

# Influence of Mechanical Activation on the Constituents of the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> System

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Original scientific paper

UDC: 669.75.018.15:620.17=20

*In this paper the effects of mechanical activation on structural and microstructural changes of the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> were analyzed. It was confirmed that mechanical activation led to the homogenization of powder particles, the comminuting of particles, and after this period, the introduced energy was used to induce changes in the crystal structure, which resulted in the emergence of defects, initially on the surface of the crystal lattice, and then inside.*

**Key words:** mechanical activation, cordierite, TiO<sub>2</sub>

## 1. INTRODUCTION

Cordierite-based ceramics (2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) has a very low temperature thermal expansion coefficient ( $20 \cdot 10^{-7}/^{\circ}\text{C}$ ), low dielectric constant (~5), and also is a material well known by its good mechanical properties [1]. Therefore, it can be applicable as a material that is exposed to sudden temperature changes [2-6] and also as a semiconducting bearer [7,8]. Temperature diapason of cordierite sintering is very narrow (1300-1400 °C).

The goal of many investigations was to lower the sintering temperature of cordierite ceramics. Oxides of boron, phosphorus, titanium and bismuth, whose atomic radius is big enough not to incorporate the crystal lattice of cordierite, were added in order to decrease the sintering temperature [9].

Preliminary investigations showed a significant influence of mechanical activation of starting components (kaolin, quartz, magnesium carbonate) on sintering processes increase the chance that during heating, processes could be observed at lower temperatures than usual [11]. Furthermore, mechanical activation could affect the final electrical characteristics, so it is very important to meet and understand changes that get introduced into the system while milling.

## 2. EXPERIMENTAL PROCEDURE

Mixtures of MgO (98.60 %, Euro Hemija), Al<sub>2</sub>O<sub>3</sub> (99.19 %, Aluminijumski kombinat, Podgorica), SiO<sub>2</sub> (96.10 %, Bela Reka), Bi<sub>2</sub>O<sub>3</sub> (99.98 %, Reahim) and TiO<sub>2</sub> (p.a.) were used in these experiments. The mixture of MgO+Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub> in the 2:2:5 ratio, with the addition of 5.00 mass% TiO<sub>2</sub>, was mechanically activated by grinding in a high-energy planetary ball mill. ZrO<sub>2</sub> vessels and balls were used with the powder to balls mass ratio of 1:40. The milling process was performed in air for 10, 20, 40 and 80 minutes. The samples were denoted as K-0 to K-80, according to the milling time.

The X-ray powder diffraction patterns after milling and sintering were obtained using a Philips PW-1050 diffractometer with  $\lambda\text{Cu-K}\alpha$  radiation and a step/time scan mode of 0.05 °/1 s.

The average particle size, particle size distribution, and the nature of agglomerates were determined by a particle size analyzer (PSA). The used instrument was Mastersizer 2000 (Malvern Instruments Ltd., UK) particle size analyzer based on laser diffraction, covering the particle size range of 0.02-2000  $\mu\text{m}$ . For the PSA measurements, the powders were dispersed in distilled water, in ultrasonic bath (low-intensity ultrasound, at a frequency of 40 kHz and power of 50 W), for 5 minutes.

The DTA measurements were performed with a SHIMADZU DTA-50 apparatus. About 10 mg sample

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Paper received: 12.04.2012.

was used for DTA testing and  $\alpha$ - $\text{Al}_2\text{O}_3$  powder as the reference sample. The heating temperature range was from room temperature to 1100 °C at heating rates of 10 °C/min. The measurements were carried out in nitrogen flow at the rate of 20 ml/min.

### 3. RESULTS AND DISCUSSION

Diffraction pattern for K-0 mixture showed the presence of starting components ( $\text{Mg}(\text{OH})_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{AlO}(\text{OH})$  and  $\text{TiO}_2$ ). All obtained intensities were identified by JCPDS cards (071-1126 for  $\text{Al}_2\text{O}_3$ , 086-1628 for  $\text{SiO}_2$ , 089-4921 for  $\text{TiO}_2$ , 083-0114 for  $\text{Mg}(\text{OH})_2$ , 074-1879 for  $\text{AlO}(\text{OH})$ ).

