

UDK: 546.824; 622.785

Fractal Corrections of BaTiO₃-ceramic Sintering Parameters

V. V.Mitić^{1,2}, Lj. Kocić^{1*}, V. Paunović¹, V. Pavlović^{2,3}

¹University of Niš, Faculty of Electronic Engineering, Aleksandra Medvedeva 14, Niš, Serbia

²Institute of Technical Sciences of SASA, Belgrade, Serbia

³University of Belgrade, Faculty of Agriculture, Belgrade, Serbia

Abstract:

Morphology of ceramics grains and pores as well as Brownian character of particle dynamics inside ceramics specimen contributes to better understanding of the sintering process. BaTiO₃-ceramics, studied in this paper, has light fractal form and it is emanated in three aspects. First, the surface of grains, even in starting green body as well as distribution of grains shows fractal behavior. Second, existence of pores and their distribution follow the rules of fractal geometry. Third, movement of particles inside viscous flow underlies the rule of Brownian motion, which is essentially a fractal category. These three elements, each in its domain influence sintering dynamics, and can be described by dimensionless quantitative factors α_S , α_P and α_M , being normalized to the interval [0,1]. Following sintering process, the associate formulae of Frenkel, Scherer and Mackenzie-Shuttleworth are shown from the angle of view of ceramics fractal dimension changing that approaches to 3. Also, it is shown that the energy balance is not violated after applying fractal correction to quasi equilibrium of the energy emanating from surface area reduction E_S and energy adopted by viscous flow E_f .

Keywords: BaTiO₃, Microstructure, Sintering, Fractal parameters

1. Introduction

The ceramics materials sintering process is characterized by an exceptional complexity, as a result of simultaneous and successive influence of elementary transport mechanisms which can not be, or can hardly be experimentally followed, and qualitatively and quantitatively described. In that case, the modeling simulation application presents a possible method of investigation. Generally speaking, defining model, as a research method, means the introduction of some assumptions and simplifications, and because of that, they represent only the approximation of real systems and processes. However, in the first stages of investigation, the model application is necessary to be justified, because it makes possible the most probable ways subset formation from sets, possible for discovering process laws and for formulating the process theory in the very physical base.

Ceramics grains contacts are essential for understanding complex sintered materials electrodynamic properties [1]. Microstructures of sintered BaTiO₃-ceramics observed by

*) Corresponding author: Ljubisa.Kocic@elfak.ni.ac.rs

SEM method are characteristic examples of a complex shape geometry which is not easy to, neither describe, nor model. A possible approach for describing contact phenomena is establishing the grains contact models. Detailed BaTiO₃-ceramics intergranular contacts research shows that they determine majority of electrical properties of the entire sample [2,3].

The process investigation on BaTiO₃-ceramics electronic materials the boundary and in the contacts two or more grains is possible. This paper supports the second mentioned access with respect to the basic physics of processes happening on the boundary and in the contact of two grains.

2. Experimental procedure

In this paper, doped BaTiO₃-ceramics were used for microstructure characterization, and modeling. The samples were prepared from high purity (>99.98%) commercial BaTiO₃ powder (MURATA) with [Ba]/[Ti]=1,005 by conventional solid state sintering procedure. Starting powders were ball-milled in ethyl alcohol for 24 hours. After drying at 200°C for several hours, the powders were pressed into disk of 7mm in diameter and 3mm in thickness under 120 MPa. The compacts were sintered at 1320°C in air for two hours. The microstructures of sintered and chemically etched samples were observed by scanning electron microscope (JEOL-JSM 5300) equipped with energy dispersive spectrometer (EDS- - QX 2000S).

3. The Stages of Sintering

It is well known that the process of BaTiO₃-ceramics the liquid (viscous) phase densification is dominant [4] over solid-state sintering. Viscous sintering constitutes of three phases.

The sintering first or initial stage corresponds to the situation when necks are forming and growing between particles. At the end of this stage, the contact area increases by approximately 1/5 due to inter-particle penetration mechanism (Fig. 1). Consequently, the compact densification is very low, only a few percent. Some decrease in the specific surface area of the compact occurs due to the surface fractal dimension lowering. Caused by the tensile stresses, the surface tension makes grain boundaries between the particles to remain in the contact plane.

