

The influence of activation and relaxation time on the synthesis of cordierite ceramics

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Abstract: Due to its properties, cordierite, $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$, is nowadays an attractive ceramic material for various applications. Mechanochemical activation of the initial components was used in order to decrease the sintering temperature. Changes in the specific surface area of the activated components were determined by the BET method. The TG and DTA methods were used to monitor the temperature induced changes in the analyzed three-component system. The influence of the relaxation time on the activated components was analyzed by FTIR spectroscopy of both the initial components and the activated mixture after 24 h and 24 months relaxation periods.

Keywords: cordierite, sintering, activation.

INTRODUCTION

Cordierite, ($2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$), ceramics have excellent thermal shock resistance, as well as low relative permittivity (≈ 5)¹ and low thermal expansions ($20\cdot 10^{-7}/^\circ\text{C}$). These properties make cordierite suitable for a wide range of high-temperature applications,² as well as in semiconductor production,³ *etc.* Cordierite can be used for various microelectronic components and applications in mechanical engineering.⁴

However, cordierite is difficult to sinter due to its very narrow range of sintering temperatures (1300–1400 °C). The thermodynamic principles of the kinetics of the syntheses of cordierite ceramics are given in the literature.⁵ The aim of this research was to decrease the sintering temperature of cordierite, and to reproducibly produce standard high quality material. The influence of mechanochemical activation on the initial mixture (caoline (Al_2O_3), quartz (SiO_2) and alkali magnesium carbonate) was analyzed and the results are presented in the literature.^{6,7}

The free surface of the initial powders increased during the mechanochemical activation and changes in the structure of the material were induced by the mechan-

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ical energy. These changes have a direct influence on properties which depend on structure, mass transport and reactivity. Due to these changes, it was necessary to analyze the possible effects and influence of the mechanical tension on the reactivity of the components during the solid-state reactions.

Mechanochemically activated samples have more accumulated energy compared to the inactivated initial components. Bearing this in mind, it was important to analyze the possible chemical changes of the activated system after certain periods of time (relaxation period) as they could have an influence on the kinetics of the sintering process. The accumulated energy can induce surface and bulk chemisorption of components in the atmosphere. If no changes of an activated sample occurred during the relaxation time, then a mechanochemically activated sample can be sintered after an unlimited period of time. FTIR Spectroscopy was used to evidence changes in the samples occurring during the relaxation time.

In this work mechanochemical energy was used to activate initial cordierite mixtures containing MgO, Al₂O₃ and SiO₂ in the ratio 2:2:5. TG and DT analyses were used to monitor the influence of the mechanical energy on attrition of the initial components and the possible occurrence of solid-state reactions in the system.

EXPERIMENTAL

The following oxides of technical quality were used in this research: MgO (98.60 %), Al₂O₃ (99.19 %) and SiO₂ (96.10 %). The system 2MgO+2Al₂O₃+5SiO₂ was mechanochemically activated for 5, 15, 30, 60, 120 and 240 minutes (samples marks A1–A6, respectively), in a laboratory scale, cylindrical ceramic ball mill (VEB, model 13×10.5).

The specific surface area changes as a function of activation time were determined by the BET method. Non-isothermal thermogravimetry (TG) and differential thermal analysis (DTA) were used to monitor the influence of mechanical activation on the samples. For this purpose, a METZSCH DTA instrument was employed in the temperature range 20 to 1500 °C, at a heating rate of 10 °C/min.

The effect of relaxation, *i.e.*, aging effect, of the activated cordierite mixture on the sintering processes was monitored by activating the initial cordierite mixture for 120 minutes and analyzing the mixture 24 hours and 24 month after the activation by FTIR spectroscopy. The purpose of this analysis was to identify possible chemical changes of the activated surface of the components in the mixture and also possible structural changes. To compare the results, a non-activated sample (zero sample) was analyzed under the established methodology,⁸ especially the components which exhibited the largest changes during mechanochemical activation (MgO and Al₂O₃).

