UTICAJ VREMENA RELAKSACIJE AKTIVIRANE SMEŠE NA SINTEZU KERAMIKE ZA NAMENU U ELEKTRONICI

IMPACT OF RELAXATION TIME OF ACTIVATED MIXTURE ON CERAMICS SYNTHESIS FOR ELECTRONICS PURPOSES

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Zahvaljujući svojim svojstvima, kordijerit, $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$, danas je atraktivan keramički materijal za razne primene, ali sa vrlo visokom temperaturom sinterovanja. Mehanohemijska aktivacija smeše početnih komponenti izvedena je da bi se snizila temperatura sinterovanja. DTA metoda je korišćena za praćenje temperaturnih promena u analiziranom trokomponentnom sistemu. Kako je ranijim istraživanjima utvrđeno da vreme relaksacije može da utiče na aktivirane komponente u smislu hemijskih promena i stepena aktiviranosti, bilo je značajno utvrditi ima li uticaj i na posmatrani aktivirani system. Uticaj vremena relaksacije na smešu aktiviranih komponenata analiziran je FT IR spektroskopijom i početnih komponenti i aktivirane smeše nakon 24h i 24 meseca perioda relaksacije.

***Ključne reči**: kordierit; sinterovanje; mehanohemijska aktivacija; DTA; FT IR*

Due to its properties, cordierite, $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$, is nowadays an attractive ceramic material for various applications but with very high sintering temperature. Mechanochemical activation of the initial components mixture was performed in order to decrease the sintering temperature. DTA method was used to monitor the temperature induced changes in the analyzed three-component system. Since previous research has pointed out that the relaxation time can influence the activated components in terms of chemical changes and the activation degree, it was important to determine whether it has an impact on the observed activated system. The influence of the relaxation time on the activated components mixture was analyzed by FT IR spectroscopy of both the initial components and the activated mixture after 24h and 24 months relaxation periods.

***Key words:** cordierite; sintering; mechanochemical activation; DTA; FT IR*

1 Introduction

Cordierite, one of the most important phases of the MgO-SiO_2-Al_2O_3 system, has a low thermal expansion coefficient, excellent thermal shock resistance, low dielectric constant, high volume resistivity, high chemical durability, and relatively high refractoriness and mechanical strength. This ceramic material is widely used in electronics, for honeycomb-shaped catalyst carriers in automobile exhaust systems, substrate material in integrated circuit boards, and also as a refractory material, owing to its stability at high temperatures [1–3].

Cordierite ceramics can be prepared by conventional sintering methods, but it is difficult to sinter cordierite because of the narrow and sintering range (1300-1400 ºC) just below its incongruent melting point [4–6]. The preparation of a homogeneous and fine cordierite powder that can be produced without sintering aids is considered to be highly desirable, due to the limiting factors of additives [7–15]. The thermodynamic principles of the kinetics of the syntheses of cordierite ceramics are given in the literature [5].

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 can have an

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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.

The aim of this research is to decrease the sintering temperature of cordierite by mechanochemical activation of the initial mixture (caoline (Al_2O_3), quartz (SiO_2), and alkali magnesium carbonate). The free surface of the initial powders increases during the mechanochemical activation and changes in the structure of the material are induced by mechanical energy. The influence of the relaxation time of this mechanochemicaly activated mixture on the sintering of cordierite ceramics was investigated.

2 Experimental

In this research the next initial raw materials of technical quality were used: MgO (98.60%), Al_2O_3 (99.19%) and SiO_2 (96.10%). The mixture composed of powdered MgO, Al_2O_3 and SiO_2 in the ratio 2:2:5 was mechanochemically activated for 5, 15, 30, 60, 120 and 240 minutes (samples marked with A1-A6, respectively), in a laboratory cylindrical ceramic ball mill (VEB, model 13x10.5). 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 1500ºC, at a heating rate of 10ºC/min.

The effect of relaxation, i.e. aging, of the activated cordierite mixture on the sintering processes was monitored by analyzing the mixture activated for 120 min using FT IR spectroscopy. FFT infrared spectra of the samples were recorded on an FFT IR spectrometer BOMEM-HARTMAN & BRAUN MICHELSON MB-100, in the range of wave numbers 4000-300 cm^{-1} at a resolution of 2 cm^{-1}. Since the samples are very sensitive to the presence of moisture, the method of making a suspension with "NuJol" was used to prepare the samples. The purpose of this analysis was to identify possible chemical changes on the activated surface of the components in the mixture as well as structural changes. A non-activated sample (zero sample) was also analyzed by the same chosen methodology [8] and the obtained results were compared.

3 Results and discussion

DTA method 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 chosen for this examination.

The obtained DTA curves are presented in Figure 4.

