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Influence of Mechanical Activation on Microstructure and Crystal Structure of Sintered $MgO\text{-}TiO_2$ System

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Abstract

Mixtures of $MgO\text{-}TiO_2$ were mechanically activated using high-energy planetary ball mill during 5, 10, 20, 40, 80 and 120 minutes. Sintering process was preformed in air at 1100°-1400°C for 2h. The decrease in powder's particle size was noticed as the time of mechanical activation increased and confirmed by particle size analyzer. XRD analyses were performed in order to acquire the information about phase composition. Different ratio mixtures of $MgTiO_3$ and Mg_2TiO_4 are present within all sintered samples. The effect of tribophysical activation on microstructure was investigated by scanning electron microscopy. The differential thermal gravimetric analysis has been performed in order to investigate thermal behaviour of the mixtures.

Keywords*: Ceramics, mechanochemical processing, sintering, X-ray diffraction.*

Introduction

Development of dielectric materials is increasing with a rapid progress in mobile and satellite communications systems, where magnesium titanates find their place owing to good dielectric properties. Recently it has been established that, these materials, which are based on binary magnesium titanates ($MgTiO_3$ and Mg_2TiO_4) can be applied in MW engineering. These materials differ extremely low dielectric loss in the microwave range and high dielectric constant [1-3]. Therefore, $MgO\text{-}TiO_2$ system has been studied extensively and the existence of three stabile phases ($MgTiO_3$, Mg_2TiO_4 and $MgTi_2O_5$) has been reported in literature. It has been established that $MgTiO_3$ posses an ilmenite structure, $MgTi_2O_5$ pseudobrookite structure and Mg_2TiO_4 inverse spinel structure [1]. The magnesium titanates are normally synthesized at relatively high temperatures of 1400°C by solid-state reactions between MgO and TiO_2.

For many solid-state reactions, the limiting stage is diffusion in the solid state. Extensive research revealed that mechanical activation could simplify or accelerate

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solid-state reaction, which normally occurs at high temperature and/or high pressure [4]. High-energy ball milling as method to synthesize nano size materials has many advantages, such as simplicity, relatively inexpensive to produce, applicable to any class of materials, etc [5]. Mechanical treatment can change the thermodynamic potentials, intensifying transport of reagents, and reducing temperatures of chemical reactions [6]. During mechanical activation, powder particles are subjected to severe plastic deformation resulting the formation of high defects concentration. This induces enhanced atomic mobility; promote different phenomena depending on the materials being milled.

Taking all this into account, in this article, the influence of mechanical activation of the MgO-TiO_2 system on phase composition, crystal structure, microstructure, as well as on thermodynamics of MgO-TiO_2 system before and after sintering process, has been reported.

Experimental procedure

Mixtures of MgO (99% Sigma-Aldrich) and TiO_2 powders (99.8% Sigma-Aldrich) at a molar ratio $MgO:TiO_2 = 2:1$ were mechanically activated by grinding in a high energy planetary ball mill device (Retsch type PH 100). The milling process was performed in air for 5, 10, 20, 40, 80 and 120 minutes at a basic disc rotation speed of 400 rpm. Ball to powder mixture mass ratio was 20:1. Samples were denoted as MT0 to MT120 according to the milling time.

The morphology of obtained powders before and after heating was characterized by scanning electron microscopy (JEOL JSM-6390 LV). The pallets were cracked and covered with gold in order to perform these measurements.

The average particle size, their distribution, and the nature of agglomerates were determined by particle size analyzer (PSA) and mastersizer (Malvern Instruments Ltd., UK). Particle size analyzer, which is based on laser diffraction, covers the particle size range of 0.02-2000 μm. 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 min.

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

Differential thermal gravimetric analyses were performed in air, during non-isothermal heating from 25^oC to 1100^oC, with a constant heating rate of 10^oC/min. For those analyses the analyzer SHIMADZU DTA-50 has been used.