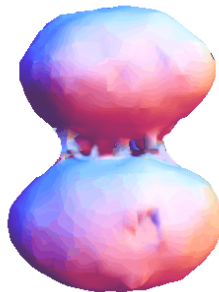


Fig. 1. Neck forming in the first stage of sintering. A computer simulation of Coble model that takes account of fractal geometry of surface of BaTiO₃ grains

The second, intermediate sintering stage is characterized by porosity increasing and by presence a more or less pore channels continuous network, along the grain resulting in a “sponge” structure (Fig. 2) having Hausdorff fractal dimension $2 < H_f < 3$. During this

stage, the pore channel shrinks and grains grow which makes H_f to increase. The reason lies in the fact that surface area increases inside the constant volume. This process contributes to higher densification.

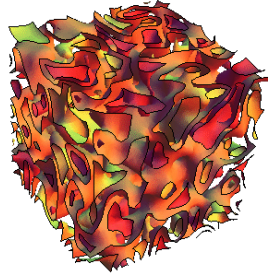


Fig. 2. Increasing porosity of sintered material in the intermediate phase increases fractal dimension due to increasing surface area.

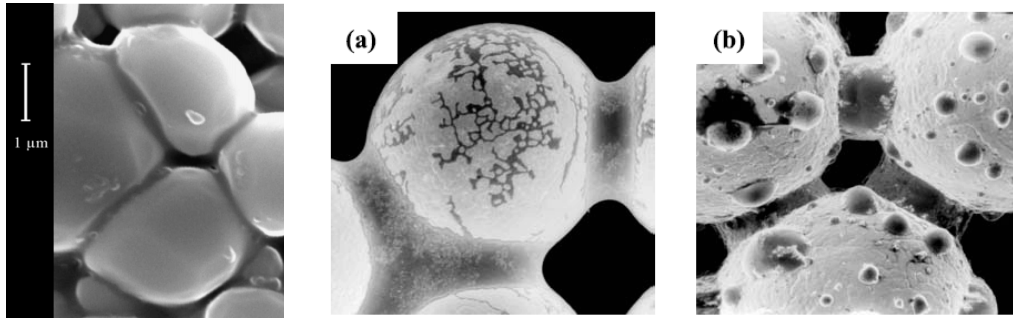


Fig. 3. Left. Microphotograph of pores BaTiO₃ ceramics sintered at 1320°C in viscous sintering processes; Right. a) and b) are examples in [13].

The pore “space” continues to shrink until it collapses to the point set of isolated pores (Fig. 3). This marks the beginning of the third or the final densification stage. In this stage, the pore volume fraction asymptotically approaches zero or $H_f \approx 3$.

Thermodynamically, the change in free energy can be written as

$$\delta G = \delta \int \gamma_{SV} dA_{SV} + \delta \int \gamma_{SS} dA_{SS} \tag{1}$$

where δG is the sintering system free energy change, γ_{SV} is the the solid – vapor interface energy per unit area, and γ_{SS} is the solid – solid interface energy/area. In this equation, during sintering, the first term is negative, since the area of the solid – vapor interface (A_{SV}) decreases. Considering that, grain growth, implies the solid – solid interface decrease, the second term may be either positive or negative; since grain boundary area (A_{SS}) may increase or decrease depending on how fast grain growth is going on. If grain growth does not occur, the second term is always positive as grain contacts grow during the sintering. As long as δG is negative, a driving force, for sintering, exists. [5]

4. Viscous sintering

The viscous sintering kinetics is driven by quasi equilibrium emanating energy from surface area reduction E_s and energy adopted by viscous flow E_f

$$\dot{E}_s + \dot{E}_f = 0 \tag{2}$$

where the over-dots denote changing rate (i.e. $\dot{E} = \frac{d}{dt} E(t)$ and this notation will be used in the sequel). This balance has also been considered by Scherer and Mackenzie and Shuttleworth [6, 7]

Frenkel analyzed the viscous sintering initial stage kinetics and developed the following relationship for the spheres sintering by viscous flow [8]

$$\beta^2 = \frac{3\gamma t}{2\pi\eta R},$$

where β is one half of the central angle in Cobble model [10] of spherical grains with radius R , η is the viscosity and γ represents the surface energy. The new model of Cobble neck formation, based on polyhedral and ellipsoid smooth geometry was developed in [11, 12]. This formula was the first fractal reduction subject, as it is discussed in [9].

