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MICROSTRUCTURE EVOLUTION AND SINTERING KINETICS OF ZnO

Darko Kosanović *
Serbian Academy of Sciences and Arts, Institute of Technical Sciences
Mr Suzana Filipović
Serbian Academy of Sciences and Arts, Institute of Technical Sciences
Dr Nina Obradović
Serbian Academy of Sciences and Arts, Institute of Technical Sciences
Dr Vladimir Pavlović
Serbian Academy of Sciences and Arts, Institute of Technical Sciences
Momčilo Ristić
Serbian Academy of Sciences and Arts

The aim of this work was to analyse the kinetics and microstructure evolution of ZnO sintering process. ZnO powder was isothermally sintered (15, 30, 60, 90 and 120 min) in the temperature range from 8000C to 12000C. The values of Lenel parameter were calculated and used for the analysis of the densification and mass transport processes. Using scanning electron microscopy the analysis of the microstructure evolution and dependence of the average grain size with temperature and time of sintering was obtained. The results of this research could enable development of a new phenomenological equations in the analyses of ZnO-based materials sintering kinetics.

Keywords: ZnO, Sintering, Kinetics.

INTRODUCTION

Complex requirements in the synthesis of materials with pre-defined functional, physical, technological and exploitage properties are the result of the rapid development in modern technology [1]. Recently, special attention was paid to the research of the ways of synthesis and properties of multifunctional materials which are used in the production of new and/or technologically advanced equipment in different fields; from electronics to medicine [2].

In the group of metal-oxide materials zinc-oxide is abstracted as a material which has been for a very long time studied whether in form of a single crystal, polycrystalline powder, film or ceramic, and in recent years in various nanostructured forms [3]. Thanks to its exceptional physical and chemical properties, ZnO has a wide range of applications, from the production of pigment, rubber, composite materials, cosmetics and pharmaceutical creams for the protection from ultraviolet (UV) radiation or anti-bacterial effect to the production of piezoelectric converters, optical wires, acoustic-wave devices, varistors, chemical and gas sensors, light emitters [4] and etc.

ZnO-based materials have been obtained by different physical and chemical methods, such as evaporation deposition, spray pyrolysis, a variety of aerosol and sol-gel techniques, ion implantation, laser ablation, etc. Using these methods significant success has been achieved recently in obtaining the various ZnO nanostructures with homogeneous and uniform particle size distribution. Sintering process has particularly important role in the synthesis of these materials. Sintering leads to shrinkage and reduce porosity which gives the possibility for obtaining materials with desired microstructural parameters [5]. Kinetics and mechanism of these macro changes have not yet been fully clarified even though the shrinkage during sintering is relatively easy to measure. Bearing all this in mind in this paper the kinetics of isothermal sintering and changes in morphology and microstructure of sintered ZnO were analyzed.

** Institute of Technical Sciences of the Serbian Academy of Sciences and Arts,Knez Mihailova 35/IV, 11000 Belgrade, Republic of Serbia; darko.kosanovic@itn.sanu.ac.rs*

EXPERIMENTAL PROCEDURE

For the experimental study in this paper commercial ZnO powder (Kemika-Zagreb, and 99%, Mr = 81.37) was used. The powder was compacted in double steel mold with diameter of 8 mm. In our research the two-sided pressing of 1 t/cm2 (98 MPa) was used.

Sintering of ZnO green samples was carried out in a laboratory chamber furnace. Green samples were directly pulled in a preheated oven at 800, 900, 1000, 1100 and 12000C and then rapidly cooled and extracted after 15, 30, 60, 90 and 120 min.

Scanning electron microscope was used to investigate the microstructural properties of ZnO sintered samples.

RESULTS AND DISCUSSION

One of the most important technological processes, used for the synthesis of modern materials that provides the possibility of obtaining materials with pre-defined properties, is certainly the process of sintering [6]. In this study, we analyzed the kinetics of ZnO isothermal sintering by monitoring the changes of Lenel parameter, morphology and microstructural characteristics of sintered samples and the dependence of average grain size of ZnO with the temperature and sintering time.