The binder-free powders were compacted using the uniaxial double action pressing process in an 8 mm diameter tool (Hydraulic press RING, P-14, VEB THURINGER). Compacts were placed in an alumna boat and heated in a tube furnace (Lenton Thermal Design Typ 1600). Compacts were sintered isothermally at 1100, 1200, 1300 and 1400^oC in air atmosphere for 120 minutes. The heating rate was 10^oC/min. The density of specimens was calculated from precise measurements of specimen's diameter, thickness and mass.

Results and Discussion

In order to investigate the effect of mechanical activation on system's microstructure, the scanning electron microscopy has been performed. Micrographs of non-activated as well as activated mixtures are presented in Fig. 1. It is well known that during mechanical attrition by ball milling, the evolution of materials phases is coupled to the mechanical properties of the powders and therefore to their microstructures [7]. It has been established that the microstructure evolution is controlled by the temperature, milling intensity and composition. The grain size, internal lattice root mean square strain and stored enthalpy are parameters characterized by the most authors [8].

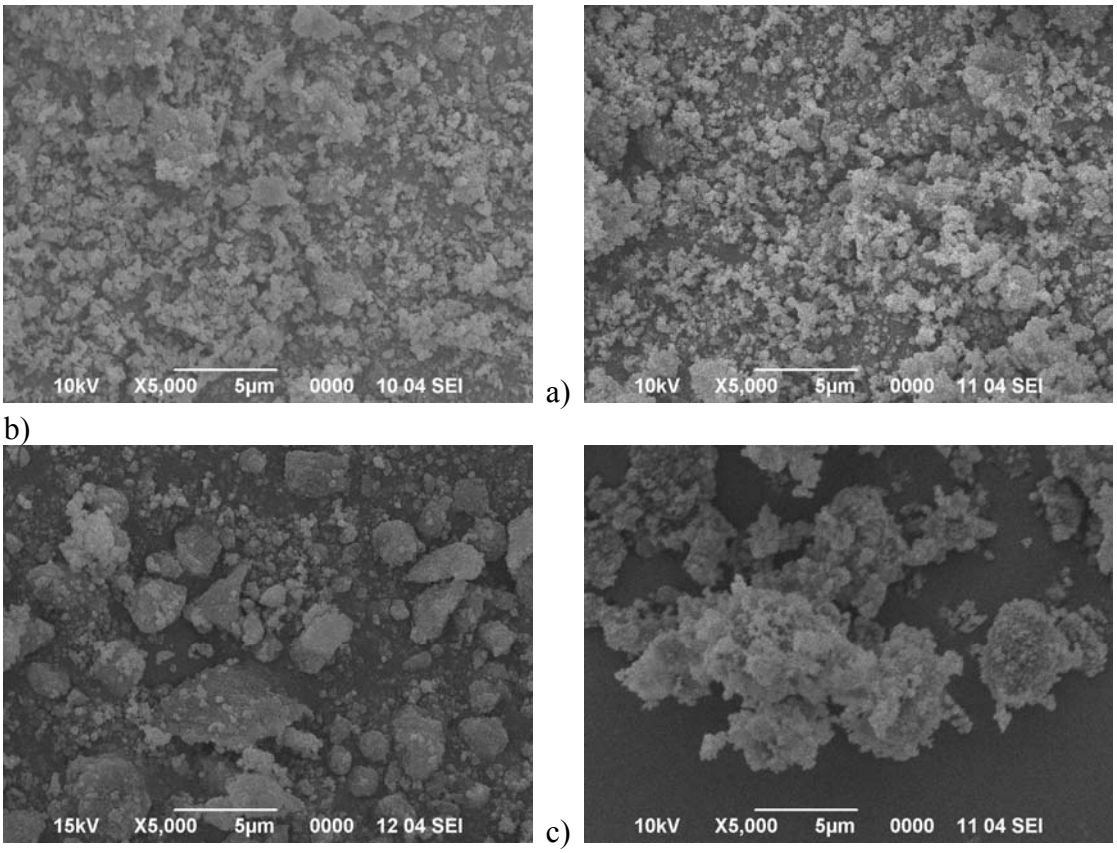

Fig. 1. Scanning electron micrographs of (a) MT0, (b) MT10, (c) MT20 and (d) MT120.

