UDK

**Sintering Kinetics of MgO-TiO₂ Systems**

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*Abstract:* Ceramic materials have been in use in many different areas of human wellbeing for a very long time. The most common way of obtaining this material is using the process of sintering. During mechanical activation inorganic materials are ground when the grain size reduced. The crystal structure distortis and also changes, leading some systems to a chemical reaction and formation of a new compound. In this work we explain the influence of mechanical activation on sintering kinetics in MgCO₃-TiO₂ systems. We noticed a temperature drop and time reduction needed for MgTiO₃ sintering when the duration of mechanical activation was longer.

**Keywords:** Sintering kinetics, MgO, TiO₂.

**Introduction**

Ceramic materials have been in use in many different areas of human wellbeing for a very long time. Ceramic materials applied in electronics occupy a significant position. Our research is focused on magnesium titanate (MgTiO₃). Magnesium titanate based dielectric materials are classically used for producing type-I ceramic multilayer capacitors [1]. Recent development of microwave communication systems requires materials that can be used at microwave frequencies as resonators in filters or oscillators in radar detectors, cellular telephones and global positioning satellite devices. During the last two decades there has been a growth of interest for preparation and characterization of low-loss dielectrics suitable for such engineering applications. Most of the ceramics exploited for communication applications have temperature-stable dielectric properties with relative permittivities in the range 20-90, and Qf products (where Q is the quality factor and f frequency in GHz) in the range 5000-400000. MgTiO₃ is one of these promising materials. Magnesium titanate also melts congruently at a temperature in the interval 1732 - 1835 °C. The mineral giekielite MgTiO₃, has many industrial applications [2,3,4].

The most common way for obtaining this material is using the process of sintering. Sintering presents a process of particle merging due to heating of a disperse mixture of crystal and non-crystal materials [5]. The essence of this process is in qualitative and quantitative changes of contacts between powder particles. In advanced technologies, preparation of powders for the synthesis of new materials is most often performed using mechanical activation – intensive transport of mechanical energy into powders, in specially constructed mechanical activators (mills). Mechanical activation leads to controlled disordering and

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destruction of materials [6]. As the reactive capability of materials is the consequence of its structural properties, the processes of disordering and destruction occurring during mechanical activation of powders later influence acceleration of the synthesis process.

**Experimental Procedure**

In this work starting powders of magnesium carbonate (MgCO$_3$) and titanium dioxide (TiO$_2$) with a rutile crystal modification were measured to attain the molar ratio of MgCO$_3$:TiO$_2$ = 1:1. Mechanical activation of the starting mixture was performed by grinding in a high energy mill in a planetary ball mill device (Fritsch Pulverisette 5) with ZrO balls and vessels where the ball to powder mass ratio was 40:1. The grinding times were 15, 30, 60 and 120 minutes. Depending on the grinding time, four mixtures were used in our work (for 15 (MT15), 30 (MT30), 60 (MT60) and 120 minutes (MT120)) and one non-activated mixture (MT0).

X-ray diffraction analysis of the starting mixture (non-activated) and activated mixtures was performed first. Investigations were performed on a Philips Analytical PW-1710 diffractometer with CuK$_\alpha$ radiation ($\lambda$=1.5418 Å) and a graphite monochromator. Investigations were performed at room temperature in the angle range of 5-60° (2θ) a step of 0.02° and holding time of 2 s per step. X-ray diffraction was used for observing the evolution of magnesium-titanate phase during research.

Differential thermal analysis (DTA) was performed with the purpose of determining characteristic temperatures on which solid-state processes occur. Starting mixture components (MgCO$_3$ and TiO$_2$), the non-activated mixture (MT0) and activated mixtures MT15, MT30, MT60 and MT120 were analyzed in air by 100ml/min, in the temperature interval from room temperature to 1100°C with a constant heating rate of 20°C/min.

XRD analysis of the non-activated mixture - MT0, heated to 300°C, 500°C, 650°C and 800°C was investigated on a Philips Analytical PW-1710 diffractometer.

**Results and discussion**

Fig. 1 shows XRD data obtained on structural changes observed in MgCO$_3$-TiO$_2$ powder mixtures induced during grinding for different times.

