

THE INFLUENCE OF MECHANICAL ACTIVATION OF STARTING COMPONENTS ON KINETICS OF CORDIERITE FORMATION

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Abstract

Mechanical activation of simple and complex powder systems is very often used as a method for modification of physico-chemical properties in technologies for obtaining advanced materials.

The present work reports on investigation of cordierite formation from starting powders mixture of basic magnesium carbonate (BMC) and kaolinite. Starting powders mixture were mechanically activated in a high energy vibro-mill. The grinding times were 10, 20 and 40 minutes. Amorphization process of starting compounds in mixtures and phase transformations during supplementary thermal treatment were examined by X-ray powder diffraction (XRPD).

Differential thermal analysis (DTA) is a convenient method for investigating chemical thermodynamics and formal kinetic descriptions of physico-chemical processes. Formal kinetic analysis of cordierite formation in non-isothermal conditions were excersited using kinetic theory in stacionary point according to Kissinger and Ozawa method. Set of DTA measurements with different heating rate of 10, 15, 20 and 30 K/min were used for determining activation energy of cordierite formation from the starting amorphous material.

Keywords: mechanical activation, non-isothermal kinetics, DTA, XRPD, cordierite

1. Introduction

Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) and cordierite based ceramics are well known for their low dielectric constant, low coefficient of thermal expansion, high thermal and chemical stability, and very good mechanical properties [1-4]. These properties enable many possibilities for wide applications.

Mechanical activation of initial powders is one of various methods used for lowering sintering temperature and time of solid state reaction synthesis [5]. It is also a method often used for the synthesis of cordierite. Mechanical treatment by grinding increases the number of contacts between powder particles, and process of generation and migration of defects occur where their mobility could be sufficient for the intensification of diffuse-controlled processes [4, 5].

There are many studies on the kinetics of various solid state reactions and phase transformation using differential thermal analysis (DTA) [6-8]. The present work reports on investigation concerning the influence of mechanical activation on cordierite formation during thermal treatment of basic magnesium carbonate (BMC) and kaolinite mixtures.

2. Experimental

Mixtures of natural kaolinite (Zettlitz, Czech Republic) and BMC (ITNMS, Yugoslavia) were used in experimental procedure as starting powders. The chemical composition of raw materials is shown in Table I. Mechanical activation was performed by grinding (dry) in a continual regime in a vibro-mill with steel rings (CUP Mill Typ MN 954/3 KHD HUMBOLDT WEDAG AG) in air (steel vessel volume was 500cm^3 , and the quantity of grinding powders was 50g). The grinding times were 10, 20 and 40 minutes and corresponding mixtures were K-KM-10, K-KM-20 and K-KM-40, respectively. The mixed powders were pressed at 1 t/cm^2 into cylindrical compacts with 8 mm in diameter. Heating in isothermal conditions was carried out in a furnace (Lenton Tube furnace LTF) at temperature of 1523 K for 120 minutes in air.

Table 1. Chemical composition of raw materials

Contents	Composition (mass%)	
	kaolinite	BMC
SiO ₂	49.15	<0.02
Al ₂ O ₃	36.03	<0.04
Fe ₂ O ₃	0.45	<0.04
TiO ₂	0.20	-
CaO	-	0.36
MgO	0.50	-
K ₂ O	0.43	-
Na ₂ O	0.06	-
MgCO ₃ ·Mg(OH) ₂ ·3H ₂ O	-	99.53
Ignition loss	13.16	-
Total	99.98	99.99

The crystal phases and crystalline structure in mechanically activated mixtures and thermally treated samples were revealed by X-ray powder diffraction (XRPD) using Philips PW-1710 Automated Diffractometer with CuK_α radiation ($\lambda=1.54178\text{\AA}$) with the step-scanning mode of 0.02°/0.25s. XRPD data were collected at room temperature in the 2 θ range of 5° – 70°.

The monitoring of cordierite formation was carried out with powder samples under non-isothermal conditions up to temperature of 1473K. The differential thermal analysis was performed using Shimadzu DTA-50 analyser in order to evaluate the kinetic parameters of cordierite formation. DTA curves was recorded using heating rate of $\beta=10, 15, 20$ and 30 K/min in nitrogen dynamic flow atmosphere. The decomposition behaviour of starting materials was also examined by DTA.