Our microstructure analyses of MgO-TiO_2 system showed that the initial MgO powder consisted of spherical particles with a size of 500 nm and irregularly shaped agglomerates with a size of 2 microns approximately. Compared to MgO particles, TiO_2 spherical particles were smaller with the particles with a size of 150 nm. It has been observed that the grain size of the starting powder mixture decreased with milling time, as observed from Fig. 1. (b).For the samples activated 20 min (MT20), as a result of mechanically induced particles deformation, formation of soft agglomerates has been noticed. SEM micrographs of MT120 clearly indicated the

presence of new phases in shape of agglomerates covered with smaller particles of starting powders.

This is in accordance with the X-ray analysis, which pointed out that mechanical activation of $MgO\text{-}TiO_2$ system is not only characterized by crystallite size reduction and increase in dislocation density and lattice strain [9], but also by formation of new magnesium-titanate phases. Fig. 2. shows frequency distribution and cumulative distribution curves of MT0, MT20, MT40 and MT120 samples.

Particle size distribution of MT0 shows that the powder consisted of three kinds of particles. The first one were about 0.5 micrometers, the second about 2 micrometers and the third about 70 microns, representing small particles of TiO_2, spherical particles of MgO and MgO agglomerates, respectively (Fig. 1. (a)). For the samples activated 20 min due to mechanically activated particle reduction, the presence of starting MgO agglomerates was not detected. Only the particles with the average size of about 0.4 micrometers and the second ones with the average size around 5 micrometers were noticed.

