UTICAJ MEHANOHEMIJSKE AKTIVACIJE KOMPONENTI NA SINTEZU KORDIJERITNE KERAMIKE ZA PRIMENU U ELEKTRONICI

INFLUENCE OF MECHANOCHEMICAL ACTIVATION OF COMPONENTS ON SYNTHESIS OF CORDIERITE CERAMICS FOR APPLICATION IN ELECTRONICS

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Kordijerit, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, zbog svojih svojstava predstavlja izuzetno atraktivan keramički materijal koji se može primeniti u elektronici za različite namene. Kako je temperatura sinterovanja kordijerita veoma visoka (1375 °C), svako sniženje temperature na kojoj se formira kordijerit donosi ekonomski benefit. Zbog toga je u ovom radu primenjena metoda mehanohemijske aktivacije smeše polaznih komponenti za sintezu kordijerita sa ciljem sniženja njegove temperature sinterovanja. Ispitivani su efekti mehanohemijske aktivacije na kordijeritnu smešu. Povećanje specifične površine aktiviranih polaznih komponenti je praćeno BET metodom. TG metoda i gubitak mase primenjeni su za praćenje promena uslovljenih temperaturom u analiziranom trokomponentnom sistemu. Na osnovu dobijenih rezultata, povećanja specifične površine i gubitka mase sa povećanjem vremena aktivacije, očekuje se sniženje temperature sinterovanja kordijerita.

Ključne reči: *kordijerit; sinterovanje; mehanohemijska aktivacija; BET; TG*

The properties of cordierite, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, makes this ceramics nowadays an attractive material, which can be used for various applications in electronics. As the sintering temperature of cordierite is very high (1375 °C), any decrease in the temperature at which cordierite is formed leads to economic benefits. Therefore, in this study, the mechanochemical activation of the initial components mixture for the synthesis of cordierite was applied with the aim to lower its sintering temperature. The effects of mechanochemical activation on the cordierite mixture were investigated. Changes in the specific surface area of the activated components were determined by the BET method. The TG method and mass loss were used to monitor the temperature- induced changes in the analyzed three-component system. Based on the obtained results, increase in specific surface area and weight loss with increasing activation time, a decrease in cordierite sintering temperature is expected.

Keywords: *cordierite; sintering; mechanochemical activation; BET; TG*

1 Introduction

Ceramics based on cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) have excellent thermal shock resistance, low dielectric constant (~5) and low thermal expansion coefficient ($20 \cdot 10^{-7}$/ °C). These properties make cordierite suitable for various microelectronic components, as well as in semiconductor production, for a wide range of high-temperature applications, and applications in mechanical engineering [1-4].

However, cordierite is difficult to sinter due to its very high and 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].

On the other hand, during the mechanochemical activation of the powders, their free surface increases and changes in the structure of the material are induced by the mechanical energy. These

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changes have a direct influence on material properties which depend on structure, mass transport and reactivity.

Mechanochemically activated samples have more accumulated energy compared to the inactivated. Bearing this in mind, it is important to analyze the possible chemical changes of the activated system after certain periods of time (relaxation period) as they can have further 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 occur during the relaxation time, then a mechanochemically activated sample can be sintered after an unlimited period of time. FT IR spectroscopy is used to make evident changes in the samples occurring during the relaxation time [6-15].

In this work mechanochemical energy was used to activate initial cordierite mixtures containing MgO, Al_2O_3 and SiO_2 in the ratio 2:2:5 with the aim to decrease the sintering temperature of cordierite. The influence of mechanochemical activation on the initial cordierite mixture was examined and analysed.

2 Experimental

The following oxides of technical quality were used in this research: MgO (98.60 %), Al_2O_3 (99.19 %) and SiO_2 (96.10 %). A powder mixture composed of oxides MgO, Al_2O_3 and SiO_2 in the ratio 2:2:5 was prepared. The system $2MgO+2Al_2O_3+5SiO_2$ 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).

The effects of mechanochemical activation on this system were investigated by monitoring the specific surface area and mass changes during time.

The specific surface area was determined by BET method. The nitrogen adsorption isotherm was determined by a standard volumetric apparatus at a temperature of -196 ºC. The samples were degasified at 110 ºC for 3 hours. Specific surface area was calculated according to the Brunauer, Emmett, Teller method from the nitrogen adsorption isotherm, using values of $0.05 < p / p0 < 0.3$.

Mass was determined by non-isothermal thermogravimetry (TG) using a NETZSCH DTA instrument with defined operating conditions: temperature range from 20 to 1500 °C, at a heating rate of 10 °C/min.