No new phases have been detected during mechanical activation. However, most of peak intensities decreased with activation time, while some peaks are broadened which indicates that processes of crystal lattice destruction and amorphization have started. Some  $\text{TiO}_2$ -anatase,  $\text{Al}_2\text{O}_3$  and  $\text{Mg}(\text{OH})_2$  peaks completely disappeared during activation process. Although no new phases have been detected, our assumption is that the formation of new phases may have started but those peaks are probably overlapped with

$\text{SiO}_2$  peaks that are broadened. Analysis of the broadening of Bragg reflections is a very convenient way to determine the size of crystalline domains from powder diffraction data. The size of crystallites has been determined by application of Scherrer's equation:

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where:  $D$ - crystallite size,  $k$ - Scherrer constant,  $\lambda$ - wavelength,  $\beta$ - integral breadth, and  $\theta$ - angular peak position. Microstructure parameters obtained from Scherrer's method: crystallite size ( $D$ ), density of dislocation ( $\rho_D$ ) and lattice strain ( $e_{hkl}$ ) are given in Tabs. I-V. These calculations have been conducted for the most intensive reflection, and reflection with no overlapping. As we can notice, for all powders with prolongation of mechanical activation crystallite size ( $D_{hkl}$ ) decreases, minimum density dislocation  $\rho_D$  increases and the intensity of microstrain increases, as well.

Due to great hardness of  $\text{SiO}_2$  powder (crystal lattice energy is 13.125 kJ/mol), minor changes are notices within.

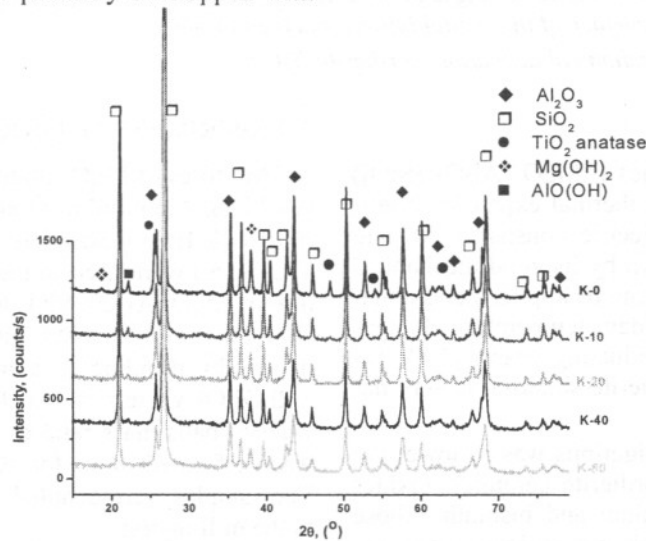


Figure 1 - XRD patterns of non activated and activated mixtures.

Table I Microstructure parameters for non-activated compounds.

compound	(hkl)	$2\theta$ (°)	$\beta$ (deg)	$D_{hkl}$ (nm)	$\rho_D \cdot 10^9 \text{ cm}^{-2}$	$e_{hkl}$
$\text{Al}_2\text{O}_3$	012	25.80	0.225	63.28	7.49	0.246
	113	43.58	0.225	66.43	6.80	0.141
	116	57.68	0.363	43.60	15.78	0.165
$\text{SiO}_2$	100	21.06	0.236	59.77	8.39	0.317
	101	26.86	0.215	66.43	6.79	0.225
	110	36.72	0.193	75.63	5.24	0.146
$\text{TiO}_2$	101	25.53	0.257	55.22	9.84	0.284
$\text{Mg}(\text{OH})_2$	011	38.00	0.279	52.57	10.85	0.203

Table II Microstructure parameters for compounds activated for 10 minutes.

compound	(hkl)	$2\theta$ (°)	$\beta$ (deg)	$D_{hkl}$ (nm)	$\rho_D \cdot 10^9 \text{ cm}^{-2}$	$e_{hkl}$
Al <sub>2</sub> O <sub>3</sub>	012	25.80	0.249	48.37	12.82	0.321
	113	43.58	0.242	61.70	7.88	0.152
	116	57.68	0.398	39.79	18.94	0.181
SiO <sub>2</sub>	100	21.06	0.279	50.56	11.74	0.375
	101	26.86	0.258	55.40	9.77	0.269
	110	36.72	0.257	56.74	9.32	0.194
TiO <sub>2</sub>	101	25.53	0.300	47.34	13.39	0.332
Mg(OH) <sub>2</sub>	011	38.00	0.322	45.57	14.45	0.234

Table III Microstructure parameters for compound activated for 20 minutes

compound	(hkl)	$2\theta$ (°)	$\beta$ (deg)	$D_{hkl}$ (nm)	$\rho_D \cdot 10^9 \text{ cm}^{-2}$	$e_{hkl}$
Al <sub>2</sub> O <sub>3</sub>	012	25.80	0.346	41.12	17.74	0.378
	113	43.58	0.311	47.99	13.03	0.195
	116	57.68	0.415	38.15	20.61	0.188
SiO <sub>2</sub>	100	21.06	0.300	46.96	13.64	0.404
	101	26.86	0.279	51.10	11.49	0.292
	110	36.72	0.279	52.39	10.93	0.210
Mg(OH) <sub>2</sub>	011	38.00	0.343	42.73	16.43	0.249