3. Results and Discussion

Fig. 1a-c presents X-ray diagrams of mechanically activated powder mixtures of K-KM-10, K-KM-20 and K-KM-40, respectively. Qualitative X-ray diffraction analysis showed the similar crystal phase composition. The presence of kaolinite, quartz and BMC was detected for

all examined samples. Also, XRPD patterns clearly distinguish the existence of the rising amorphization trend of present crystal phases. The amorphization process is in direct proportion to the time of powders grinding, and therefore the K-KM-40 mixture is the most amorphous one. The higher level of amorphization was noticed for kaolinite and BMC, while quartz was subjected to minor changes.

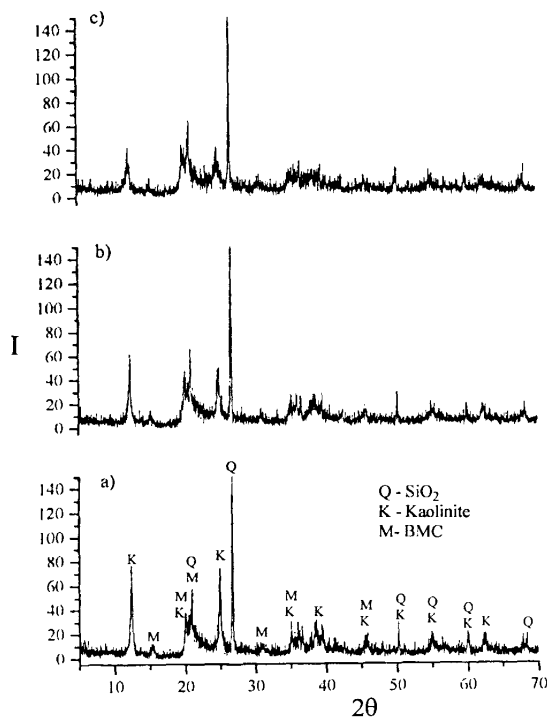


Fig. 1 X-ray patterns of powder mixtures a) K-KM-10, b) K-KM-20 and c) K-KM-40.

X-ray diagrams of thermally treated samples are presented in Fig. 2. Sample mineral content is: α -cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), quartz (SiO_2), corundum (Al_2O_3), spinel (MgAl_2O_4), enstatite (MgSiO_3) and periklase (MgO). The predominant phases are α -cordierite and quartz, and corundum in a smaller amount, while the existence of other phases (spinel, enstatite, periklase) is insignificant. It is important to underline the different quantitative ratios. Namely, the predominant phase of the K-KM-10 sample is α -cordierite, with significantly lower content of other phases

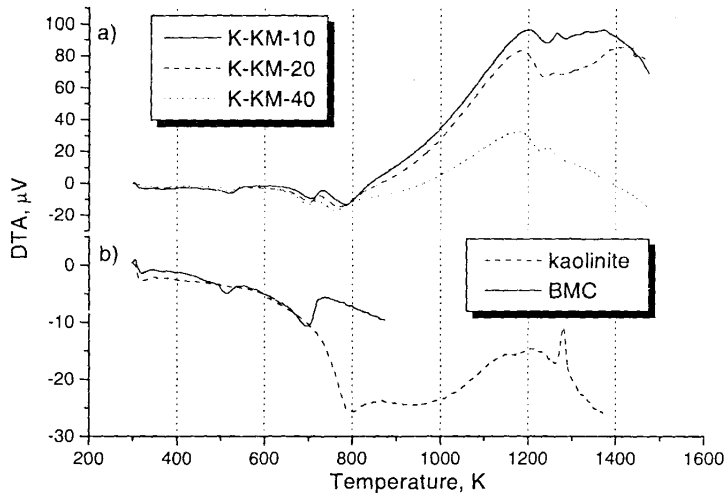


Fig. 3 DTA curves: a) starting mixture and b) raw materials.

The existence of a broad exothermic peak at about 1200 K in all examined mixtures (Fig.3a) point to the formation of μ -cordierite, spinel and enstatite, while the next exothermic one corresponds to the $\mu \rightarrow \alpha$ cordierite transformation [1, 2, 9].

Table II contains the characteristic temperatures obtained by the DTA. It could be seen that temperature of dehydration and decomposition of BMC and kaolinite, and $\mu \rightarrow \alpha$ cordierite phase transition move towards lower values with the increase of grinding time.

