infty$ polyhedral grain becomes a spherical grain. In presented model, this number was 1,000,000, so originally polyhedral grains became spherical and further treated as a spherical. Structural motive of three grains repeats through the whole cubic sample volume and the grains of different radii are contacted. Using the fundamental methods of stereology technique, cutting of modelled 3D sample by parallel planes is done, and on these planes the developed program for the grain contact identification calculates their number.

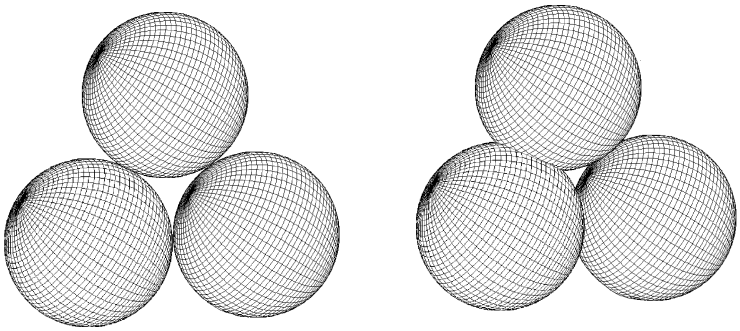
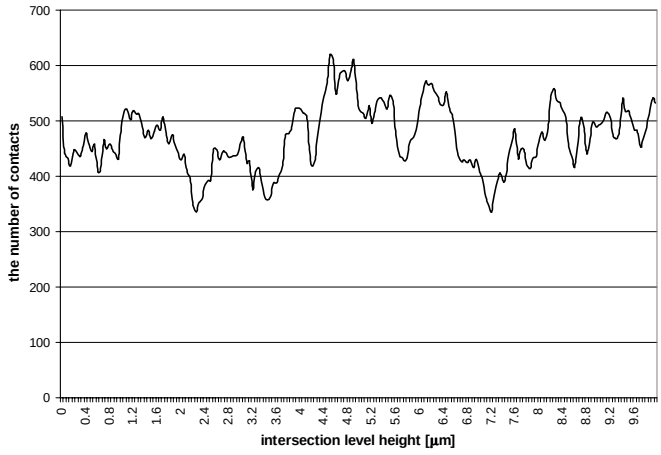


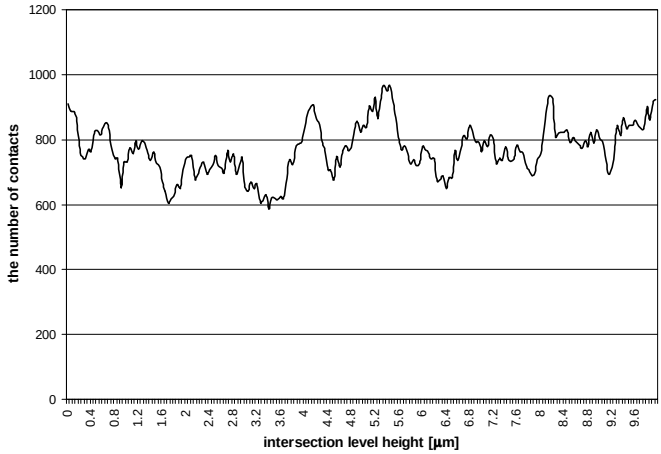
Fig. 2. *A structural pattern of three sphere-shaped ceramic grains: contacting only in one point (left) and making contacts (right).*

RESULTS AND DISCUSSION

According to the described method for calculating the contact surfaces number, 3D model of $BaTiO_3$-ceramic sample internal microstructure pressed under the pressure of 105 MPa is developed (Fig. 1a). For this case, parameters of the distribution density function in the Eq. 2 are as follows: $\overline{l} = 0.65$ μm and $\sigma = 0.43$ (Table 1). The sample is presented by the 3D cube of 10 μm × 10 μm × 10 μm. According to the given radii distribution, the putting of spherical grains inside the cube is done. Two cases are tested: 1) the case when 500 grains in the modelled sample exist and 2) 700 grains. The last one corresponds to the situation of grains' high compactness (the porosity percentage is smaller). The 3D modelled sample is, in both cases, cut by planes, and the minimum distance between neighboring planes was $z = 0.05$ μm. Results of calculating the numbers of contacts through the intersection planes for the system of $BaTiO_3$-ceramic sample of 500 and 700 grains are presented in Figs. 3a and b, respectively. As it can be seen, *x*-axis presents intersection level height of the cube (range 0 to 10 μm) and *y*-axis shows the number of contacts at each intersection level. In this way, the developed model gives the distribution of grain contacts through the sample volume. For the system of 500 grains, the biggest number of contacts is calculated for the intersection level height of 4.9 μm, so at the middle of the modelled sample the biggest number of contacts is concentrated. The similar situation is valid for the system of 700 grains, although this number is shifted towards intersection level of about 5.6 μm height. Also, in Figs. 4a and b are shown looks of intersection planes (intersection level height of 2 μm) for the system of 500 and 700 grains, respectively, generated by the program for grains contact identification. This program is developed in the program package Borland C++.