Table IV Microstructure parameters for compounds activated for 40 minutes.

compound	(hkl)	$2\theta$ (°)	$\beta$ (deg)	$D_{hkl}$ (nm)	$\rho_D \cdot 10^9 \text{ cm}^{-2}$	$e_{hkl}$
Al <sub>2</sub> O <sub>3</sub>	012	25.80	0.363	39.17	19.55	0.397
	113	43.58	0.398	37.55	21.28	0.249
	116	57.68	0.433	36.62	22.37	0.196
SiO <sub>2</sub>	100	21.06	0.322	43.82	15.62	0.433
	101	26.86	0.300	47.46	13.32	0.314
	110	36.72	0.300	48.63	12.69	0.226
Mg(OH) <sub>2</sub>	011	38.00	0.386	37.98	20.80	0.280

Table V Microstructure parameters for compounds activated for 80 minutes.

compound	(hkl)	$2\theta$ (°)	$\beta$ (deg)	$D_{hkl}$ (nm)	$\rho_D \cdot 10^9 \text{ cm}^{-2}$	$e_{hkl}$
Al <sub>2</sub> O <sub>3</sub>	012	25.80	0.433	32.91	27.69	0.472
	113	43.58	0.450	33.21	27.20	0.282
	116	57.68	0.485	32.68	28.08	0.220
SiO <sub>2</sub>	100	21.06	0.365	38.66	20.06	0.491
	101	26.86	0.322	44.29	15.28	0.337
	110	36.72	0.343	42.57	16.55	0.259
Mg(OH) <sub>2</sub>	011	38.00	0.387	37.95	20.82	0.282

Table VI Characteristic temperatures for cordierite.

sample	T1 (oC)	Q1 (J/g)	T2 (oC)	Q2 (J/g)	T3 (oC)	Q3 (J/g)
K-0	525.76	130.00	-	-	1050.51	310.00
K-10	504.65	130.00	851.86	12.77	1054.68	130.00
K-20	522.82	100.00	884.52	12.38	1055.95	84.54
K-40	555.57	84.85	879.02	12.86	1054.70	59.48
K-80	553.75	89.10	882.58	5.87	1056.31	48.04

Particle size analysis, presented on Figure 2, showed that average particle size for non-activated mixture is around 5 μm, while the value decreased with increase in activation time. Average particle size for mixture activated for 80 minutes is around 1.5 μm. This is in accordance with XRD results, where destruction of crystal lattice was noticed as well as peak intensities decreasing as a function of activation time.

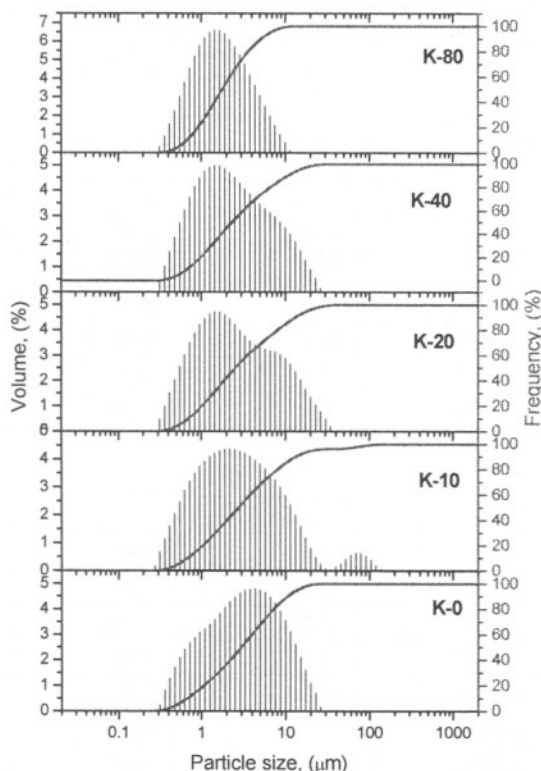


Figure 2 - Particle size analysis of mixtures non-activated and activated for 10-80 minutes.

Diagram presented at Figure 3, clearly showed that the decrease in particle size reaches its minimum within 20 minutes of activation. Further activation leads to smaller decrease in particle size, while after 40 minutes of activation saturation in average particle size value appears indicating at the amorphization process.