RESULTS AND DISCUSSION

The results obtained by the BET method showed that the specific surface of the cordierite powder mixture (2MgO+2Al₂O₃+SiO₂) changed as a function of activation time. The sample activated for 5 min had a specific surface area of 7.19 m²/g, while the sample activated for 240 min had a specific surface area of 8.45 m²/g. The changes of the specific surface as the function of the activation period are shown in Fig. 1, from which it can be seen that the size of the particles decreased and the specific surface of the activated powders increased with time of mechanochemical activation, especially during the first 120 min. Longer activation resulted in only a small increase in the specific surface area.

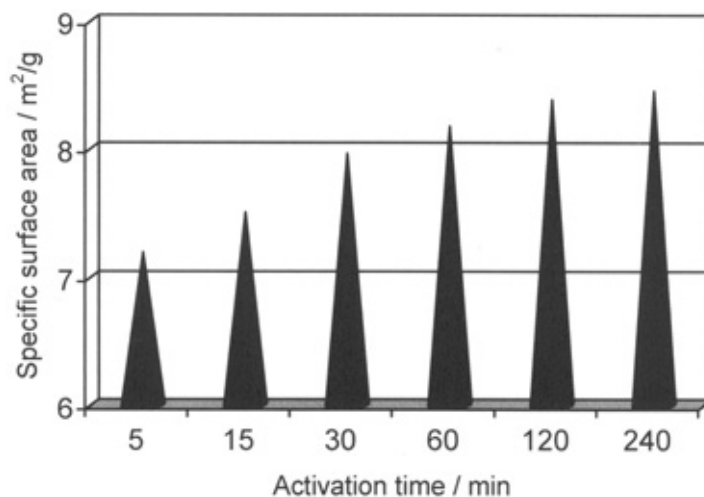


Fig. 1. Specific surface changes of the cordierite mixture as a function of the time of mechanochemical activation.

The obtained experimental results of the changes in the specific surface the activated cordierite mixture can be expressed by the following kinetic equation:

$$(S_{\infty} - S)/(S_{\infty} - S_0) = \exp(-kt) \quad (1)$$

where S , S_0 and S_{∞} are the specific surface area of the powder after time t , the starting specific surface area and the final specific surface area, respectively, and k is the rate constant of the activation process, $k = 3.1 \times 10^{-2} \text{s}^{-1}$.

The activated mechanochemical samples showed the presence of magnesium hydroxyl carbonate after 24-month relaxation. This is due to the reaction of humid

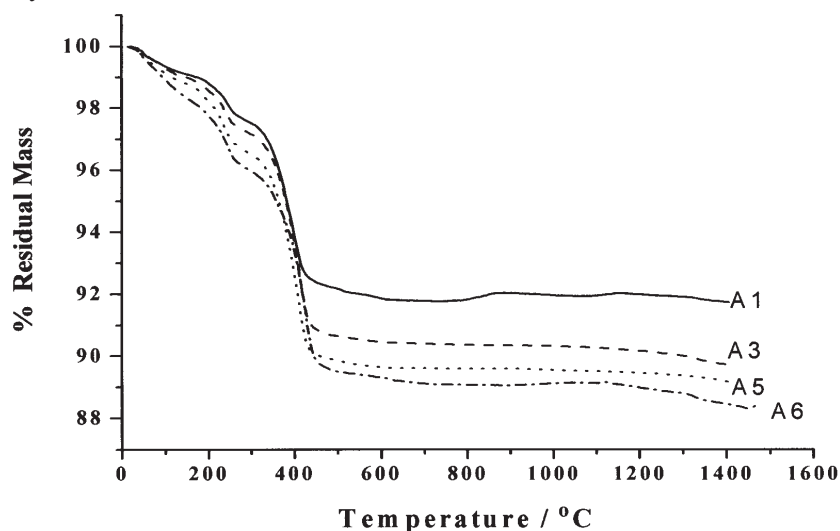


Fig. 2. Non-isothermal TG curves of the cordierite mixture mechanochemically activated for different periods of time.

air with MgO from the activated mixture of cordierite. In this case, the relaxation time should be minimal and the initial cordierite mixture should be activated just before the sintering process.