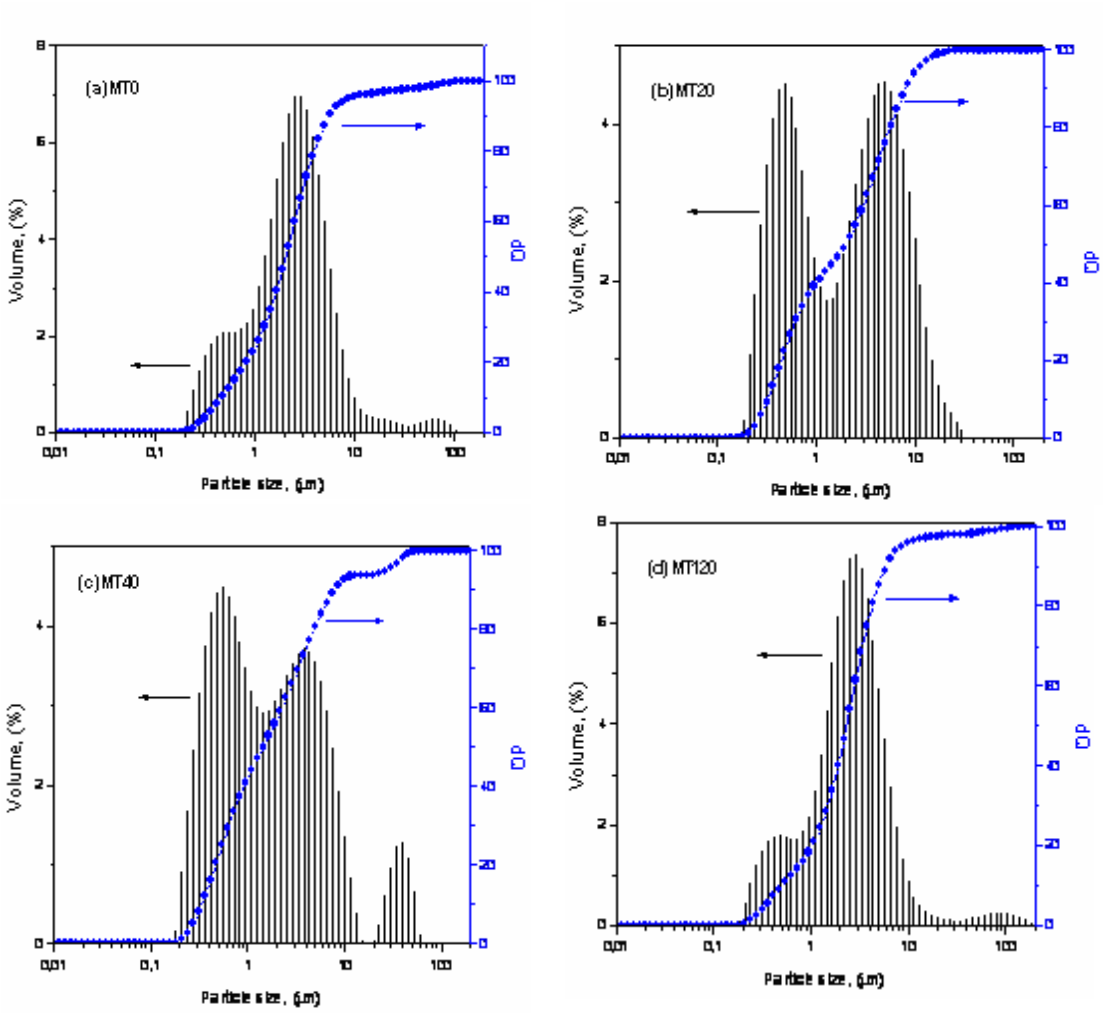

Fig. 2. Cumulative and frequency distribution curves for (a) MT0, (b) MT20, (c) MT40 and (d) MT120.

According to microstructure analysis we suppose that the MT40 and MT120 particle size distributions belong to the three differently sized agglomerates – about 0.5, 4 and 35 microns within MT40 and 0.4, 2.5 and, finally, 50 microns within MT120, representing the agglomerates of some new phases covered with smaller ones of starting powders. This is in a great accordance with the results obtained by XRD analysis. X-ray diffraction patterns of non-milled and ball-milled MgO and TiO_2 powders are given in Fig. 3. and reveal the phase composition and changes within powder during milling process.

MT0 is the X-ray pattern of the non-milled starting mixture containing MgO, $Mg(OH)_2$ and TiO_2 (anatase and rutile modification). The identification of all obtained reflections has been accomplished using the JCPDS cards (65-5714 for TiO_2 anatase, 77-0443 for TiO_2 rutile, 72-0021 for TiO_2 **II** (brookite), 71-1176 for MgO, 82-2453 for $Mg(OH)_2$, 79-0831 for $MgTiO_3$ and 76-2373 for $MgTi_2O_5$).

