Kinetics of Specific Surface Area Change Using the Boltzmann Model

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Abstract:

During sintering of the 2MgO-2Al$_2$O$_3$-5SiO$_2$ system, cordierite, an attractive ceramic material because of its properties, is obtained. Effects of mechanochemical activation of stoichiometric mixtures, performed to investigate possibilities of lowering cordierite formation temperature during sintering, were monitored by thermogravimetric and differential thermal analyses. Specific surface areas of the mechanically activated powder mixtures were determined by the BET method. Kinetics of the specific surface area increase was analyzed using the Boltzmann model. It was confirmed that with activation time increase, temperatures of phase transformations were shifted to lower values and, according to FTIR analysis no significant changes occurred during material aging. According to the obtained results, it may be concluded that since mechanochemical activation has an influence on the treated powder mixture, lowering of the cordierite formation temperature during the sintering process is expected.

Keywords: Cordierite, Kinetics, Boltzmann model.

Introduction

Cordierite (2MgO·2Al$_2$O$_3$·5SiO$_2$) is a material with a very low coefficient of thermal expansion (20·10^{-7}/°C) and low dielectric constant (~5), also known for its good mechanical properties [1]. Because of such properties, it can be used as a component in products exposed to high temperatures [2-6] and as a semiconductor carrier [7, 8].

The temperature range of cordierite sintering is very narrow (1300–1400 °C). The aim of many previous researches was to decrease the sintering temperature of this material. The basic components of the cordierite mixture are often mixed with different additives with lower melting points so that the liquid phase present can enable better contact among the reacting substances. Therefore, cordierite is mixed with the oxides of boron, phosphorus, titanium, bismuth and other metals, that can't be built into the crystal lattice of cordierite because of their atomic radii [9].

Preliminary research has shown a significant influence of mechanochemical activation on lowering the sintering temperature of the starting components (kaolin, quartz and basic magnesium carbonate). Mechanochemically activated samples contain more energy in relation to non-activated starting components. During mechanochemical activation, the

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material is milled to a powder, the crystal lattice structure is destroyed and defects occur, which increases the possibility that phase changes during heating appear at lower temperatures than usually [10]. Furthermore, mechanochemical activation can have an effect on the final, especially electrical properties of the sintered material. Therefore, it is very important to get acquainted with changes that occur during mechanochemical activation of the $2MgO-2Al_2O_3-5SiO_2$ system.

Experimental work

The cordierite mixture was synthesized with the following powders: magnesia, alumina and silica. Chemical compositions of the initial components are shown in Tab. I.

Tab. I Chemical compositions of the initial components

Composition	Alumina, (%)	Magnesia, (%)	Silica, (%)
SiO_2	0.17	-	96.10
Al_2O_3	99.19	-	0.14
Fe_2O_3	0.089	-	0.243
CaO	0.07	1.40	0.112
MgO	0.049	98.60	-
Na_2O	0.236	-	-
K_2O	0.012	-	1.16
LOI	0.18	-	2.22

The powder mixture of the $2MgO-2Al_2O_3-5SiO_2$ stoichiometric composition was homogenized and mechanochemically activated by milling in a laboratory cylindrical ball mill of the VEB type.

Mechanochemical activation was carried out for 5, 15, 30, 60, 120 and 240 minutes (Tab. II). Activated cordierite mixtures were exposed to air for 24 hours and 24 months. During this resting period, moisture and carbon dioxide from the atmosphere can be absorbed by magnesia, and magnesium hydroxycarbonate can be formed. If air exposure changes activated powders, i.e. if so-called "aging" of materials occurs, it is necessary to carry out sintering immediately after mechanochemical activation, or store powders in an inert atmosphere. However, if the time of powder resting has no effect on the sintering process, the synthesis which has influence on the structure will be less complex and subsequently sintering that has influence on the properties of material will be simpler.

Samples A1, A3, A5 and A6 were subjected to thermogravimetric and differential thermal analyses (DTA/TG) within the temperature range of 20−1500 °C, and heating velocity of 10 °C/min.

Tab. II Mechanochemically activated starting $2MgO-2Al_2O_3-5SiO_2$ mixture

Sample	Activation Time (min)
A1	5
A2	15
A3	30
A4	60
A5	120
A6	240

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Sample A5 after the resting period of 24 h and 24 months was subjected to FTIR analysis.