The samples activated 5, 30, 120 and 240 min (A1, A3, A5 and A6) were allowed to relax for 24 months. Non-isothermal TG analysis showed that all these samples had rapid loss of mass at a temperature of about 400 °C and that the mass loss increased with increasing activation time, Fig. 2.

Three mass loss steps are visible on the TG curves. The first step occurred at temperatures up to 100 °C, which indicates loss of humidity, amounting to a mass loss of $\approx 1\%$ for all samples. The second mass loss step occurred in the temperature range of 230 °C to 300 °C. Preliminary research showed that this mass loss corresponded to the dehydration of $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. The mass loss was in the range from 1 % to 3 %, depending on the activation time. Third step is very rapid and represents the largest mass changes in the system. It occurred in the temperature range from 390 °C to 420 °C, which is the temperature range of the decomposition of magnesium hydroxyl carbonate. The mass loss in step 3 was 4 % for the sample activated for 5 min and 6 % for the sample activated for 240 min.

The overall mass loss at 500 °C of the examined samples as a function of the activation time is presented in Fig. 3. The total mass loss increased with increasing activation time and was in the range of 8 to 12 %, depending on the sample.

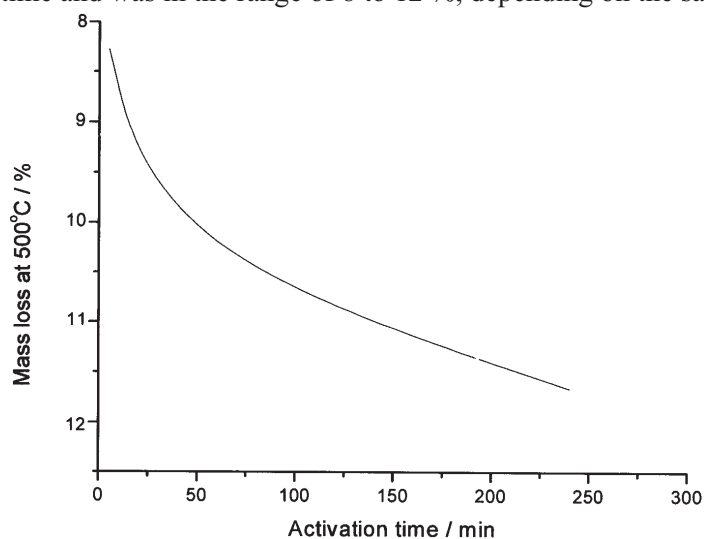


Fig. 3. Total mass loss at 500 °C as a function of activation time.

DTA was used to investigate the changes in the activated cordierite system during the sintering process at temperatures up to 1600 °C. The samples activated for 5, 60 and 120 minutes were used for this examination.

The DTA curves, Fig. 4, show large effects up to the temperature of 400 °C, while all the samples showed similar behavior up to the temperature of 600 °C. As

with the TG analysis, three characteristics peaks are visible. The first up to 100 °C, resulting from loss of humidity, the second in temperature range from 230 to 300 °C from dehydration of $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ and the third in the range from 390 to 420 °C from the decomposition of magnesium hydroxyl carbonate.

Indications of the commencement of cordierite formation were detected in the temperature range of 1200–1400 °C for the initial mixture. The corresponding endothermic and exothermic effects were shifted to lower temperatures with increasing duration of mechanical energy activation.