3 Results and discussion

Specific surface area values of the cordierite mixture during mechanochemical activation, obtained by the BET method, are presented in Figure 1.

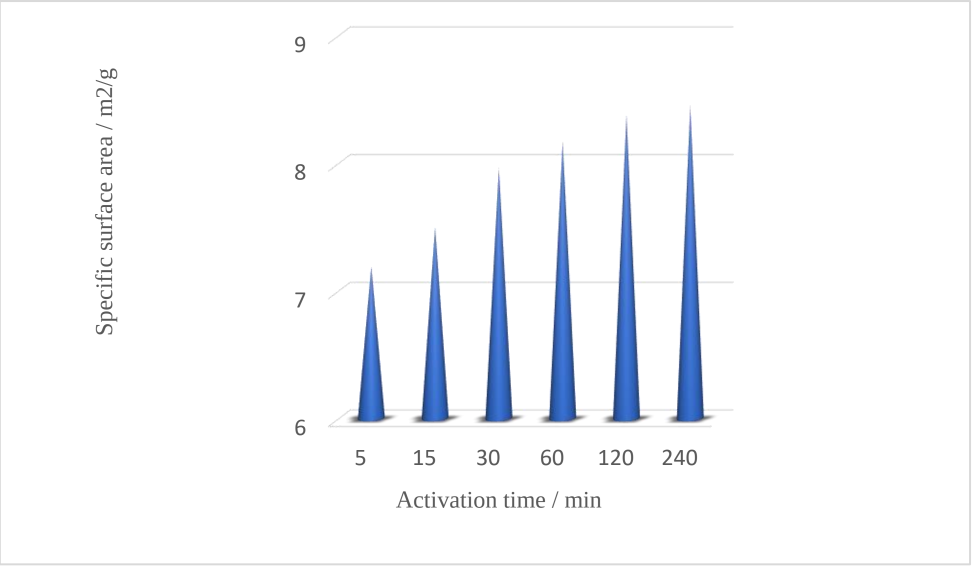

Figure 1. Specific surface changes of the cordierite mixture as a function of the time of mechanochemical activation

The results given in Figure 1 showed that the specific surface of the cordierite powder mixture ($2MgO+2Al_2O_3+SiO_2$) changed as a function of activation time in a way that longer activation time caused higher specific surface area values. The sample activated for 5 min had a specific surface area value of 7.19 m^2/g, while the sample activated for 240 min had a specific surface area of 8.45 m^2/g. This dependence is not linear but S-shaped, with a plateau from 0 to 50 minutes and another one from 120 to 240 minutes.

It can be concluded that the size of the particles decreased and therefore the specific surface of the activated powders increased with time of mechanochemical activation. These changes are especially pronounced during the first 120 minutes. Further activation resulted in only a small increase in the specific surface area.

The obtained experimental results of the changes in the specific surface area of the activated cordierite mixture can be expressed by the following kinetics equation (Eq. 1):

$$(S_\infty-S)/(S_\infty-S_o) = \exp(-kt) \qquad (1)$$

where S, S_o and S_∞ are the specific surface areas of the powder: after time t, the starting specific surface area (before mechanochemical activation), and the final specific surface area (at the end of mechanochemical activation), respectively, and k is the rate constant of the activation process, $k = 3.1\cdot10^{-2}\ s^{-1}$.

The chosen samples, A1, A3, A5, and A6, activated for 5, 30, 120, and 240 minutes, respectively, were allowed to relax for 24 months.

Chemical analysis of mechanochemically activated samples showed the presence of magnesium hydroxyl carbonate after 24-month relaxation. This can be explained by the reaction of hygroscopic MgO from the activated cordierite mixture with humid air. In this case, the relaxation time should be minimal and the initial cordierite mixture should be activated just before the sintering process. It can be concluded that the relaxation time of the mechanochemically activated mixture should be minimal, that is the sintering process have to be performed immediately after activation.

Non-isothermal TG analysis showed that all these samples had a rapid loss of mass at a temperature of about 400 °C and that the mass loss increased with increasing the activation time, Figure 2.