Analysis of the densification process, in other words the reduction of pore volume, usually has a phenomenological character, but based on the obtained relations, using different models, some information on the mechanism of mass transport that are essential to the process of sintering could be obtained. The course of densification could be characterized using the changes in relative density, porosity, volume and linear shrinkage or through some of the relations that connect the initial, sintered and theoretical density [7]. In this work the changes of relative density and porosity were investigated.

Theoretical density (TG) of ZnO is ρT = 5,657g/cm3, while the densities of the sintered samples (ρs) were determined based on the measurenents of the mass (ms) and sample dimensions: height (h) and diameter (D), a relative density of sintered samples were determined as a ratio between theoretic and measured density values (ρs) and (ρT), as shown in Table 1.

The analysis of the results given in Table 1, clearly have shown that the values of the relative densities of sintered ZnO samples increased with the temperature and the time of sintering. Maximum values are obtained for ZnO samples activated for 90 and 120 minutes and sintered at 1100oC. Based on our previous investigations, prolonged milling times can cause formation of agglomerates that can prevent sintering process at high temperatures.

Table 1. Relative densities of ZnO sintered samples expressed in (%)TG.

T(0C)	Time (min)				
	15	30	60	90	120
800	71,68	72,51	74,61	75,05	76,31
900	82,73	83,33	84,20	84,33	84,58
1000	86,62	86,95	88,19	89,27	89,66
1100	91,23	91,79	92,36	93,19	93,58
1200	91,67	91,78	92,75	92,98	92,98

The degree of densification during sintering is usually characterized with Lenel parameter, L [8], which describes a simple relation between the sintered Ps and the initial porosity P0 i.e. theoretical ρT, sintered ρS and initial ρ0 density of the samples:

$$L = 1 - \frac{P_s}{P_0} = \frac{\rho_s - \rho_0}{\rho_T - \rho_0} \quad (1)$$

The usage of Lenel parameter, the variable dependent with temperature and sintering time, in our analysis, was conditioned by the fact that it is connected with simple relations to the other parameters used in such investigations, that simplifies the comparison of the results.

A mathematical analysis of the obtained experimental values of Lanel parameter was performed with sufficient accuracy by fitting the results with the equation:

$$L = L_0 + A \cdot t^n, \quad (2)$$

L_0, A and n are constants, t is time of sintering. L_0 corresponds to the value of Lanel parameter at the beginning of isothermal sintering, therefore it represents the degree of densification at the beginning of isothermal heating regime. The calculated values of Lenel parameter for the sintered samples at different temperatures during isothermal sintering, are graphically presented in Fig. 1.

From obtained results for L_0 can be seen to be increasing with temperatures up to 11000C, which indicates that at a given mode the system enters the final stage of sintering, in which the density approaches its maximum (relative density of these samples is about 95%), as shown in Table 2.