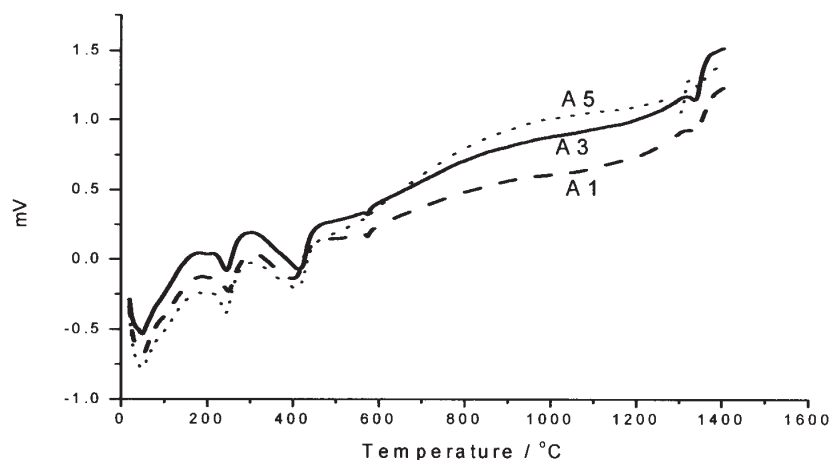


Fig. 4. DTA Curves of the starting cordierite mixture activated for 5, 60 and 120 min.

Analysis of the derivative of the DTA curve of the sample after a relaxation time of 24 months, Fig. 5, showed very rapid changes below 600 °C, which indicate transformation reactions in the system at these temperatures. The endothermic change at 1315 °C, indicating the transformation temperature in the sintering process, is clearly visible.

The temperature change of the endothermic effect in the cordierite sintering process from the initial cordierite mixture as the function of the duration mechanochemical activation is presented Fig. 6. The curve is S-shaped with two plateaus, which are separated by a region of significant changes in the system. The transformation model indicates that the temperature of cordierite sintering decreases with increasing activation time.

The first plateau lasts to 50 min of activation, indicating that the changes in the system in this time period were not high enough to have any influence on the sintering process. From 50 to 160 min of activation, the changes in the reaction system have the effect of decreasing the sintering temperature. In this range of activation times, it can be seen that the mechanochemical activation had an influence on the kinetics of cordierite sintering, *i.e.*, the activity of the sample increased with increasing activation time. The mechanical energy was used not only for particle attrition, but also for increasing the active surface of the particles. This accumulated energy has influence on the affinity of the components to interact with each other at lower temperatures than in the non activated systems.

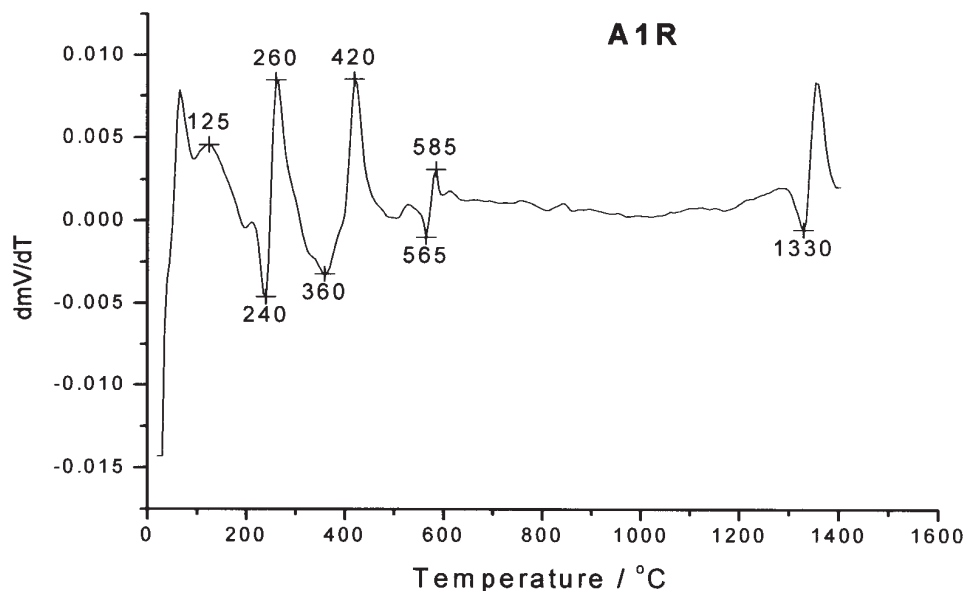


Fig. 5. Differential DTA curve for the sample activated for 5 min.