Specific surface area of all samples was determined by the BET method.

Results and discussion

TG/DTA analyses of cordierite mixtures mechanically activated for different time periods and exposed to air during 24 months are shown in Fig. 1.
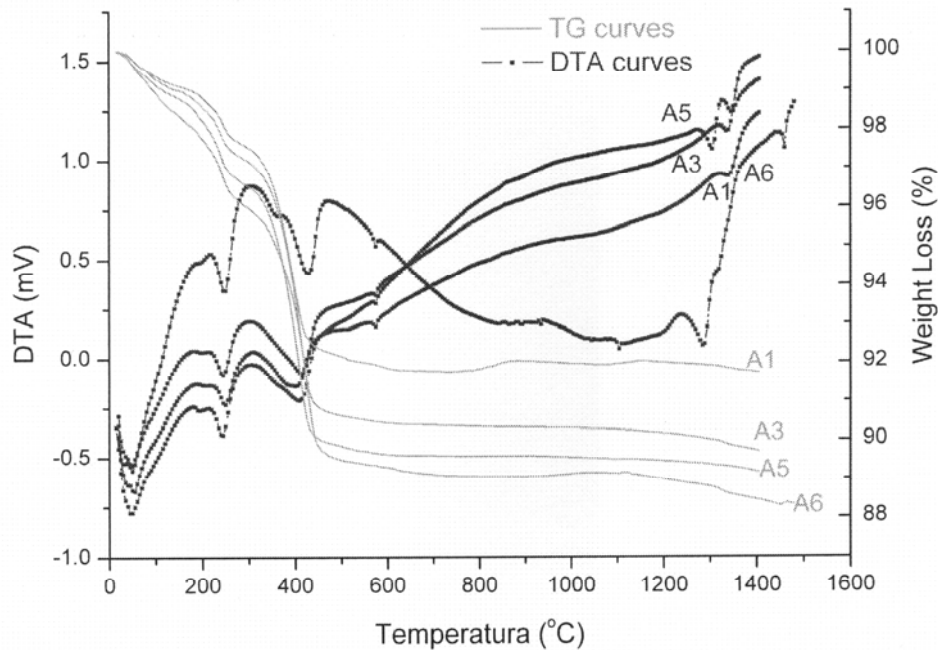

Fig. 1. TG/DTA diagram of samples A1, A3, A5 and A6, after the resting period

All three characteristic mass changes noticed on the TG diagram refer to mass reduction. The first one is noticed below 100 ºC and represents free water elimination, with the mass change for all investigated samples of about 1%, regardless of the activation time. The second one occurs within the temperature range of 230-300 ºC, with the mass change between 1 and 3% depending on the activation time. The third one, extremely pronounced representing the biggest change in the system, is noticed in the temperature range of 390-420 ºC with the mass change of 4% for sample A1 and 6% for sample A6. It can be noticed that mass reduction increases with the activation time, so that the overall mass reduction is between 8 and 12 % for samples activated in the period between 5 and 240 min, respectively. Differential thermal analysis (DTA) was done with the aim to investigate changes in the activated system within the sintering temperature range, up to 1500 ºC. Samples marked A1, A3, A5 and A6, that are actually powders activated for 5, 30, 120 and 240 min, were used in the DTA analysis and are shown together in Fig. 1. It can be noticed that all investigated samples behave in a similar way, in other words there are no significant behavior differences within the temperature range up to 600 ºC. However, it is noticeable that in the temperature range from 1200 to 1400 ºC, endothermic picks are slightly shifted towards lower temperatures. Based on the obtained results, it can be assumed that during sintering of the

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activated system $2MgO-2Al_2O_3-5SiO_2$, the temperature of cordierite formation will be reduced by increasing the activation time.