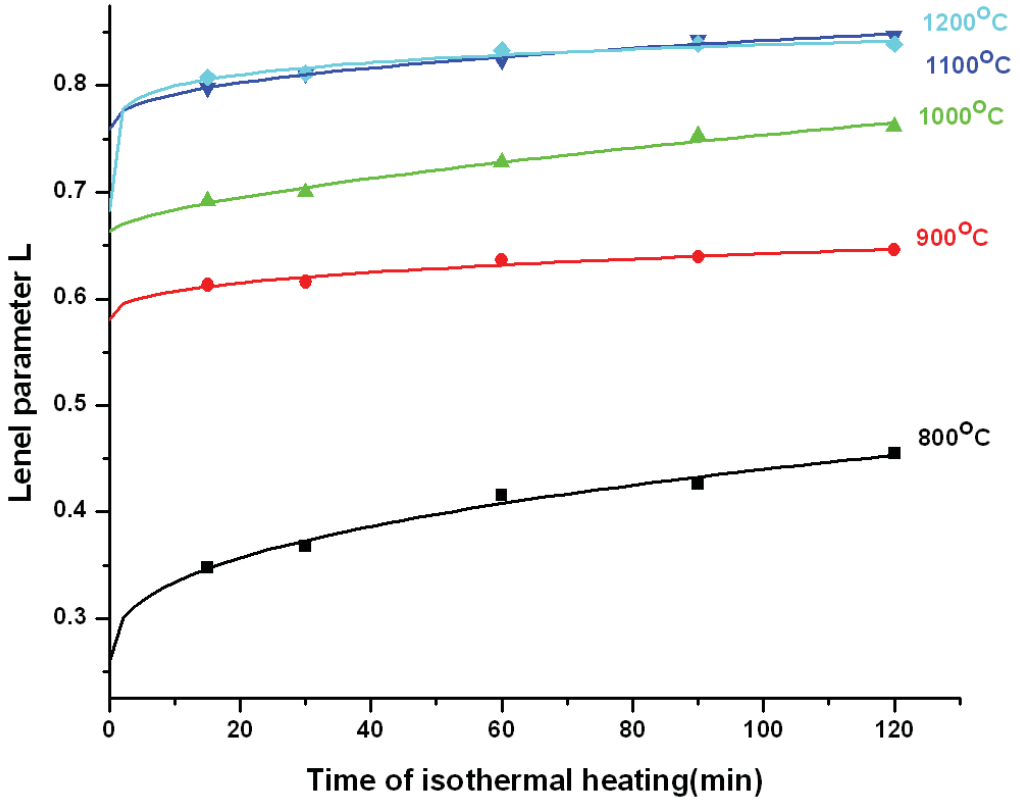

Figure 1. Changes of Lenel parameter during ZnO isothermal sintering.

Table 2. Values of L0, A and n parameters at different temperatures obtained by fitting.

T(0C) / Parameters	800	900	1000	1100	1200
L_0	0,259	0,580	0,663	0,760	0,682
A	0,031	0,012	0,004	0,013	0,088
n	0,383	0,563	0,654	0,405	0,124

The other two parameters A and n that characterize, in fact, the rate of the densification process during sintering, have a little more complexed dependence with temperature.

The parameter n is increased to temperature of 10000C, which affects the increase in density, while lowering the temperature parameter A points to the the initial stage of sintering is still present (Tab.2).

On the basis of this it could be concluded that the process of mass transport during sintering of ZnO was intensified in the temperature range 800-10000C, which certainly had to do with the system's increased activity due to its higher porosity at lower temperatures.

Scanning electron micrograph of the initial ZnO powder is shown in Fig. 2. It indicated the uniform distribution of particles and their polygonal shape.

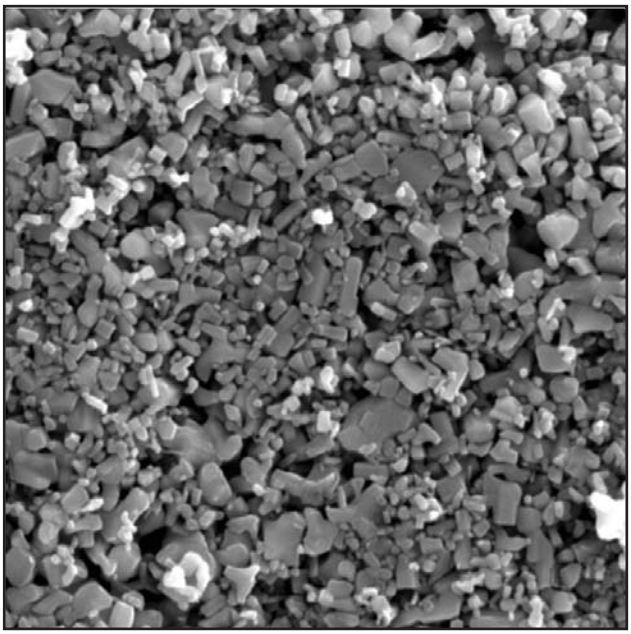

Figure 2. SEM of ZnO initial powder.