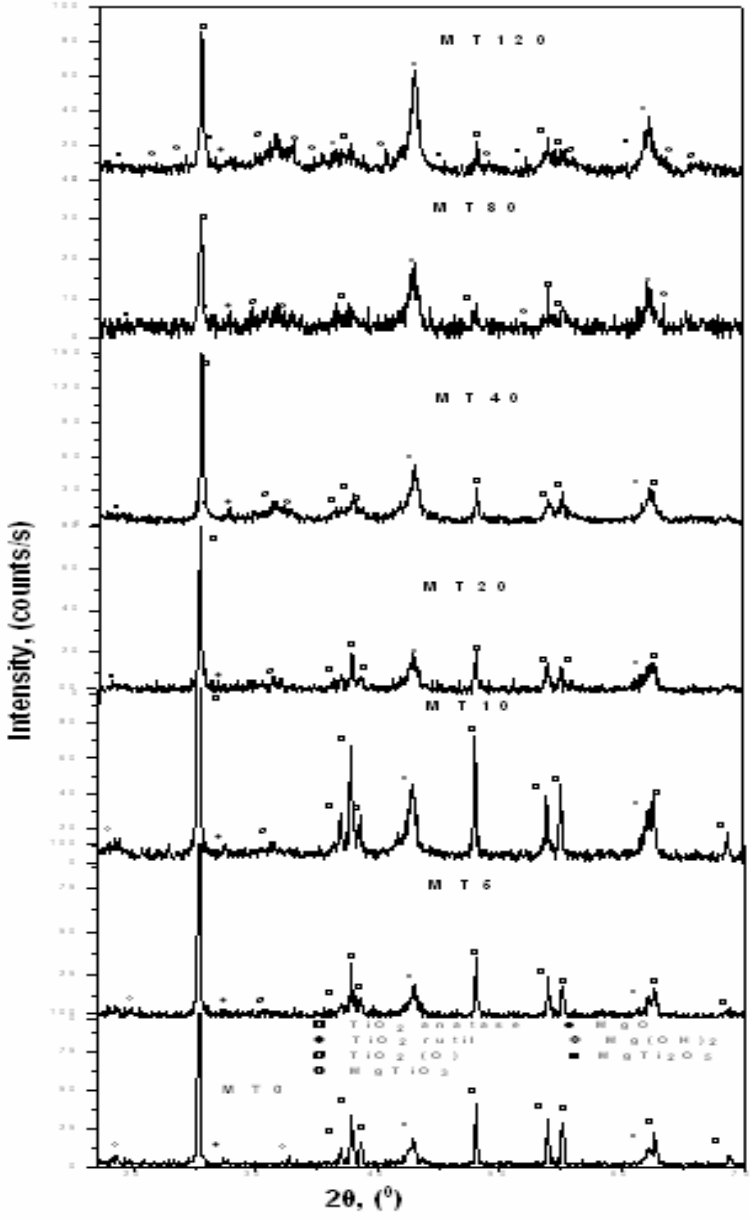

Fig. 3. XRD patterns of non-activated and activated mixtures.

After 5 minutes of mechanical treatment, intensities of some anatase and magnesium-oxide peaks are lowered and the phase transition of some anatase into high pressure form TiO_2 **II** has been observed.

After 20 minutes, due to diminution of crystallite size, defect formation and amorphisation, intensities of all starting phases were significantly lowered and smoothly broadening of magnesium-oxide peaks was noticed. Furthermore, the very first traces of metastable compound $MgTi_2O_5$ became detectable.

Moreover, as the time of activation is prolonged, further broadening and lowering of intensities of all peaks has been observed. Due to phase transition from anatase over TiO_2 **II** to the most stabile form of TiO_2-rutile decrease of anatase phase concentration has been also noticed [10, 11]. In the MT40 pattern, we have noticed the simultaneous decrease of TiO_2 anatase along with the first traces of perovskite phase $MgTiO_3$. No spinel phase Mg_2TiO_4 has been detected. After 80 minutes of activation, all phases mentioned above were still present except for the strongest anatase reflection. This reflection is drastically lowered and broadened, because of overlapping with the most intensive $MgTi_2O_5$ peak and the peak of TiO_2 **II** [12]. Finally a mixture of $MgTi_2O_5$, $MgTiO_3$ and MgO along with very small concentration of TiO_2 phases is observed for the samples activated 120 min.

In order to determine characteristic temperatures at which solid-state processes are taking place, DTA and TGA analyses have been performed. DTA and TGA curves of the non-activated sample and sample activated for 120 minutes are presented in Fig. 4.

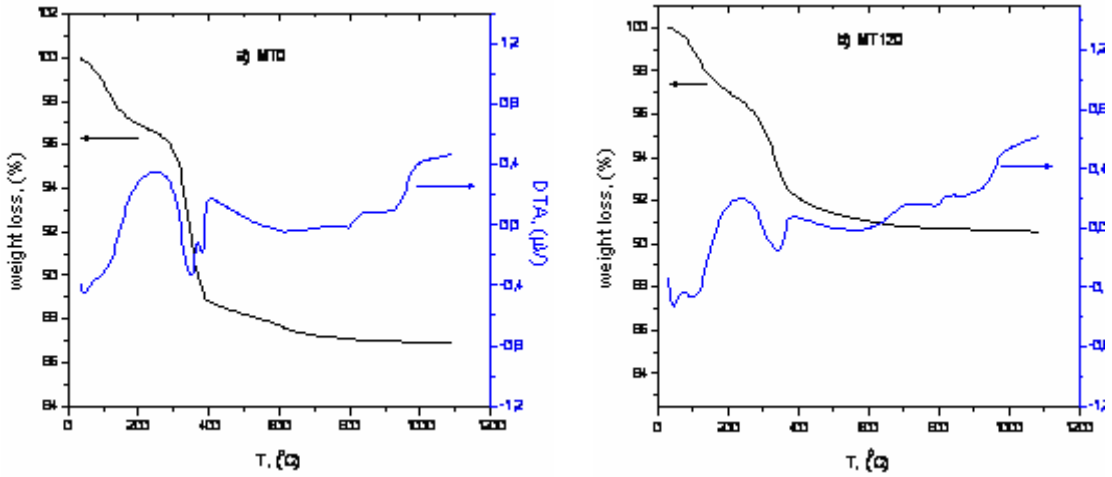

Fig. 4. DTG curves of (a) non-activated MT0 mixture and (b) MT120.