The diffractograms obtained show that due to mechanical activation disassembling and decomposition of MgCO$_3$ occurs, which is indicated by a decreased intensity of peaks as the temperature rises.

The influence of mechanical activation on the behavior of the system during thermal treatment can be analyzed in thermograms of differently activated mixtures. The DTA curves are given in fig. 2 and weight loss of MgO-TiO$_2$ during heating (TG curves) are given in fig. 3.

With the increase of the activation time the reaction occurs at a lower temperature in comparison with non-activated samples. This confirms that the basic material changes during mechanical activation are related to physical-chemical surface parameters, resulting in the occurrence of changes in the materials reactivity. Decomposition of the material gives an increased specific surface and thus reactive capability. Thus, grinding ceramic powders increases their reactivity and accelerates solid-state reactions.

Up to 100°C the process of drying, i.e. loss of water occurred. Weight loss, also indicated on fig. 3 up to 100°C, is the consequence of water absorption. Mechanical activation supports hygroscopy, so weight loss is the highest for the sample with the longest period of grinding - MT120. On 400°C an exothermal peak indicates loss of residues of CO$_2$,
which is shown on the figure of weight loss, where weight loss to 400°C is clearly stated. A large number of phase changes is noticeable as well. Additional analyses by XRD confirm the appearance of phase changes.

**Fig. 1** Diffractograms of non-activated mixture, and mixtures activated for 30 and 120 minutes.

**Fig. 2** DTA curves of MgO-TiO₂
Fig. 3 Weight loss of MgO-TiO$_2$ during heating

Fig. 4 shows diffractograms of starting non-activated mixtures heated to temperatures of 300 °C, 500 °C, 650 °C and 800 °C. The diffractograms obtained show that due to heating disassembling and decomposition of MgCO$_3$ occurred, indicated by a decreased intensity of peaks as the temperature rises.

Fig. 4 Diffractograms non-activated mixtures MT0, warmed on 300 °C, 500 °C, 650 °C and 800°C.
Intermediate phases between MgO and TiO$_2$ exist: Mg$_2$TiO$_4$ (qandilite), MgTi$_2$O$_5$ (karrooite) and MgTiO$_3$ (geikielite). These phases can form by reactions between MgO and TiO$_2$ powder at high temperatures. Only geikielite is stable at room temperature and qandilite and geikielite are in equilibrium only at high temperatures. Qandilite and karrooite are supposed to decompose at lower temperatures by reactions or phase transitions [7, 8].

Mg$_2$TiO$_4$ has an inverse spinel structure although one cannot rule out absolutely the possibility of a small deviation from a completely inverse character. The observation of Fd$3m$ symmetry implies that, on average, the distribution of Mg and Ti over octahedral sites is random. MgTi$_2$O$_5$ has a pseudobrookite structure. The space group is Bbmm, and the structure consists of bands of edge-sharing octahedra extending in the $b$ direction [9].

On 300 °C traces of MgTi$_2$O$_5$ forming existing up to the temperature of 800 °C are visible. Mg$_2$TiO$_4$ is formed after 450 °C so the XRD on 500 °C indicates its formation. Its intensity is higher with the rise of temperature and on 800 °C it dominates.

On diffractograms of non-activated mixtures even at 800 °C no MgTiO$_3$ has formed, but for activated powders it has formed even after 60 minutes of grinding as indicated by the diffractograms given in fig. 1.

Conclusions

Obtaining materials with properties defined in advance is one of the basic tasks of materials science. Based on analysis of all given results it can be concluded that mechanical activation of a mixture of magnesium carbonate and titanium-dioxide powders leads to reduction of the size of the material, deformation of the crystal structure of the dispersed material and generation of point and line defects. It was established that after 15 minutes of grinding the influence of mechanical activation can be noted. All above mentioned analyses indicate that mechanical activation enables sintering of initial powders on lower temperatures and for a shorter period of time. These results will be used for future work.

References

кинетику синтеровања система MgCO₃-TiO₂. Утврђено је да се температура и време који су потребни за синтеровање MgTiO₃ смањују са продужавањем времена механичке активације.

Кључне речи: Кинетика синтеровања, MgO, TiO₂.