Figure 3. shows the micrographs of samples sintered for 90 min at different temperatures. SEM micrograph of sample sintered at 8000C (Fig. 3.a) shown that the microstructure of this sample was characterized by large, open porosity and inhomogeneity, which is in accordance with the principles of the recrystallization and grain growth theory [9], present within initial sintering stage. The grains with irregular polygonal shapes were observed as well. It may be noticed that some grains were consisted of a number of particles and that the process of grain growth was intensified. It was found that large grains retained their polygonal shape which led to their merger, while the mass transport through the contact zone and surface diffusion was dominant in the smaller grains. Increasing sintering time intensified the process of mass transport and grain polygonisation. Increased sintering temperature led to the grain growth and caused the formation of irregularly shaped, closed pores, clearly seen in Figure 3.b.

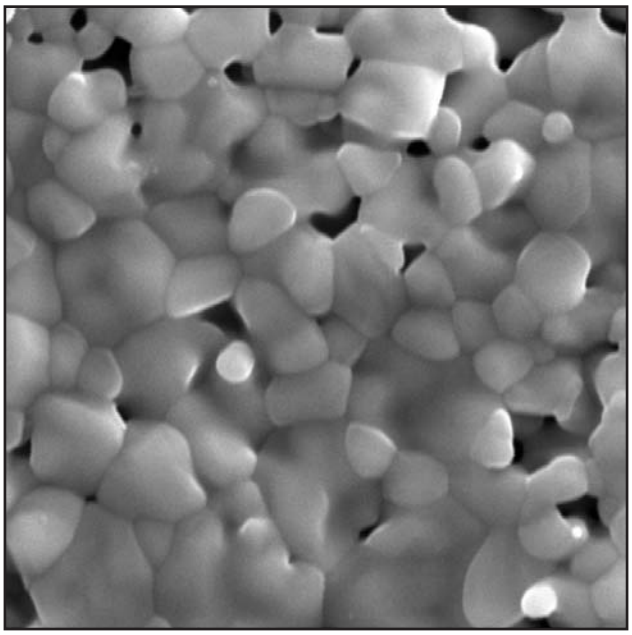

Figure 3b. SEM of ZnO sintered for 90 min at 1000 ^{0}C

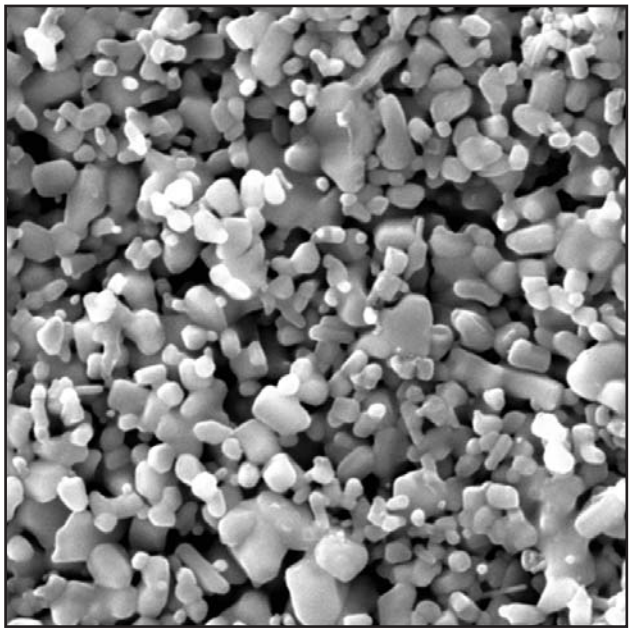

Figure 3a. SEM of ZnO sintered for 90 min at 800 ^{0}C

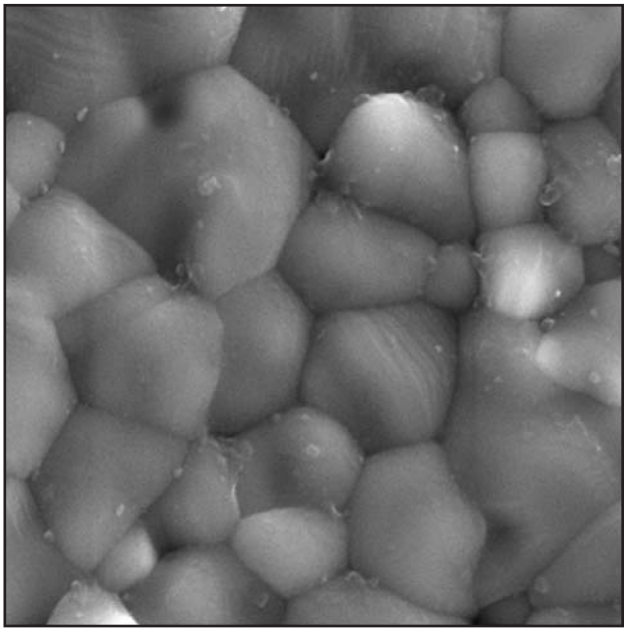

Figure 3c. SEM of ZnO sintered for 90 min at 1100^{0}C

Sintering at 11000C, presented in Figure 3. c. led to anisotropic grain growth and mass transport which consequently created spheroide, closed pores, characteristic for final sintering stage. The microstructure of samples sintered at 12000C was not much different from the microstructures of the samples sintered at 11000C (the calculated densities indicated this as well), but the uniform grain growth and the disappearance of open porosity was still noticed.

Fig. 4. shows the dependence of average grain size G of ZnO with the temperature and time of sintering. This diagram shows that after sintering at 1000, 1100 and 12000C the grains remain approximately with same size, but with increasing sintering temperature, up to 12000C (more than 60 minutes), leads to further grain growth.