First weight loss of 4% was assigned to some humidity evaporation during powder's preparation route. Our DTA curves showed three endothermal and one exothermal peak. The first and the second ones, around 400°C, are very sublime and are assigned to the formation of $MgTi_2O_5$ phase [13] and transition of some TiO_2 anatase into rutile modification. This is accompanied with a weight loss of 8% (see Fig. 4.). The endothermic peak at 800°C, represents the beggining of $MgTiO_3$ formation. The fourth, exo-peak which occurs around 1000°C can be assigned to reaction completing and high temperature crystal growth [14].

DTA curve for MT120 shows no endo-peak of TiO_2 transition, which is in accordance with the X-ray diffraction data (phase transition is observed within MT5

pattern and transition of anatase into rutile is finished until 120 minutes). Also, since the formation of $MgTi_2O_5$ phase occurs after 20 min of mechanical activation, the weight loss is less than within MT0.

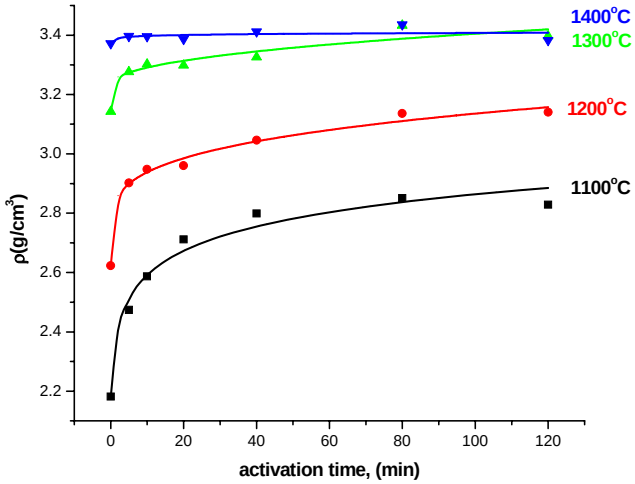

Fig. 5. Compacts densities of the samples isothermally sintered at various temperatures for 2h.

Compact densities of the ball-milled powder after its sintering at 1100, 1200, 1300 and 1400°C for 2h are shown on Fig. 5. The maximum change in densification rate is observed within powders activated 40 minutes, and the greatest values are obtained at 1400°C, as expected. Regarding previous analysis based on SEM and XRD measurements, it is clear why prolonged milling time inhibits densification. Namely, it is known that a high content of hard agglomerates is not suitable for good sinterability.