The influence of the resting time, also called "aging" or relaxation, on the chemical composition of the mixtures activated for 120 min after resting of 24 h and 24 months was carried out by FTIR analysis, Fig. 2. Since the initial components are considered, it is assumed that the surface adsorption of moisture and CO_2 from the atmosphere occurs, and hence relatively unstable hydromagnesite compounds. So, "aging", or resting of the activated samples should not have a significant influence on the sintering process. According to the obtained results of IR analysis, it can be concluded that regardless of the resting period, i.e. time elapsed from the initiation of activation the activated sample does not undergo significant changes until sintering. In this way, undesirable aspects in the process of synthesis can be avoided, and at the same time possible changes in the structure and properties.
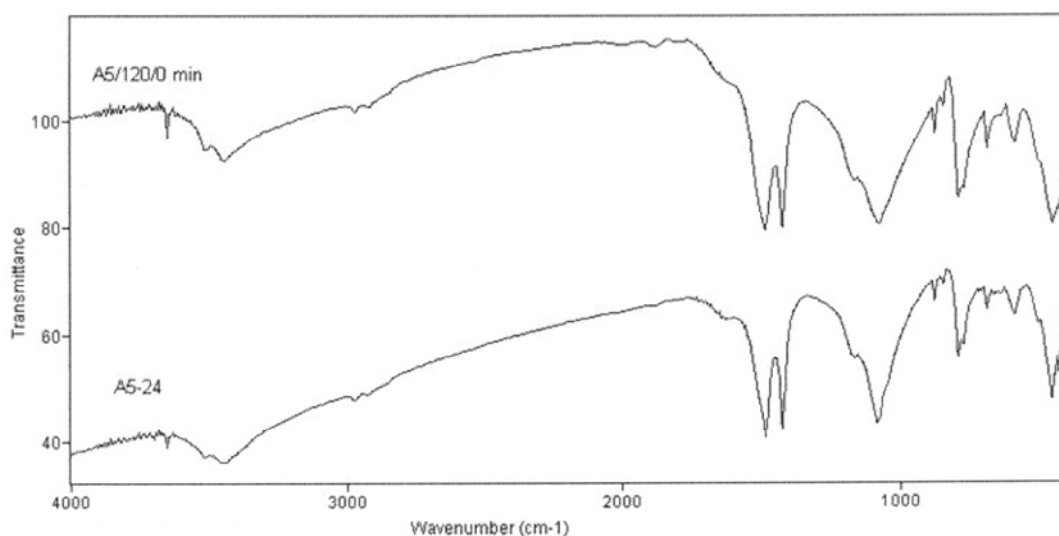

Fig. 2. FTIR of samples activated for 120 min, after the resting period

BET analysis, Fig. 3, showed that the value of specific surface area of sample A1, activated for 5 min is 7.19 m^2/g and that other values of specific surface areas are increasing sequentially, reaching 8.45 m^2/g for sample A6. These results indicate the fact that the reactive surface areas of mixture oxides increase by milling, that is mechanochemical activation. Furthermore, values of the specific surface areas suggest that sizes of the powder particles are reduced in the activation period up to 15 min. By prolonging the comminution process, the increase of specific surface area is primarily the consequence of particle surface "roughness" rise.

Increasing of the powder specific surface area determined by the BET method depending on mechanochemical activation time is shown in Fig. 3. The highest level of both size degradation and free powder surface area was achieved in the first 50 min of activation (Segment a, Fig. 3). In the activation period of 50-120 min (Segment b, Fig. 3), the specific surface area still increases, and after this period slightly increases (Segment c, Fig. 3) with prolonging the milling process, so it can be assumed that the maximum value of the specific surface area is achieved after 120 min of grinding.
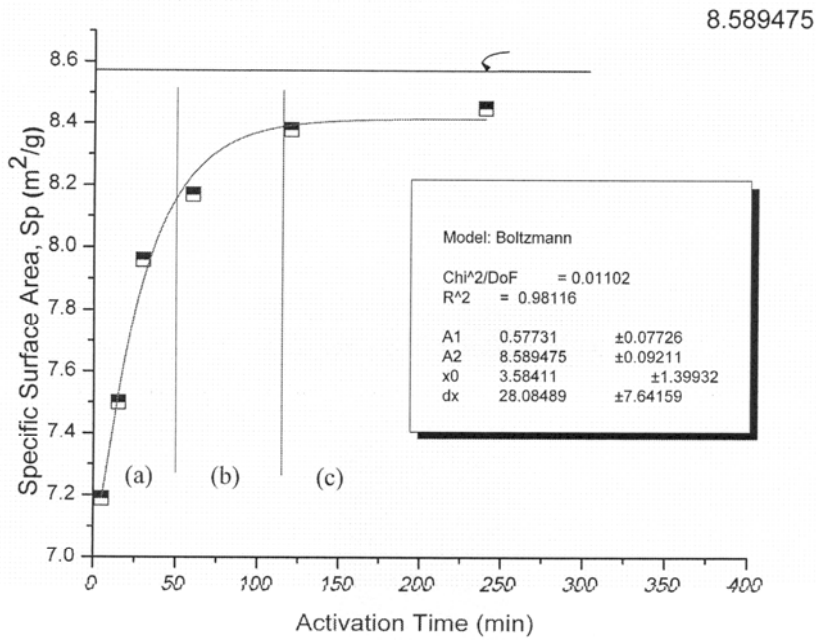
Fig. 3. Specific surface area by BET method