Fractality of BaTiO₃ (and similar) -ceramics appears in the sintering process very early stage, even in green body stage. Namely, due to Stöber method [4], the BaTiO₃ monodisperse particles substructure shows fractal morphology.

So, fractality exists during all sintering phases. Exploring the box counting methods and variable measure unit length Richardson method as well as log-log diagrams [9,10] a typical BaTiO₃ grain contour, with Hausdorff fractal dimension being estimated to $H_f=1.16596$. Further measurements and calculations by different models yield, that the fractal dimension of BaTiO₃-sintered ceramics grains, should fall into the range $2.010 \leq H_f \leq 2.085$.

The sintered bulk fractal dimension is changing, although, in a tiny range. For ex., consider an isolated pore being filled by viscous material schematically shown in Fig. 4.

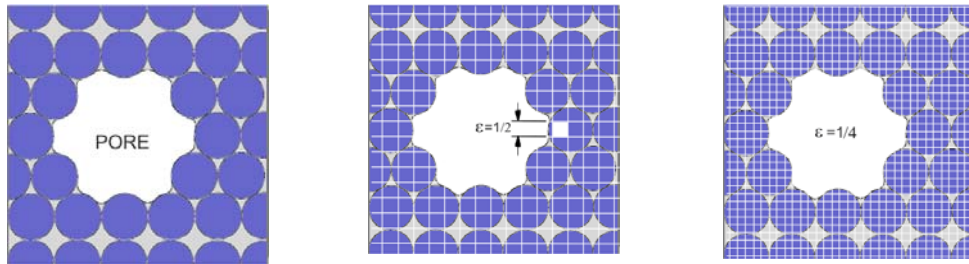


Fig. 4. Fractal dimension of porous material.

Using the box counting method, let $N(\varepsilon, t)$ be the boxes number, which cover sintered specimen solid matter (emptiness does not count) after time t . The dynamic fractal dimension function would be then

$$H_f(t) = \lim_{\varepsilon \rightarrow 0} \frac{\ln N(\varepsilon, t)}{\ln(1/\varepsilon)}, \quad (3)$$

which, after taking regular subdivision usual setting of $\varepsilon = 1/2^n$, turns into

$$H_f(t) = \lim_{n \rightarrow \infty} \frac{\ln N(2^{-n}, t)}{\ln(2^n)}.$$

Since $N(\varepsilon, t)$ is growing with t , while pores went smaller and smaller, there is a strong argument to believe that $D_f(t)$ will approach to 3, which is bulk's topological dimension. It has its justification in well-known densification and coarsening process. Note that, pores decrease, as much as, the elasticity module permits it.

Indeed, if using definition formula (3), it follows that

$$\frac{d}{dt}N(\varepsilon, t) = \frac{1}{\varepsilon^3} \frac{dV(t)}{dt} \Rightarrow N(\varepsilon, t) = N_0(\varepsilon) + \frac{1}{\varepsilon^3} \Delta V(t)$$

which results in

$$H_f(t) = \lim_{\varepsilon \rightarrow 0} \frac{\ln\left(N_0(\varepsilon) + \frac{1}{\varepsilon^3} \Delta V(t)\right)}{\ln(1/\varepsilon)} \tag{4}$$

Using the known three sintering formulae phase described above, formula (4) can be refined. Namely, for the sintering initial phase, the Frenkel formula takes place [8]

$$\frac{dV}{dt} = -3\pi \frac{\sigma}{\eta} \left(R_0 - \frac{4}{3} \frac{\sigma}{\eta} t\right)^2, \tag{5}$$

where σ is crystal lattice constant, η is the material viscosity, R_0 stands for initial pore radius, n is the pores number per unit volume, ρ is the normalized density (normalized by the theoretical density).