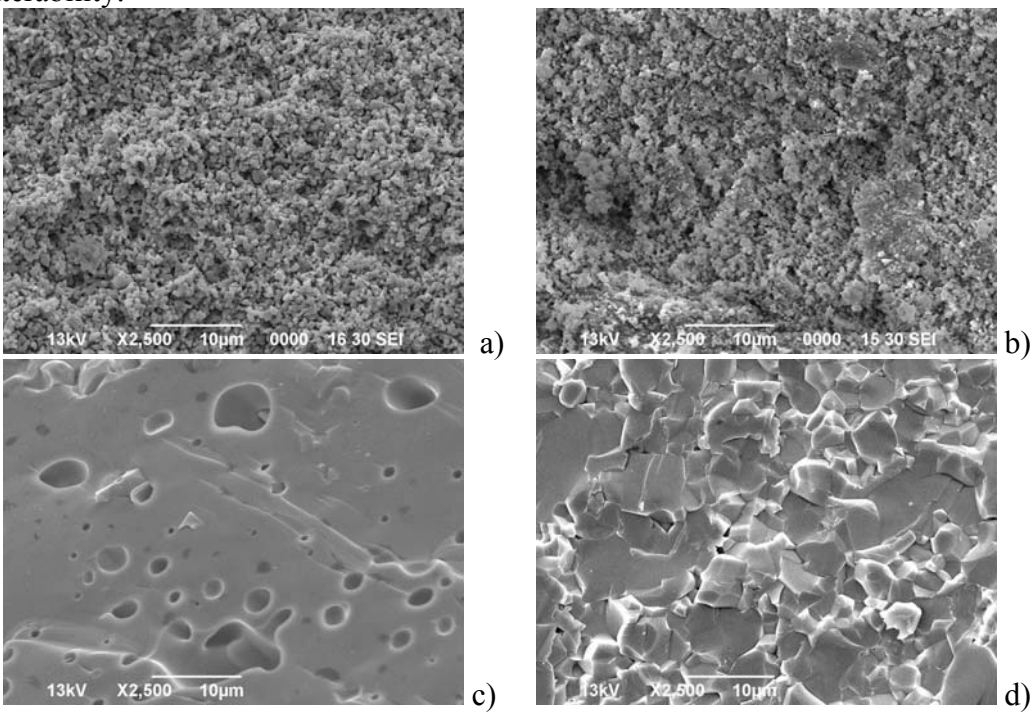

Fig. 6. SEM micrographs of (a) MT0 and (b) MT120 sintered at 1100°C for 2h and (c) MT0 and (d) MT120 sintered at 1400°C for 2h.

Micrographs of some sintered samples are given in Fig. 6. Formation of contact necks at the beginning stadium of sintering process is clearly visible at Fig. 6. (a). Grains still own their starting shape, no relevant mass transport has been observed. Due to activation process, particles between agglomerates were more active, so the greater conglomeration is present.

Spherical pores and very porous microstructure were the main characteristics for sample MT0 sintered at 1400°C for 2h. For the activated samples (especially for the samples activated 120 min) due to sintering of hard agglomerates, anisotropic distribution of phase particles and irregularly shaped closed pores has been observed.