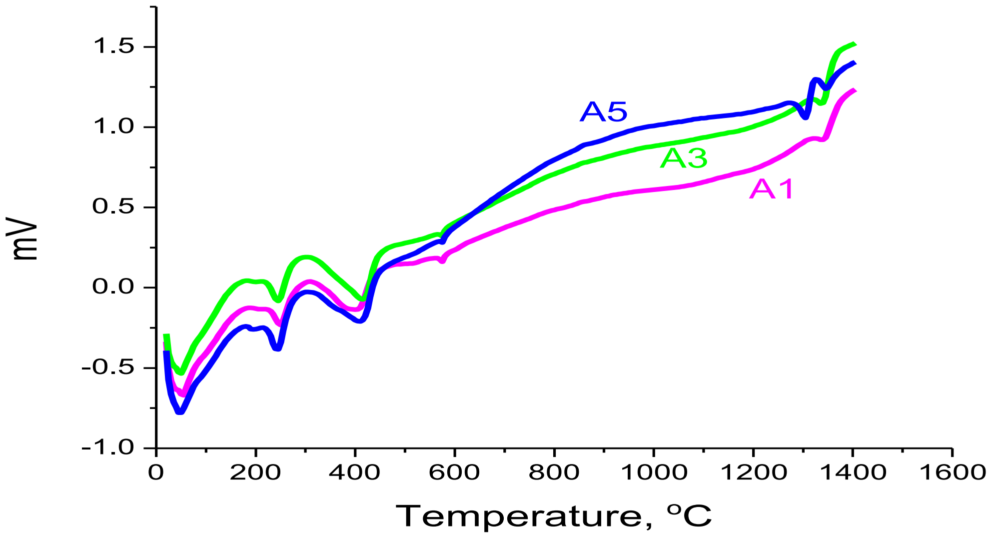

Figure 4. DTA curves of the cordierite mixture activated for 5, 60 and 120 minutes.

As seen in Figure 4, all investigated samples exhibite significant changes up to the temperature of 400 °C, while all the samples behaved quite similarly up to the temperature of 600 °C. Three characteristic peaks are visible: The first peak is up to 100 °C, resulting from loss of humidity. The second in temperature range from 230 to 300 °C which corresponds to the dehydration of $MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, and the third peak in the range from 390 to 420 °C and it can be attributed to 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 activation.

Derivative of the DTA curve of the sample activated for 5 minutes after a relaxation time of 24 months is presented in Figure 5.

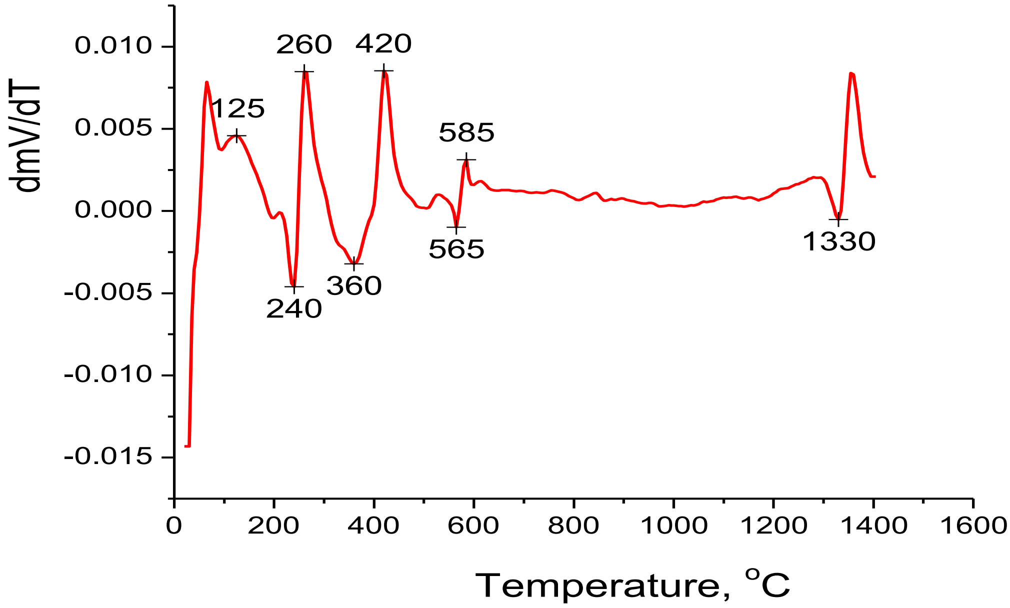

Figure 5. Derivative of the DTA curve for the sample activated for 5 minutes.

By analyzing the curve in Figure 5 it can be noticed that very rapid changes are taking place below the temperature of 600 °C. This indicates transformation reactions in the system at these temperatures. The clearly visible endothermic change at 1315 °C indicates the transformation temperature in the sintering process.

The temperature change of the endothermic effect in the cordierite sintering process from the initial cordierite mixture as a function of the mechanochemical activation duration is presented Figure 6.

As seen in Figure 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 minutes of activation, indicating that the changes in the system in this time period were not pronounced enough to have any influence on the sintering process. From 50 to 160 minutes of activation, the changes in the reaction system cause 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 an influence on the affinity of the components to interact with each other at lower temperatures than in the non-activated systems.

After this period of 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.