The intermediate state is characterized by Scherer formula [6]

$$\frac{dV}{dt} = -\frac{4\pi}{3} \left(\frac{\gamma n^{1/3}}{\eta}\right) \frac{(\pi - 4\sqrt{2}R_0) R_0^{8/3}}{(3\pi - 8\sqrt{2}R_0)^{2/3}}, \tag{6}$$

where γ represents the surface energy. Finally, Mackenzie-Shuttleworth [7] (MS) formula describes the final stage

$$\frac{dV}{dt} = -\frac{1}{2} \left(\frac{4\pi}{3}\right)^{4/3} \left(\frac{\gamma n^{1/3}}{\eta}\right) \left(\frac{1}{\rho} - 1\right)^{2/3} R_0^3. \tag{7}$$

By applying formula (4) to (5), (6) and (7) brings more refined expressions for fractal dimension estimation in each of sintering phases, separately,

$$H_f(t) = \lim_{\varepsilon \rightarrow 0} \frac{\ln\left(N_0(\varepsilon) - \frac{3\pi}{4\varepsilon^3} \left(R_0 - \frac{4}{3} \frac{\sigma}{\eta} t\right)^3\right)}{\ln(1/\varepsilon)}, \text{ (for initial phase),} \tag{8}$$

$$H_f(t) = \lim_{\varepsilon \rightarrow 0} \frac{\ln\left(N_0(\varepsilon) - \frac{4\pi t}{3\varepsilon^3} \left(\frac{\gamma n^{1/3}}{\eta}\right) \frac{(\pi - 4\sqrt{2}R_0) R_0^{-2/3} R(t)}{(3\pi - 8\sqrt{2}R_0)^{2/3}}\right)}{\ln(1/\varepsilon)}, \text{ (for intermediate phase),} \tag{9}$$

$$H_f(t) = \lim_{\varepsilon \rightarrow 0} \frac{\ln\left(N_0(\varepsilon) - \frac{t}{2\varepsilon^3} \left(\frac{4\pi}{3}\right)^{1/3} \left(\frac{\gamma n^{4/3}}{\eta}\right) \left(\frac{1}{\rho} - 1\right)^{2/3} R(t)^3\right)}{\ln(1/\varepsilon)}, \text{ (for final phase),} \tag{10}$$

where $R(t)$ is pore radius as time function (Fig. 5).

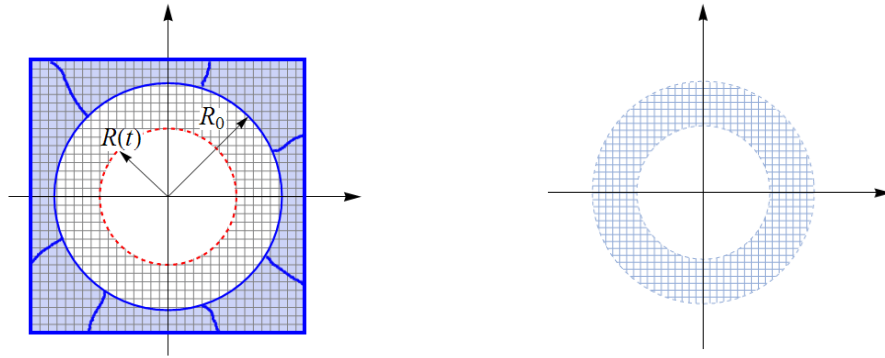


Fig. 5. Isolated pores and their flooding in the liquid phase of sintering.
 Left: The initial value R_0 of pore radius is decreasing with time.
 Right: The positive volume difference $\Delta V(\varepsilon, t)$ after time t .