After this period of large change, a second plateau appeared when the reactivity of the system ceased to change. Further energy input due to mechanochemical activation results in no significant increase in the reactivity of the system and, hence, there was no further decrease in the cordierite sintering temperature. Thus, prolonging the milling would have no effect.

The temperature decrease of the endothermic and exothermic effects can be described by kinetic equations similar to Eq. (1):

$$(T_k - T_\infty)/(T_0 - T_k) = \exp(-mt) \quad (2)$$

where T_k is the characteristic endothermic or exothermic temperature effect, m – the coefficient of the process, $m_I = 1.5 \times 10^{-2} \text{ s}^{-1}$, $m_{II} = 5 \times 10^{-2} \text{ s}^{-1}$, respectively. The endothermic effect favors the transformation of β -quartz to α -quartz, while the exothermic effect results from solid-state reactions between MgO and SiO₂, resulting in the formation of forsterite.

FTIR spectroscopy was used to analyze eventual chemical changes of the activated cordierite mixture during the relaxation time (ambient conditions for up to 24 months). The IR spectra of a sample activated for 120 min after relaxation for 24 h and after 24 months are shown in Fig. 7.

From the spectra shown in Fig. 7, it can be seen that hydroxyl and carbonate-magnesium compounds were present as impurities in the mixture. The characteristic peaks of bound crystal water are sharp at the wavenumbers 3445 cm⁻¹, 3512 cm⁻¹ and 3649 cm⁻¹. The carbonates are visible at wavenumbers 1425 cm⁻¹ and 1485 cm⁻¹, which indicates that the compounds are only impurities due to

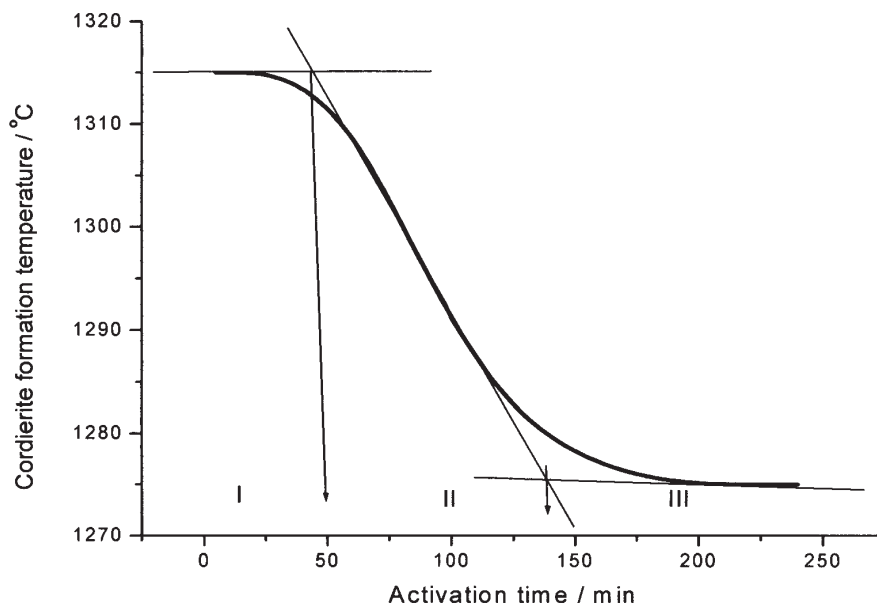
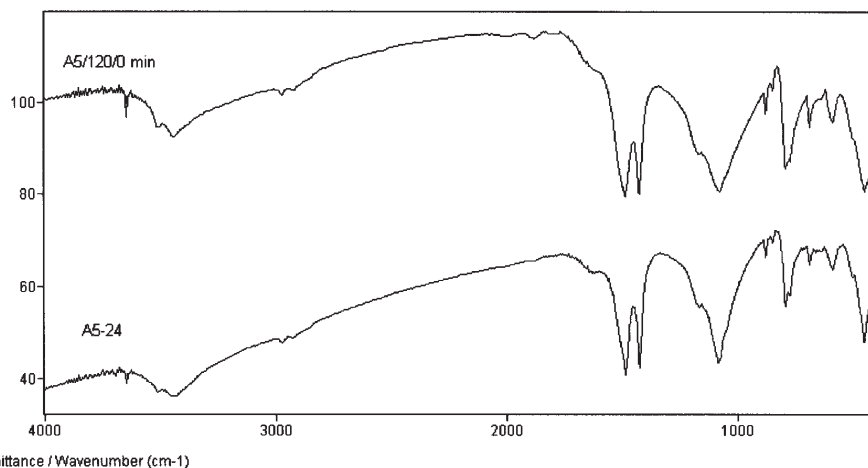