Kinetics of the specific surface area increase during mechanochemical activation can be monitored by the gradient change (velocity) of creating the surface area during the process of introducing energy into the system, Fig. 4. The change of gradients can indicate on the system resistance to introducing energy by mechanochemical activation. Hence, by analyzing the model, it is also possible to obtain specific properties of the used powders, i.e. limited values of the changes that are in this case the specific surface areas due to activation.
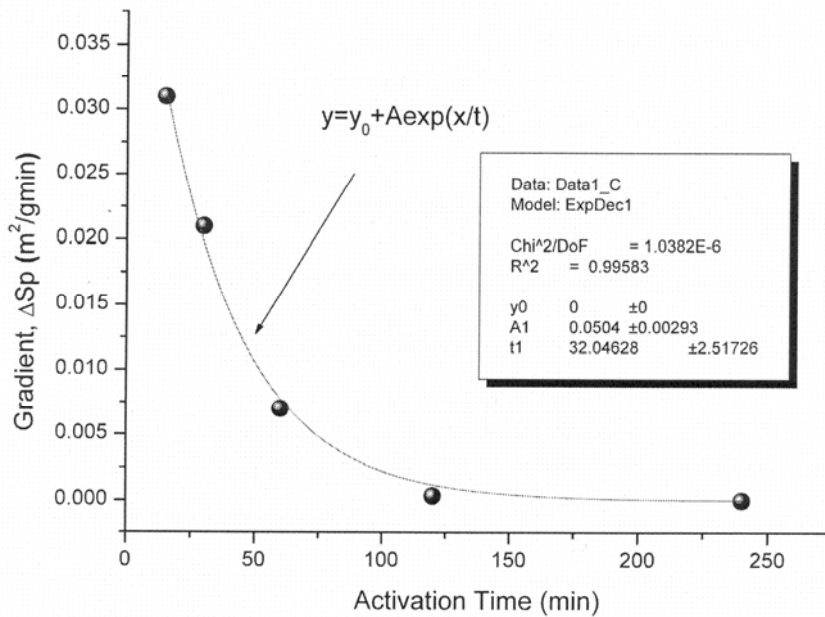

Fig. 4. Gradient of specific surface area change

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The velocity of free surface area changes of activated initial powders mixtures can be described by the following kinetic equation:

$$y = y_0 - A\exp(-kt) \tag{1}$$

Where y−gradient, y_0−initial gradient, k−constant of process velocity, A−constant, t−activation time.

Based on the experimental results, the velocity constant of the process is obtained, $k = 0.0312$ min^{-1}, which is in accordance with the literature data [11]. The obtained value for constant A is 0.05 m^2/gmin, and it indicates maximum possible velocity of the specific surface area change in the investigated system, which occurs in the activation period between 0 and 5 minutes. By analyzing the data shown in Fig. 4, in order to define the highest possible specific surface area generated for the investigated system during activation, it was found that the best results are obtained by using the so-called Boltzmann model [12], equation (2).