Table II The results of DTA measurements

Sample	Temperature (K)					
	Dehydration	Decomposition	Dehydration	I exo-effect	Transition $\mu \rightarrow \alpha$	II exo-effect
BMC	513.8	697.2	-	-	-	-
kaolinite	-	-	795.4	-	-	-
K-KM-10	522.9	709.6	785.6	1203.3	1265.6	1373.6
K-KM-20	518.5	703.9	771.9	1186.5	1262.9	1406.6
K-KM-40	523.5	700.3	762.8	1185.3	1244.1	-

The activation energy of a thermally activated transformation is very important parameter that reflects the nature of transformation. The energy value is obtained by measuring the peak temperature at different constant heating rates and working out the slope of a plot of either $\log(\beta/T_m^2)$ or $\log\beta$ against $1/T_m$. The principles behind these plots were developed by Kissinger [7] and Ozawa [8], respectively. According to the theory, a series of DTA measurements with different heating rates for K-KM-10, K-KM-20 and K-KM-40 mixtures were performed in order to determine the activation energy of α -cordierite formation. For example, the obtained DTA traces for K-KM-10 are presented in Fig. 4. After fitting the data to Kissinger and Ozawa equations using the least square method, the obtained activation energies of α -cordierite formation are presented in Table III. The small differences in activation energies calculated by the Kissinger and Ozawa methods arise from different mathematical approximations used in developing the two methods. Fig. 5 illustrates the plot as a result of the fitting process. Experimental data are in pretty good agreement with the fitted lines, which guarantees correct values of activation energies. It can be seen that the activation energies derived from the different plots using the same data are found to be very close to each other and relative differences are within 5%.

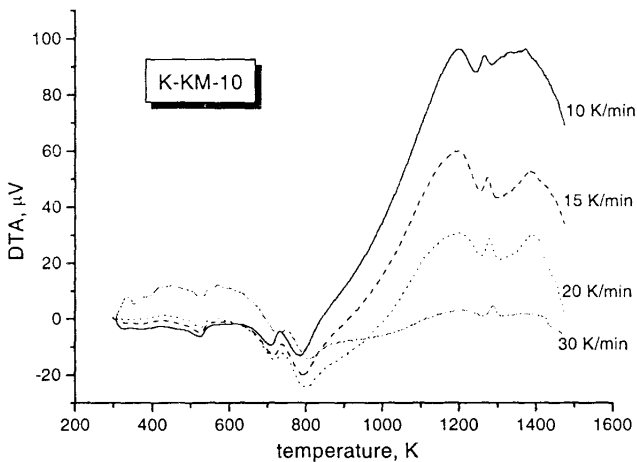


Fig. 4 Series of DTA traces obtained with different heating rates for the K-KM-10 mixture.

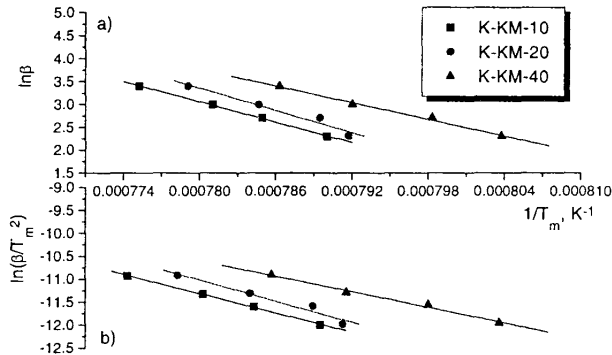


Fig. 5 a) Ozawa and b) Kissinger plots for the cordierite formation process.

The α -cordierite was formed through sequential formation of crystalline cordierite (amorphous $\rightarrow \mu \rightarrow \alpha$). In the synthesis of cordierite, the formation of μ -phase reduced the possibilities of forming other silicate compounds. The highest value of activation energy for cordierite formation was calculated for the K-KM-20 sample, which is given in Table III. The explanation of such behavior could be sample phase composition, i.e. the equal presence of two phases - α -cordierite and quartz.

Table III Calculated values for the activation energy of α -cordierite formation in non-isothermal conditions

Sample	Activation energy (kJ/mol)	
	Kissinger method	Ozawa method
K-KM-10	595	616
K-KM-20	653	674
K-KM-40	486	507

4. Conclusions

It was noticed that during mechanical activation of initial mixtures destruction of components crystal structure occur. Kaolinite and BMC are mostly subjected to amorphization, while changes of quartz structure are insignificant. Characteristic temperatures of dehydration and decomposition of initial components, as well as the temperature of cordierite formation move towards lower values with the increase of the time of mechanical treatment. The phase composition of all samples is the same after thermal treatment at 1520 K, but the quantitative ratio between some phases is different. The dominant phase for K-KM-10 and K-KM-40 sample is α -cordierite, while the K-KM-20 sample contains equal amounts of α -cordierite and quartz. Activation energies for the formation of cordierite were calculated according to Kissinger and Ozawa methods. The highest value of activation energy obtained for the K-KM-20 sample point to the conclusion that the formation of α -cordierite is hindered in this sample.

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