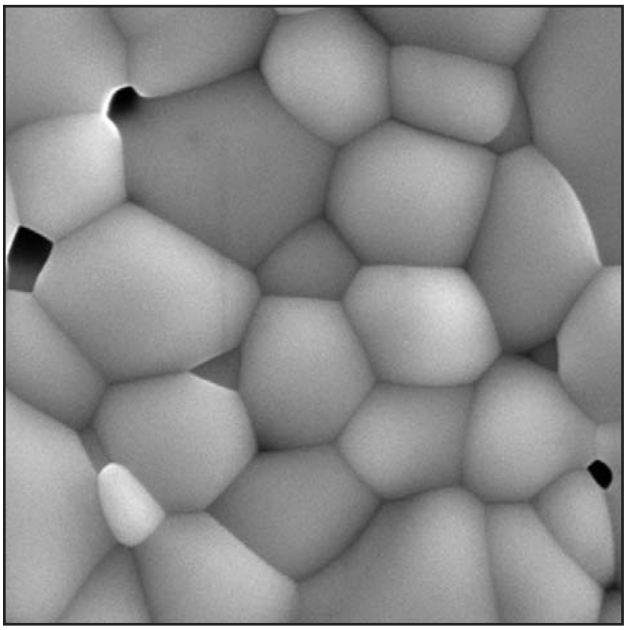

Figure 3d. SEM of ZnO sintered for 90 min at 1200^{0}C

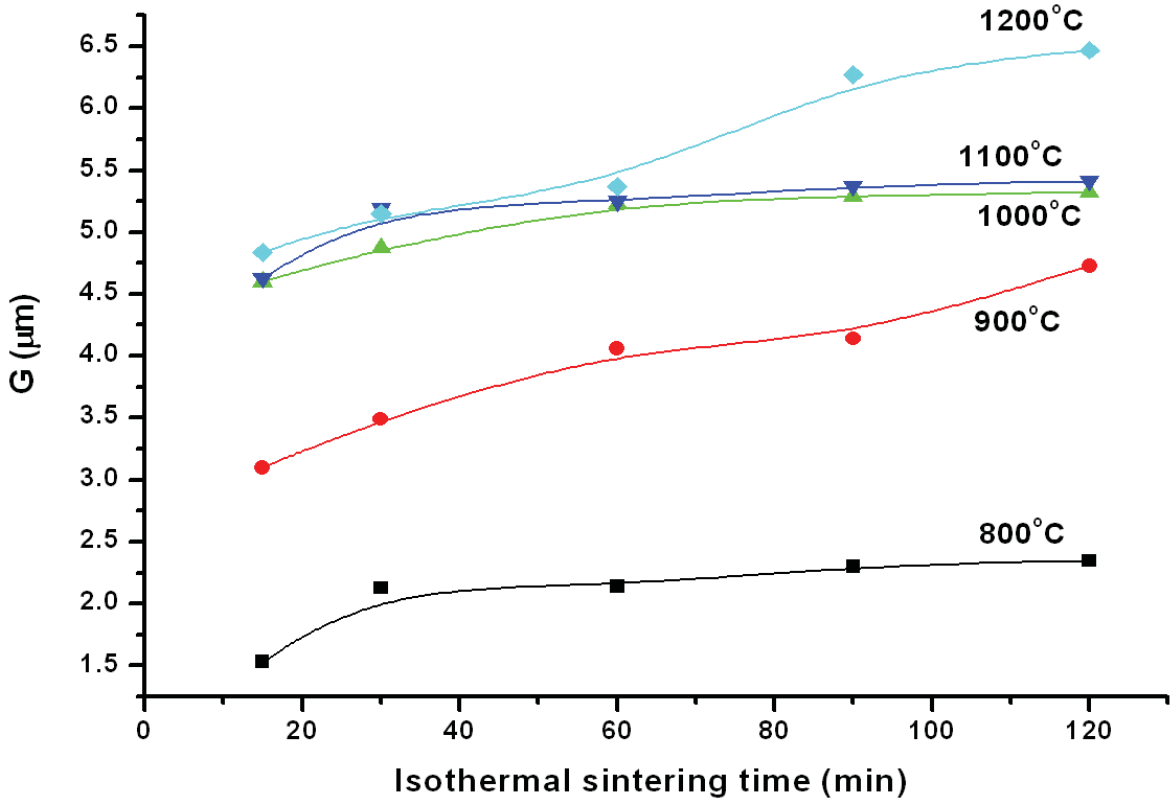

Figure 4. The dependency of the grain size of ZnO with the temperature and time of sintering.

CONCLUSION

In this work we analyzed the kinetics of sintering and changes in the microstructure of sintered ZnO. It was also found that the initial sintering process is characterized by intensive mass transport during sintering of ZnO in the temperature range from 8000C to 10000C, which certainly had to do with the system's activity due to its higher porosity at lower temperatures. Based on the experimental results the values of Lanel parameter were determined and it was found that it reaches its maximum values for samples activated for 90 and 120 min and sintered at

11000C, indicated the final sintering stage.

SEM analysis determined a balanced densification of the material with the increase of sintering temperature, as well as the pore spheroidization and reduction. It was noted that the system entered the final stage of sintering at temperatures above 11000C, while the grains were in uniform polygonal shape. The results of these research is a contribution to the existing investigations of the ZnO-based materials sintering kinetics.

