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Reaction Sintering of the 2ZnO-TiO$_2$ System

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Abstract:

Sintering kinetics of the mechanically activated ZnO-TiO$_2$ system was studied. Mixtures of ZnO and TiO$_2$ powders were mechanically activated using a high-energy ball mill for different time intervals from 0 to 300 minutes. Formal phenomenological analyses were performed in order to describe the specimen's behavior during isothermal sintering at 1100°C. Non-isothermal sintering was investigated by dilatometer measurements up to 1100°C with a constant heating rate. The Dorn method was applied in order to give information on the activation energy.

Keywords: Sintering kinetics, Mechanical activation, ZnO-TiO$_2$ system.

Introduction

Zinc titanates applied as dielectric resonators and filters in microwave devices occupy a significant place in the field of material science due to their good semi-conducting and dielectric properties [1,2]. Also, recent investigation of regenerable sorbents for desulfurization of hot coal gases, a relatively new and important task, use zinc titanate as a sorbent [3,4].

A variety of titanates, such as ZnTiO$_3$, Zn$_2$Ti$_3$O$_8$ and Zn$_2$TiO$_4$, can be simultaneously obtained by a classic solid-state route [5,6]. Mechanical activation is also a common part of the powder preparation route in the field of ceramics.

Due to complexity of each technique, mechanical activation along with reaction sintering deserves a special approach. The aim of the present paper was to investigate the sintering kinetics of a mechanically activated ZnO-TiO$_2$ system.

Experimental procedure

Commercially available ZnO (99.9% Kemika-Zagreb) and TiO$_2$ (99.9% Alfa product-Ventron) were chosen as starting materials. Appropriate amounts of the compositional constituents at the 66 mol% ZnO to 33 mol% TiO$_2$ ratio, that corresponds to the required stoichiometric ratio of 2:1, were weighed out and homogenized. The powder mixture was afterwards mechanically activated in a planetary ball mill device (Fritsch Pulverisette 5), with

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ZrO balls and vessels where the ball to powder mass ratio was 40:1. The time of milling was varied from 0 to 300 minutes and the mixtures, as appropriate samples, were denoted according to the applied time of activation as ZTO-000, ZTO-005, ZTO-015, ZTO-030, ZTO-090, ZTO-180 and ZTO-300. The mixture labeled as ZTO-000 was not mechanically activated.

Powders were compacted using an uniaxial double action pressing process in an 8 mm diameter tool (Hydraulic press RING, P-14, VEB THURINGER). Based on our previous investigation of the behavior of non-activated and activated mixtures [7], the compaction pressure was varied in order to achieve almost identical green densities for dilatometer measurements. Compacts obtained from the non-activated mixture without a binder are extremely fragile and thus not convenient for handling, which is not the case with compacts of mechanically activated mixtures.

Isothermal sintering was performed in air with the heating rate $10^{o}C/min$. Compacts were placed in an alumina boat and heated in a tube furnace (Lenton Thermal Design Typ 1600). When the temperature of the furnace and samples achieved $1100^{o}C$, compacts were sintered isothermally for 0, 15, 30 and 160 minutes.

The relative shrinkage of samples in order to investigate the reactive sintering process was followed by a sensitive dilatometer Bähr Gerätebau GmbH Type 702s. Heating was carried out in air with a constant heating rate of $10°C/min$, from room temperature to $1100°C$, and with a holding time of 2 hours.

Results and discussion

As shown in Fig. 1, the maximum change in densification rate was registered after about 15 minutes of isothermal sintering regardless of green densities or the fact that samples were activated or not.
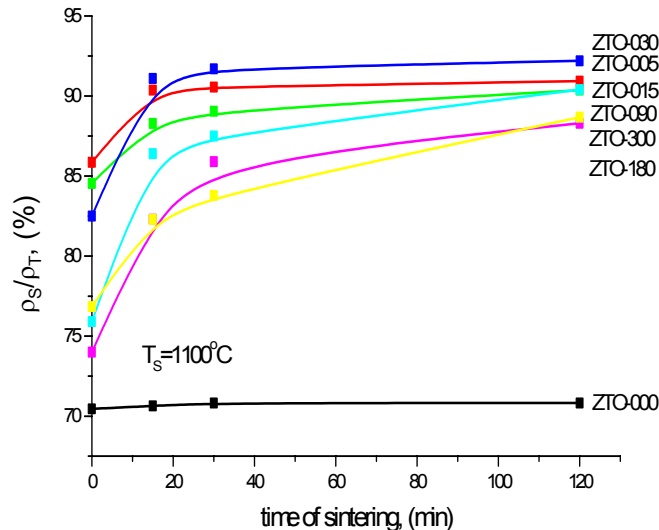
Fig. 1 Percentage ratio of obtained sintered to theoretical density as a function of thr sintering time