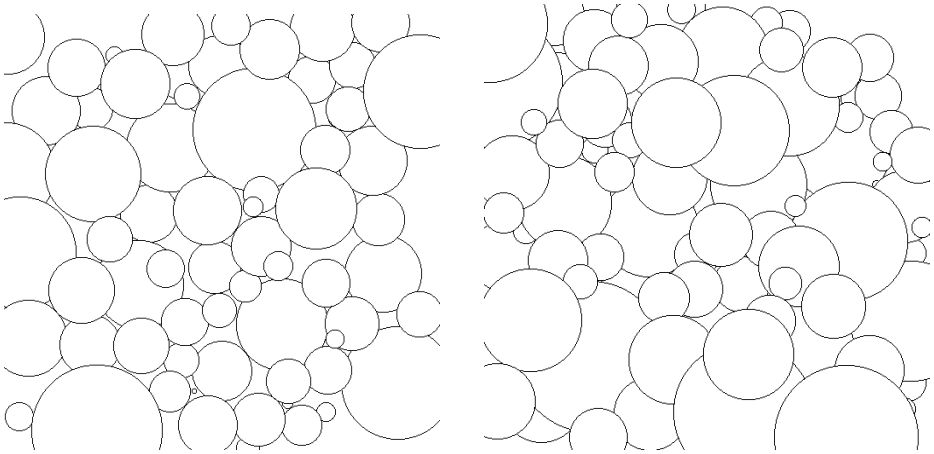


a)



b)

Fig 3. *Generated curves for the contact surfaces number through the intersection planes of the $BaTiO_3$-ceramic sample system with: a) 500 grains and b) 700 grains.*



a) b)

Fig. 4. *A look of intersection levels for z = 2 μm in modelled $BaTiO_3$-ceramic sample structure with: a) 500 and b) 700 grains.*

It should be emphasized that all calculated values are valid for the assumed microstructure model of pressed $BaTiO_3$-ceramic sample. It is valid for the assigned assumptions of the grain shape, grain size distribution and grain center distribution in the modelled sample. Fig. 1a show the deviation of grain shape from spherical one, and give the information of contact distribution in 2D plane. The true reconstruction of this microstructure in 3D plane by the model demands the knowledge of grain contact parameters by 2D microphotographs made in more different planes of the unique sample. According to this, further experimental research aim to this direction, will influence further developments and improvement of the presented model, with the aim to show more truly the real geometry of $BaTiO_3$-ceramic sample microstructure which essentially defines dielectric properties of this ceramics. Further research is in progress.

CONCLUSION

Modern methods of stereology technique in the area of microstructure research of $BaTiO_3$-ceramic materials demand the development of special mathematical models, which simulate the microstructure (grain shapes and contacts), in the given 3D-sample volume. Presented stereology method enables the calculation of numbers of $BaTiO_3$-ceramic grains contact surfaces in 3D making the basis for calculating the integral contact surface, important in the prognosis of dielectric properties of this ceramics. The experimental base of method consists of results obtained by the stereological method for determination the grain size values and the method of scanning electronic microscopy. By the control of shapes and numbers of contact surfaces on the level of the entire $BaTiO_3$-ceramic sample, the control over structural properties of this ceramics is made, with the aim of correlation between material electronic properties and corresponding microstructure.

ACKNOWLEDGEMENT

This research has been supported by the projects: "Prognosis of material characteristics" financed by the Ministry of Science and Technology of Republic of Serbia and "Physical chemistry processes of technology of modern materials" financed by Serbian Academy of Sciences and Arts.

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