Having in mind energies formula (1) balance, and the fact that the sintering process overall energy of the decreases due to its engagement in atomic material transport of inside the specimen, it is reasonable to post a hypothesis that this energy part spends in overcoming surfaces irregularity, having Hausdorff fractal dimension $2.010 \leq H_f \leq 2.085$ [9,10]. This fractal structure impact may be “measured” by a non-dimensional parameter α_s that should be between $\min(H_f - 2) = 0$ and $\max(H_f - 2) = 1$. Here, the number 2, is the surface topological dimension. This means that $0 < \alpha_s < 1$. Next, the “sponginess” of porous material may also have additional affect, which may be materialized by “porosity factor” α_p which ranges for 0 to 1. Finally, there is a third factor α_M , caused by disorder ferroelectric particles movement influence which is the fractal movements factor. It is connected with Brownian kind moving particles inside the sintering process. This movement has fractal dimension H_M which ranges from 1 to 3. So, it is reasonable to take $\alpha_M = \frac{1}{2}(H_M - 1)$, so that $0 < \alpha_M < 1$ is valid. In this way, all three factors α_s, α_p , and α_M are normalized. All these factors influence the overall fractality correction factor φ that is function of above three, and so it may valid

$$\varphi = \Phi(\alpha_s, \alpha_p, \alpha_M), \quad (11)$$

where the function Φ is unknown by now, but a good approximation would be a linear combination of α_s, α_p , and α_M ,

$$\Phi(\alpha_s, \alpha_p, \alpha_M) = \omega_1 \alpha_s + \omega_2 \alpha_p + \omega_3 \alpha_M, \quad \omega_1, \omega_2, \omega_3 \geq 0, \quad \omega_1 + \omega_2 + \omega_3 = 1. \quad (12)$$

Getting back to the surface area energy reduction E_s and energy adopted by viscous flow E_f , our hypothesis is that a part of both energies dissipates on “struggle” with grains’ surfaces fractal structure of (factor α_s), porosity (α_p) and Brownian motion (α_M). As a consequence, effective surface area reduction energy of is not, E_s but $E_s - \Delta E_s$

$$E_s - \Delta E_s = \varphi_s E_s, \quad (13)$$

and similarly

$$E_f - \Delta E_f = \varphi_f E_f, \quad (14)$$

where φ_s and φ_f are of the form (11) with different linear coefficients choice ω_1, ω_2 and ω_3 . Obviously, the “fractal” dissipation parts ΔE_s and ΔE_f are small comparing to E_s and E_f , which makes factors φ_s and φ_f close to 1. Also, note that formula (2) which is fundamental for energy equilibrium will not suffer changes, namely ΔE_s and ΔE_f may consider to be constant functions of time, so

$$\frac{d}{dt}(E_s - DE_s) + \frac{d}{dt}(E_f - DE_f) = \dot{E}_s + \dot{E}_f = 0. \quad (15)$$

Two facts give rise from the last formula. First, that energy losses ΔE_s and ΔE_f may justify our heuristic hypothesis of being constant, which might be too simplified but truthful. If it will not be the case, then it have to be supposed that the Δ operator is distributive one. Under this circumstance, it directly follows from (2) that $\Delta(\dot{E}_s + \dot{E}_f) = \Delta \dot{E}_s + \Delta \dot{E}_f = 0$, and therefore (15) holds. But, either situation shows that fractal approach supports and improves way of looking on the sintering processes in the natural way.

5. Conclusion

Process of sintering is a complex operation on which a lot of parameters have influence. Here, the impact of morphology of ceramics grains and pores as well as Brownian character of particle dynamics inside ceramics specimen is studied. In this study, available micrograph data of BaTiO₃-ceramics are used. Based on our earlier works, it is established fact that such ceramics has light fractal form which emanates in three aspects. First, the shape and distribution of grains in prepared powder show fractal elements. Second, existence and distribution of pores obeys fractal geometry rules. Third, movement of particles inside viscous flow is nothing but Brownian motion, which is itself a fractal. These three elements, each in its domain influence sintering dynamics, and can be described by dimensionless quantitative factors α_s, α_p and α_M , being normalized to the interval [0, 1]. Following the associate formulae of Frenkel, Scherer and Mackenzie-Shuttleworth are used to determine that fractal ceramics dimension during sintering process approaches to 3. It is shown that after applying fractal correction the total energy remain constant.