Fig. 6. Temperature changes of the endothermic effect in the process of cordierite sintering as a function of the activation time.

bound water and carbon dioxide, originating from the atmosphere. Since the initial components are well defined, it is supposed that this analysis proves surface adsorption of humidity and CO_2 from atmosphere, which resulted in the formation of unstable compounds of hydromagnesite. The IR spectrum of Al_2O_3 shows the existence of $-\text{OH}$ groups at 3443 cm^{-1} , the origin of which is air humidity. These results are to be expected since in all experiments technical quality components were used. A relaxation period of 24 months had no influence on the sample, since no noticeable changes were visible in the IR spectrum of this sample.



Transmittance / Wavenumber (cm^{-1})

Fig. 7. FTIR Spectra of sample A5 after relaxation for 24 h and 24 months.

CONCLUSIONS

The results of an investigation of the mechanochemical activation of a powder mixture initially consisting of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ in the ratio 2:2:5 have been presented. With increasing duration of mechanochemical activation, the value of the specific surface area of the activated samples increased from $7.19 \text{ m}^2/\text{g}$ for the sample activated 5 min to $8.45 \text{ m}^2/\text{g}$ for the mixture activated for 240 min. The increase was not linear with activation but S-shaped, with a plateau from 0 to 50 minutes and another one from 120 to 240 minutes.

TG Analyses of the initial cordierite mixture activated for 5 to 240 min showed mass losses at 400°C of from 8 to 12 %, depending on the time of activation. The mass loss occurred in three stages, due to humidity loss (up to 100°C), dehydration (240°C) and decomposition of the formed hydroxymagnesite (400°C). This was proved by FTIR spectroscopy. The mass loss registered by TG analysis had no influence on the further process of cordierite synthesis at sintering temperatures above 1250°C .

DTA proved that the influence of mechanochemical activation of the initial components was caused by an increase in energy of the initial cordierite mixture, which resulted in the endothermic and exothermic sintering reactions being shifted to lower temperatures. The decreasing of these temperatures was about 100°C , depending on the activation time.

IR Analyses showed that relaxation had no influence on the activated mixtures. It can be concluded that the mechanochemically-activated samples did not change at all up to the moment of sintering, regardless of the activation time. The presented spectra explain the mass losses at the temperatures of 240 and 400°C registered on the TG curves, *i.e.*, less-stable compounds (hydroxide and carbonate bonded to hydroxymagnesite) were generated during mechanochemical activation.

ИЗВОД

УТИЦАЈ АКТИВАЦИЈЕ И ВРЕМЕНА РЕЛАКСАЦИЈЕ НА СИНТЕЗУ
КОРДИЈЕРИТНЕ КЕРАМИКЕ

НАТАША ЂОРЂЕВИЋ и ЉУБИЦА ПAVЛОВИЋ

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Кордијерит, $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$, због својих својстава представља изузетно атрактиван керамички материјал. У циљу снижења температуре синтеровања, користи се метода механохемијске активације полазних компоненти. Повећање специфичне површине активираних полазних компоненти је праћено ВЕТ методом. Понашање трокомпонентног система праћено је методом TG и DTA. У циљу утврђивања утицаја времена релаксације на полазну кордијеритну смешу извршена је FTIR анализа појединачних полазних компоненти, као и механохемијски активираних кордијеритних смеша након 24 сата и 24 месеца од тренутка активације.

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