It is clearly visible that the best results were obtained with ZTO-030, ZTO-005 and ZTO-015, respectively. Non-activated powder had the lowest densification rate compared to the other samples, as expected. A formal phenomenological analyses of results obtained using

activated samples shows that the sintering process can be described quite well by the following equation:

$$\rho = \rho_0 + \frac{At}{(B + t)} \tag{1}$$

ρ –density of activated samples, t – sintering time, ρ_0 – green density at t = 0 min, A – inverse sinterability coefficient and B – constant (tab. I).

Dependences of parameters A and B vs. milling time are presented on Fig. 2. We can divide the dependence of parameter A vs. milling time into two categories. The minimal values of parameter A (<10) were obtained using powders activated 5, 15 and 30 minutes. Higher densities after sintering were obtained for lower parameter values. The inverse sinterabillity values increased until aproximately 50 minutes of activation and then the slope changed and we have a slight decrease of coefficient A.

We can also split the results of the dependence of B vs. milling time into two ranges (first range - 5, 15 and 30 minutes and the second one - 90, 180 and 300 minutes).

The first stage is characterized by reaction sintering (during the heating up regime, both a mechanochemical reaction along with the sintering process are taking place).

Tab. I Parameter values for differently activated samples

sample	ρ_0	A	B
ZTO-005	86	5	2
ZTO-015	88	4	57
ZTO-030	82	10	2
ZTO-090	76	15	7
ZTO-180	74	16	12
ZTO-300	77	14	29

The second stage is characterized by sintering of the reaction product (at the beginning of the sintering process we have a pure zinc-titanate phase).
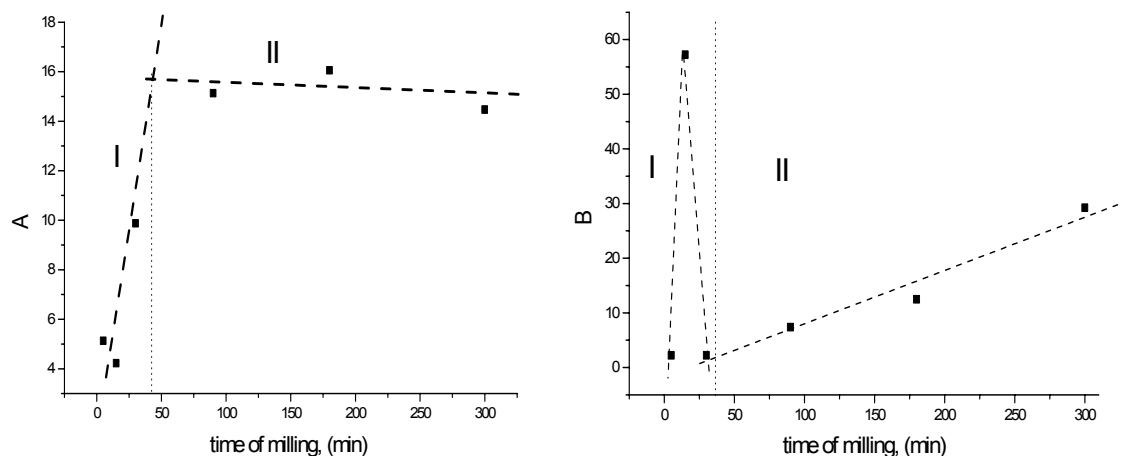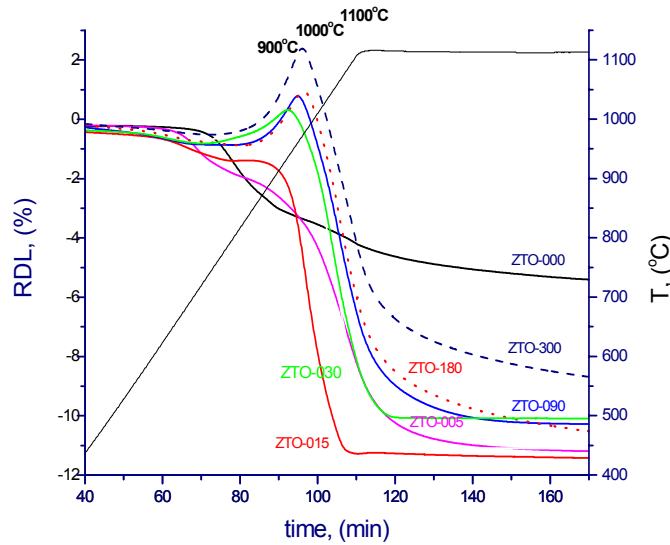