Acknowledgements

This research is a part of the project „Directed synthesis, structure and properties of multifunctional materials“ (172057). The authors gratefully acknowledge the financial support of Serbian Ministry of Education and Science for this work.

6. References

1. Y.K. Cho, S.L.Kang, D.Y. Yoon, J. Am. Ceram. Soc., 87 (2004) 119-124.
2. V. V. Mitić, V. B. Pavlović, Lj. Kocić, V. Paunović, D. Mancić, Science of Sintering, 41 [3] (2009) 247-256.
3. V. Mitić, V. Paunović, D. Mančić, Lj. Kocić, Lj. Zivković, V.B. Pavlović, Ceramic Transactions, 204 (2009) 137-144.

4. L. DeJonge, M.N.Rahman, Sintering of Ceramics, In: Handbook of Advanced Ceramics, S.Somiya et al. (Eds.), Elsevier 2003.
5. R.K.Bordia, H.Camacho-Montes, Sintering Fundamentals and Practice, In: Ceramics and Composites Processing Methods (N. P. Bansal, A. R. Boccaccini eds.), Wiley 2012
6. G. W. Scherer, J. Am. Ceram. Soc. , (1991) 74 [7] 1523–1531. ,
7. J. K. Mackenzie and R. Shuttleworth, Proc. Phys. Soc. B, (1949) 62 [12] 833–852.
8. J. Frenkel, J. Phys. USSR, (1945) 9 385–391
9. V. V. Mitić, Lj. M. Kocić, I. Mitrović, Science of Sintering, Vol. 30 (1), pp. 97-104, 1998.
10. V.V.Mitić, V. Paunović, J. Purenović, S. Janković, Lj. Kocić, I.Antolović, D.Rančić, Ceramics International 2012 38 (2):1295-1301.
11. V.V. Mitić, I. Mitrović, B. Jordović, V. Brankov, "The Application of Stereology Method for Estimating the Number of 3D BaTiO₃-Ceramics Grains Contact Surfaces", 7th European Congress for Stereology, Book of Abstracts, Amsterdam, The Netherlands, April 20-23, P47, p. 131, 1998.
12. Lj.M. Kocić, V.V. Mitić, M.M. Ristić, "Stereological Models Simulation of BaTiO₃-Ceramics Grains", Journal of Materials Synthesis and Processing, Vol. 6, No. 5, pp. 339-344, 1998.
13. Kang Suk-Joong L., "Sintering. Densification, Grain Growth, and Microstructure", Elsevier 2005.

Садржај: Морфологија керамичких зрна и пора као и брауновски карактер динамике честица унутар узорка керамике свакако утичу на процес синтеровања. ВаТiО₃-керамика, која се разматра у овом раду, има слабо фракталну форму и она се испољава у три аспекта. Прво, површина зрна као и њихова дистрибуција чак и у почетном „green body“ узорку, указују на фракталну структуру и понашање. Друго, постојање пора и њихов распоред такође следе обрасце фракталне геометрије. Треће, кретање честица у фази вискозног синтеровања подлеже правилима брауновског кретања које представља једну од основних фракталних категорија. Ова три фактора, сваки у свом домену утичу на динамику синтеровања и могу бити описана бездимензионим квантитативним факторима α_S , α_P и α_M , нормализованих на [0, 1]. Пратећи процес синтеровања по фазама, одговарајуће формуле Френкеља, Шерера и Мекензи-Сатлворта се могу употребити да би се показала промена фракталне димензије керамике која, може се показати, током процера синтеровања тежи ка граничној вредности 3. Такође, показано је да се равнотежа енергија не нарушава након примене фракталне корекције на квази-равнотежу енергије која настаје из редуције површине површи зрна E_S и енергије потрошене на вискозни ток E_f .

Кључне речи: ВаТiО₃, микроструктура, синтеровање, фрактални параметри