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RERERENCES

1) Minić V. M., (1998) Dijagrami sinterovanja oksida cinka i kadmijuma, Magistarska teza, Univerzitet u Beogradu
2) Brown E. H., (1976) Zinc oxide: Properties and application, Pergamon pres, New York.
3) Klingshirn C., (2007) ZnO: Material, Physics and Applications, ChemPhysChem.
4) Ristić M. M. (1993) Principi nauke o materijalima, SANU, Beograd.
5) Ristić M. M., Pryadko L. F., Kunicki Ja. A., Nikolić Z. S., Živković M. M., Radić S. M. (1996) Prognoza fizičkohemijskih svojstava materijala, CMS, Beograd
6) Ивенсен В. А., (1985) Феноменология спекания и некоторые вопросы теории, Металлургия, Москва.
7) Lee W. S., Chen W. T., Lee Y. C., Yang T., Su C. Y., Hu C. L., (2007) Influence of sintering on microstructure and electrical properties of ZnO-based multilayer varistor (MLV), Ceram. Int., 33, 1001-1005.
8) Exner H. E., (1979) Principles of Single Phase Sintering, in Reviews on Powder Metallurgy and Physical Ceramics, Edited by Fritz V. Lenel, Freund Publishing H o u s e LTD, Tel-Aviv. Israel.
9) Ristić M.M., Maričić A. M., Kosanović D.A., (2009). Rekristalizacija i rast zrna, ITN-SANU i TFČ Čačak, Čačak.

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