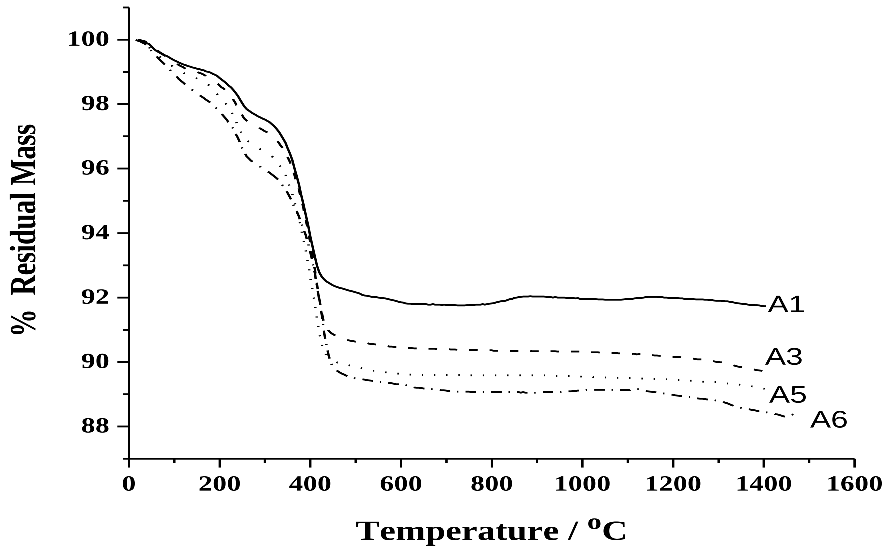

Figure 2. Non-isothermal TG curves of the cordierite mixture mechanochemically activated for different periods of time

Three mass loss steps are visible on the TG curves.

The first mass loss step occurred at temperatures up to 100 °C, which indicates loss of humidity, amounting to a mass loss of ~1 % for all samples.

The second mass loss step occurred in the temperature range from 230 °C to 300 °C. Preliminary research showed that this mass loss corresponded to the dehydration of $MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. The mass loss was in the range from 1 % to 3 %, depending on the activation time.

The third mass loss step is very rapid and represents the greatest mass changes in the system. It occurred in the temperature range from 390 °C to 420 °C, which corresponds to the temperature range of the decomposition of magnesium hydroxyl carbonate. The mass loss in this step was 4 % for the sample activated for 5 minutes and 6 % for the sample activated for 240 minutes.

The overall mass loss of the examined samples at a temperature of 400 °C as a function of the activation time is presented in Figure 3.

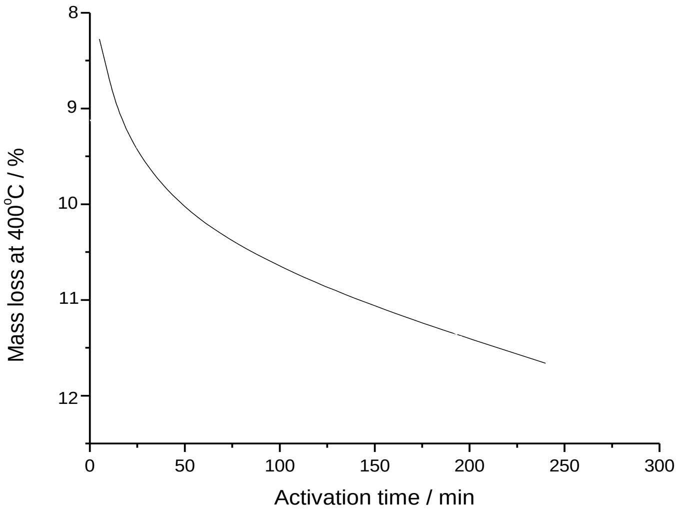

Figure 3. Total mass loss at 400 °C as a function of activation time

As seen in Figure 3, TG analyses of the cordierite mixture activated from 5 to 240 minutes exhibited a total mass loss from 8 to 12 % at 400 °C in a way that mass loss is increasing for longer activation times.

4 Conclusions

The results of an investigation of the mechanochemical activation effects on a powder mixture initially consisting of MgO-Al_2O_3-SiO_2 in the ratio 2:2:5 have been presented. According to the obtained BET method results, with increasing duration of mechanochemical activation, the value of the specific surface area of the samples increased from 7.19 m^2/g for the sample activated 5 minutes to 8.45 m^2/g for the sample activated for 240 minutes. The mass loss, determined by TG method, after relaxation period of 24 months, occurred in three stages: at temperatures up to 100 °C, due to humidity loss; at temperatures about 240 °C, as a result of dehydration; and at temperatures around 400 °C owing to decomposition of the formed hydroxymagnesite. The total mass loss at a temperature of 400 °C increased from 8 to 12 % with increasing the activation time. Based on the obtained results, using mechanochemically activated cordierite mixture, lowering the sintering temperature of cordierite can be expected. Recommendation is to sinter the mixture as soon as possible after the activation to avoid moisture absorption by MgO.

Acknowledgments

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