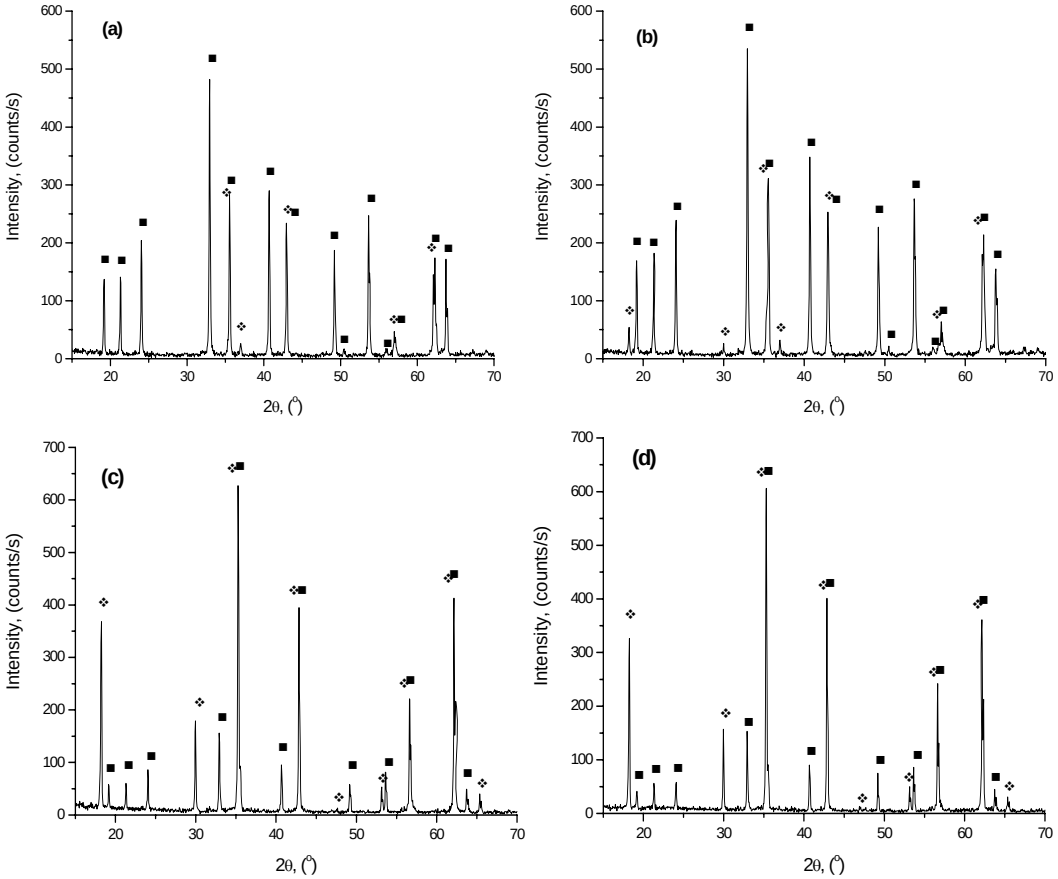

Fig. 7. XRD patterns of (a) MT0 and (b) MT120 sintered at 1100°C for 2h and (c) MT0 and (d) MT120 sintered at 1400°C for 2h (■-$MgTiO_3$, ❖-Mg_2TiO_4).

XRD patterns of sintered samples are presented in Fig. 7. All sintered samples consist of two phases: perovskite phase $MgTiO_3$ and spinel phase Mg_2TiO_4. Some reflections of these two compounds are overlapped. With the increasing sintering temperature, intensities are sharper and the ratio between two phases is changing. Based on the analysis of peak's intensities, one can notice that spinel phase concentration is more dominant within samples activated at 1400°C for 2h. The pure Mg_2TiO_4 phase was not obtained with the milling and sintering conditions we used.

Conclusion

In this paper, the influence of mechanical activation on microstructure and crystal structure, as well as the isothermal sintering of MgO-TiO_2 system, was studied. Scanning electron micrographs indicate a difference between the starting and activated powders morphology confirming the changes taking place during the mechanical activation. Based on XRD results, the phase transition of TiO_2 anatase $\rightarrow$ TiO_2 **II** brookite $\rightarrow$ TiO_2 rutile is observed after 5 minutes of mechanical treatment; the first appearance of the magnesium-titanate phase $MgTi_2O_5$ was found to occur after 20 minutes of mechanical treatment; the $MgTiO_3$ perovskite phase was noticed after 40 minutes. Spinel Mg_2TiO_4 phase is not possible to obtain using these milling conditions (times of activation and balls to powder mass ratio).

Also, it has been found that mechanical activation leads to particle size reduction. Differential thermal gravimetric analyses established the temperatures at which the solid state reactions begin and showed no phase transition from TiO_2 anatase $\rightarrow$ TiO_2 **II** $\rightarrow$ TiO_2 rutile for non-activated heated sample.

XRD data of sintered samples gave information on their phase composition. After sintering, we obtained two-phase system consisted of $MgTiO_3$ and Mg_2TiO_4 phases. The ratio between these two compounds varied and with the increase in sintering temperature, the concentration of spinel phase, Mg_2TiO_4, is increasing. The pure spinel phase is not possible to obtain using these conditions, as a consequence of the thermodynamic instability of spinel phase [4].

Acknowledgement

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Садржај: *Смеше MgO-TiO_2 су механички активиране у високо-енергетском планетарном млину током 5, 10, 20, 40, 80 и 120 минута. Фазни састав је одређен рендгенском дифракцијом. Са порастом времена млевења, примећено је смањење величине честица праха. Такође, испитан је и ефекат трибофизичке активације на микроструктуру праха методом скенирајуће електронске микроскопије. Ради испитивања термичких својстава праха, урађена је диференцијална термијска анализа. Процес синтеровања изведен је у ваздуху у температурном опсегу од 1100^o-1400^oC током 2 сата. У свим синтерованим узорцима уочено је присуство две фазе $MgTiO_3$ и Mg_2TiO_4 али њихов међусобни однос концентрација варира у односу на температуру синтеровања.*

Кључне речи*: Керамика, механичка активација, синтеровање, рендгенска дифракција.*