Figure 4, shows a termogram of sample activated for 10 minutes. Three exothermic effects are noticed during heating. The first one around 500 °C is due to allotropic change of TiO<sub>2</sub> from anatase to rutile modification (which is in accordance with the XRD data, showing the decrease in anatase peaks with activation time). It is accompanied with smaller one endothermic which is due to kaollinite dehydroxilation [12]. Table VI shows obvious influence of mechanical energy that is brought into the system during activation process. Its influence is observed as crystal lattice destruction; less energy is needed for transfor-

mation process as the time of activation is prolonged. Energy needed for anatase to rutile transformation

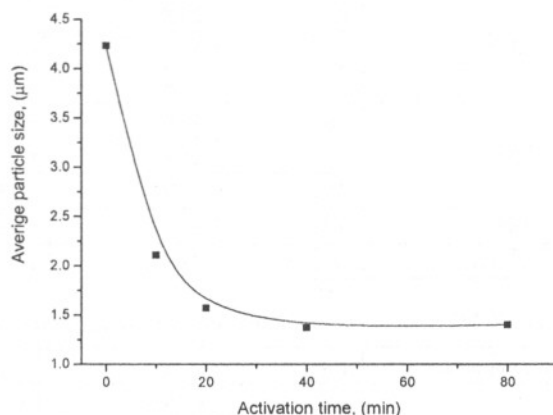


Figure 3 - Influence of mechanical activation on particle size.

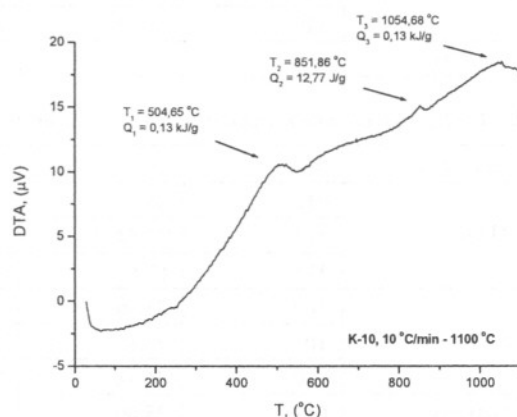


Figure 4 - DTA termogram for K-10 sample.

decreases from 130 J/g for non activated system to 89 J/g for system activated for 80 minutes. Second exothermic peak noticed at 850 °C is due to the transformation of the non-crystalline structure of a kaolinite into a spinel or premullite phase. This phase transformation is not present within non activated system. The third exothermic peak around 1050 °C is due to crystal growth owing to sintering process. Contrary to previous two phase transformations, energy needed for the third one is significantly lowered with prolonged activation time ( $\Delta Q = 250$  J/g).

#### 4. CONCLUSION

In this paper the effects of mechanical activation on structural and microstructural changes of the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub> were analyzed. Based on our previous investigation [13], we confirmed that mechanical activation led to the homogenization of powder particles, the comminuting of particles, and after this period, the introduced energy was used to induce changes in the crystal structure, which resulted



in the emergence of defects, initially on the surface of the crystal lattice, and then inside.

XRD results indicate no new phase formation although intensive decrease in peak's intensities along with amorphization and peak broadening have been noticed. In addition, based on powder diffraction patterns of non-activated and mechanically activated 10, 20, 40 and 80 minutes powders, we got values for the density of dislocations, microstrains and the average dimension of crystallites of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{Mg}(\text{OH})_2$ . Based on obtained results, we concluded that with increase of mechanical activation time the average crystallite size decreases, while the minimum size of microstrain and dislocation density increases..

PSA confirm results obtained with the X-ray analysis, indicating the attrition of starting powders. DTA has given us a characteristic temperatures for the processes occurring in the system during heating up to  $1100^\circ\text{C}$ . Based on these results, the further course of our research will study the sintering of mechanically activated systems as well as the influence of mechanical activation and addition of  $\text{TiO}_2$  on sintering process of cordierite ceramics.

## 5. ACKNOWLEDGEMENTS

This research was performed within the project 172057, funded by the Ministry for Education and Science of the Republic of Serbia and project F-7/II funded by the Serbian Academy of Sciences and Arts.

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## REZIME

### UTICAJ MEHANIČKE ENERGIJE NA KOMPONENTE $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ SISTEMA

*U ovom radu je ispitivan uticaj mehanicke energije na strukturu i promene u mikrostrukturi sistema  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ . Utvrđeno je da mehanicka energija pospesuje homogenizaciju polaznih komponenti, utice na velicinu i oblik zrna praskastih materijala i podstice promene u kristalnoj strukturi polaznih cestica, sto utice na pojavu defekata u ispitivanom sistemu.*

*Ove promene su utvrđene difraktometrijskom analizom, kao i PSA i DTA metodom.*

**Ključne reči:** mehanicka aktivacija, kordijerit  $\text{TiO}_2$