$$y = \frac{a_1 + a_2}{1 + \exp^{(x - x_0)/dx}} + a_2 \tag{2}$$

Constants a_1 and a_2 are asymptotic values that should show the limits where the corresponding changes happened. In a particular case, these are minimum and maximum values of the specific surface area for the investigated three-component system. Results of the analysis are shown in Fig. 5, and parameter values in Tab. III.
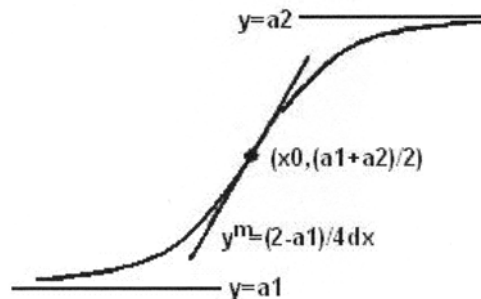

Fig. 5. Graphical shape of the Boltzmann model

The value obtained for limited values of the specific surface areas indicates that the maximum specific surface area that can be achieved by mechanochemical activation is 8,589 m^2/g. Considering that the values of the specific surface areas after 120 min of activation are over 8 m^2/g, it can be supposed that in this way, the objective practical measure of activation time is obtained, after which energy addition has a minimum effect on the system changes.

Tab. III. Boltzmann model parametars

Parameter	Value
a_1	0,57 ± 0,08
a_2	8,59 ± 0,09
x_0	3,58 ± 1,40
dx	28,08 ± 7,64
R^2	0,9812

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The value of parameter a_1 would represent the initial theoretical value of the specific surface area of the starting powders, which is not significant for the analysis carried out in this paper. The value of parameter x_0 indicates the time during which the half value of the specific surface area range defined by the model (from 0.5 to 8.58 m^2/g) is reached. Knowing that the experimental value of the specific surface area after 5 min of activation is 7.19m^2/g, the value x_0 seems real.

Conclusion

This research has ascertained that mechanochemical activation has an evident effect on the changes when the system $2MgO-2Al_2O_3-5SiO_2$ is heated to the cordierite sintering temperature. Also, lowering of the cordierite formation temperature during the sintering process occurred. TG analysis has confirmed that during the activation time of 5-240 minutes, mass reduction probably as a result of moisture and carbon dioxide desorption from the surface of the activated samples is 8-12%, which has also been confirmed by FTIR analysis.
BET method has confirmed that there is significant increase of the specific surface area with increase of the activation time. Kinetics of the specific surface area change was analyzed using the Boltzmann model. The velocity constant of the process calculated from this model is 0.0356 min^{-1}, which is slightly higher than the value given in the literature.

On the basis of the experimental results, it may be assumed that by introducing energy by mechanochemical activation into the system, the comminution of particles was realized first, and after this period, the introduced energy was used for the changes within the crystal structure, which resulted in the appearance of defects, initially on the surface of the crystal lattice, and then inside. Dislocations and other defects of the lattice are the centers of further changes in the system.

Assuming that potential centers for further transformations are created with the application of mechanochemical activation, then it is reasonable to expect lower sintering temperatures in order to obtain the desired product. From the triad aspect *synthesis-structure-properties,* additional synthesis parameters as well as their effect on the properties of the investigated material should be analyzed. Materials with familiar properties may be obtained only with the combination of synthesis and with the knowledge of the structure of the familiar material.

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Садржај: *Синтеровањем система 2MgO·2Al₂O₃·5SiO₂, добија се кордијерит, који због својих својстава представља изузетно атрактиван керамички материјал. У циљу испитивања могућности снижења температуре формирања кордијерита током процеса синтеровања, извршена су прелиминарна испитивања механохемијске активације стехиометријске смеше полазних компоненти. Ефекти механохемијске активације су праћени термогравиметријском и диференцијалном термијском анализом. Специфична површина механички активиране смеше прахова је одређивана BET и Coulter методом. Кинетика повећања специфичне површине је анализирана тзв. Boltzmann-овим моделом. Утврђено је да се са повећањем времена активације температуре на којима се уочавају фазне промене померају ка нижим вредностима. FFT IR анализа механохемијски активираног праха након 24 месеци је показала да није дошло до битних промена током „старења" материјала. На основу добијених резултата може се закључити да је механохемијска активација имала утицаја на третирану прашкасту смешу, па се очекује да се овај утицај одрази и на снижење температуре формирања кордијерита током процеса синтеровања.*
Кључне речи: *Кордиерит, кинетика, Болтзманов модел.*