Fig. 2 Parameters A and B vs. milling time

Fig. 3. shows the relative shrinkage of samples as a function of time during heating and holding at 1100°C for various activated samples, obtained by the dilatometer.

Intensive sintering of mixture mechanically activated for 15 minutes starts at 900°C (in lit. 1100°C) accompanied by characteristic shrinkage.

According to the fact that in samples of the mixtures activated for 30, 90, 180 and 300 minutes non-reacted compounds are present in lower quantities than in the one activated 15 minutes, spinel formation is the dominant process and more pronounced with a displayed characteristic expansion.

Fig. 3 The relative shrinkage of samples as a function of time during heating and holding at 1100°C

Also, the onset of sintering shifts to higher temperatures for longer activation times. However, the curve for the non-activated sample proceeds in quite a different manner. First, the characteristic maximum of zinc-titanate formation is not observed, and secondly the sintering process is far away from the final stage. All these facts lead us to conclude that in the absence of mechanical activation the formation of Zn_2TiO_4 is to slow to be the dominant process in the observed temperature range.

J. L. Woolfrey and M. J. Bannister [8] suggested a non-isothermal technique for studying initial-stage sintering. It is shown that in principle they permit determination of all sintering parameters (rate law, activation energy and diffusion coefficients).

(1) Dorn method

This technique consists of determining the instantaneous effect of a small step change in temperature on the shrinkage rate. If V_1 is the shrinkage rate at temperature T_1 just before the temperature change and V_2 is the shrinkage rate at T_2 just after the change, the apparent activation energy of the process responsible for sintering is given by:

$$E_a = \left[\frac{RT_1T_2}{(T_1 - T_2)}\right]\ln\left(\frac{V_1}{V_2}\right) \tag{2}$$

where R is the gas constant. According to the suggested equation, the values of activation energy responsible for the sintering process are given in tab. II.

The results obtained using Dorn's method are in accordance with the experimental results. Sintering of ZnO anticipates a reaction within ZTO-000 that is not accompanied by a great shrinkage rate - thereby a relatively low activation energy value.

Tab. II Activation energies for various activated samples

sample	E_a (KJmol^{-1})
ZTO-000	117.7
ZTO-005	100.4
ZTO-015	150.6
ZTO-030	352.3
ZTO-090	590.9
ZTO-180	728.3
ZTO-300	1114.0

Sintering of ZnO takes place within ZTO-005, only this time a small amount of the remaining of ZnO has already started to react with TiO_2. Starting from ZTO-015 and all the way to ZTO-300, activation energies increase with the increase of milling time and accompany the shrinkage rate-the presence of agglomerates inhibits the sintering process and therefore the system needs higher activation energy values.

Conclusions

In this paper the reaction sintering of $2ZnO-TiO_2$ system was studied. Based on these results, the maximum shrinkage rates were obtained using powers activated 5, 15 and 30 minutes. The most productive influence of mechanical activation was noticed on the ZTO-015 powder. Namely, the sintering process started at 900°C (in lit. 1100°C), and the process of zinc-titanate formation already started at 814°C (in lit. 945°C).

A formal-fenomenological equation that describes the isothermal sintering process was recommended and is yet to be studied. Also, we assumed that viscous flow is the mechanism responsible for the initial stage sintering process.

Acknowledgements

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Садржај:*. У овом раду проучавана је кинетика синтеровања механички активираног система ZnO-TiO₂. Смеше прахова ZnO и TiO₂ механички су активиране у високо-енергетском планетарном млину од 0 до 300 минута. Употребљена је формална феноменолошка анализа са циљем да опише понашање узорака синтерованих изотермски на 1100ᵒC. Неизотермско синтеровање до 1100ᵒC праћено је на дилатометру са константном брзином загревања. Дорнов метод је примењен за израчунавање енергије активације.*
Кључне речи*: кинетика синтеровања, механичка активација, систем ZnO-TiO₂*