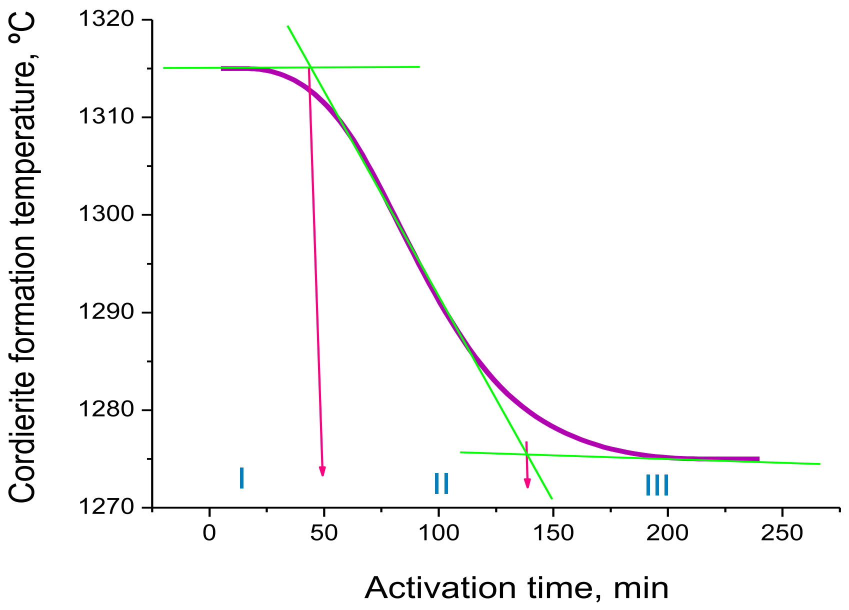

Figure 6. Temperature changes of the endothermic effect in the process of cordierite sintering as a function of the activation time

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

$$(T_k - T_\infty) / (T_o - T_k) = \exp(-mt) \qquad (1)$$

where T_k is the characteristic endothermic or exothermic temperature effect, m is the coefficient of the process, $m = 1.5 \cdot 10^{-2} s^{-1}$. The endothermic effect favors the transformation of β-quartz to α-quartz, while the exothermic effect results from solid-state reactions between MgO and SiO_2, resulting in the formation of forsterite.

FT IR 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 minutes after relaxation for 24 hours and after 24 months are shown in Figure 7.

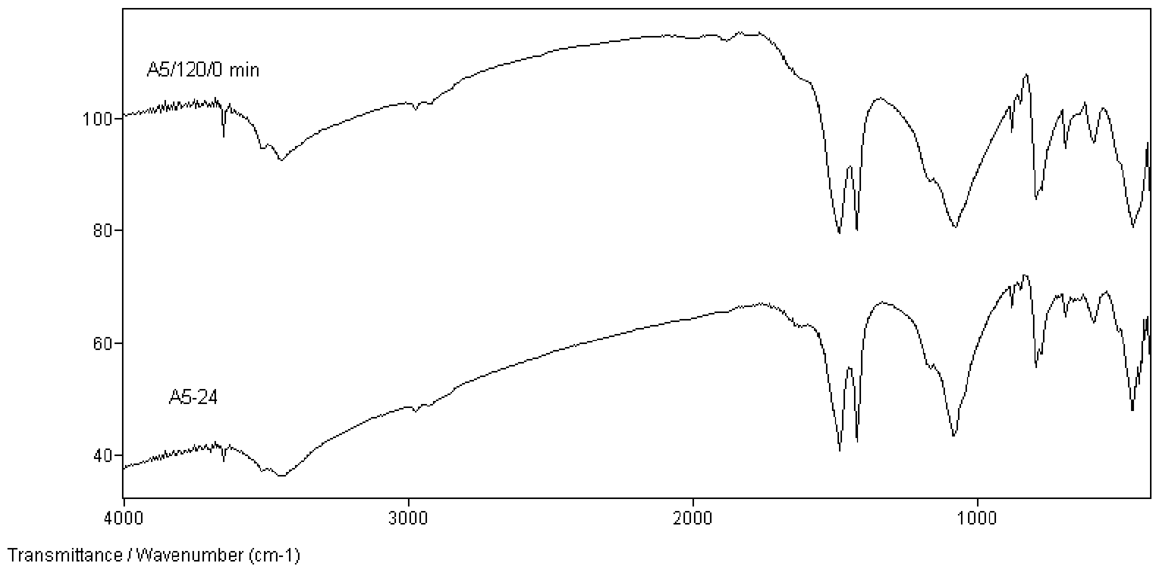

Figure 7. FT IR spectra of sample A5 after relaxation for 24 hours and 24 months.

From the spectra shown in Figure 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 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 the atmosphere, which resulted in the formation of unstable compounds of hydromagnesite. The IR spectrum of Al_2O_3 shows the existence of –OH groups at 3443 cm^{-1}, the origin of which originated 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.

4 Conclusions

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 decrease in these temperatures was about 100°C, depending on the activation time.

FT IR analyses showed that relaxation time 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, i.e., less-stable compounds (hydroxide and carbonate bonded to hydroxymagnesite) were generated during mechanochemical activation.

Acknowledgments

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