Synthesis of alumomagnesian spinel by mechanical activation method

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Synthesis of alumomagnesian spinel by mechanical activation method

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Abstract. The influence of the mechanical activation of the initial alumina and magnesium oxide powders on the formation of alumomagnesian spinel has been studied. It has been established that the mechanical activation of the starting powders accelerates the formation of alumomagnesian spinel, significantly reducing the temperature of the subsequent heat treatment.

1. Introduction

Alumomagnesian spinel is used as a structural and refractory material for modern technology, due to such important technological properties as high melting point, increased mechanical strength, high resistance to neutron irradiation and low neutron capture cross section with the formation of radioactive products [1].

Much attention is paid in the literature to the synthesis of stoichiometric $MgAl_2O_4$. The difficulty of obtaining alumomagnesian spinel from aluminum and magnesium oxides during their solid-phase reaction is the formation of the $MgAl_2O_4$ phase at sufficiently high temperatures above 1400 ° C [2]. Mainly chemical methods based on the processes of wet chemistry (coprecipitation, sol-gel methods, SHS processes, hydrothermal method, Pechini method, etc.) are used to obtain a reactive and single-phase material based on $MgAl_2O_4$ [3,4]. However, these chemical methods of obtaining imply the use of chemicals that are sensitive to the environment (sol-gel process, Pechini method), the possibility of leaching cations during filtration (coprecipitation process), complex instrumentation (hydrothermal method). Mechanically activated synthesis exceeds the methods of wet chemistry, allows mixing and grinding of components, and solid-phase reactions of a multicomponent system in one process, significantly reducing the subsequent heat treatment temperature. Mechanically activated synthesis is actively used to obtain various ceramic materials of functional purpose [5].

The main objective of this study is to establish the effect of mechanical activation in the dry grinding of magnesium and aluminum oxides on the heat treatment temperature in order to synthesize alumomagnesian spinel. The production of $MgAl_2O_4$ is possible directly during grinding as a result of physicochemical processes associated with the effect of mechanical energy on powder particles.

2. Materials and methods

The initial components are γ-form of aluminum oxide (99.999%, produced by Nanocorund LLC, Sarov, the average size of the agglomerates is 5 μm) and magnesium oxide (the average size of the aggregates is 4 μm). Highly dispersed magnesium oxide was obtained by thermal decomposition of magnesium

carbonate. To obtain stoichiometric alumomagnesian spinel, γ-alumina and magnesium oxide were taken in a molar ratio of 1: 1. Mechanical activation was performed in a planetary mill (Fritsch Pulverisette 5) at room temperature in air, in corundum drums (volume 250 ml) with grinding corundum bodies (diameter 15 mm), the rotation speed of the mill was 400 revolutions per minute. The duration of grinding varied from 30 to 120 minutes (composition M30, M60 and M120), the ratio of material and grinding media was 1:10. The obtained powders after mechanical activation were investigated by the methods of differential thermal (EXSTAR TG / DTA 7300 (SII)) and X-ray phase analyzes (D2 PHASER, Bruker). Heat treatment of the mixtures was carried out in the temperature range of 500-1400°C, holding at the maximum temperature was 1 hour. The crystallite sizes for all the studied powders were calculated from the broadening of the peaks in the diffractograms according to the Scherrer equation: $D = K \cdot \lambda / (\beta \cdot \cos \theta)$, where D is the average particle size, K is the Scherrer constant or form factor (0.89–0, 90), λ is the wavelength of the incident X-ray radiation (copper - 0.15406 nm), β is the full width of the peak at the level of half the intensity, θ is the angle of diffraction.

3. Results and discussion

Figure 1 shows the X-ray patterns of the obtained powders after dry grinding at different duration mechanical activation. Diffraction peaks correspond to the MgO (JCPDS No. 78-0430), gamma-Al_2O_3 (JCPDS No. 77-0403) and $MgAl_2O_4$ (JCPDS No. 73-1959) phases. As a result of mechanical action on the charge (γ-Al2O3: MgO) over time, the intensity of the diffraction peaks of γ-alumina and magnesium oxide is significantly reduced with simultaneous broadening of the peaks and is primarily due to a decrease in the particle size of the charge during the grinding process. The formation of the primary crystallites of alumomagnesian spinel phase on the surface of oxide particles occurs during the first 30 minutes of mechanical activation. An increase in the time of mechanical treatment of powders up to 120 minutes leads to an increase of aluminomagnesian spinel phase during mechanical action, as well as on the size and degree of crystallinity of the initial particles of the mixture.

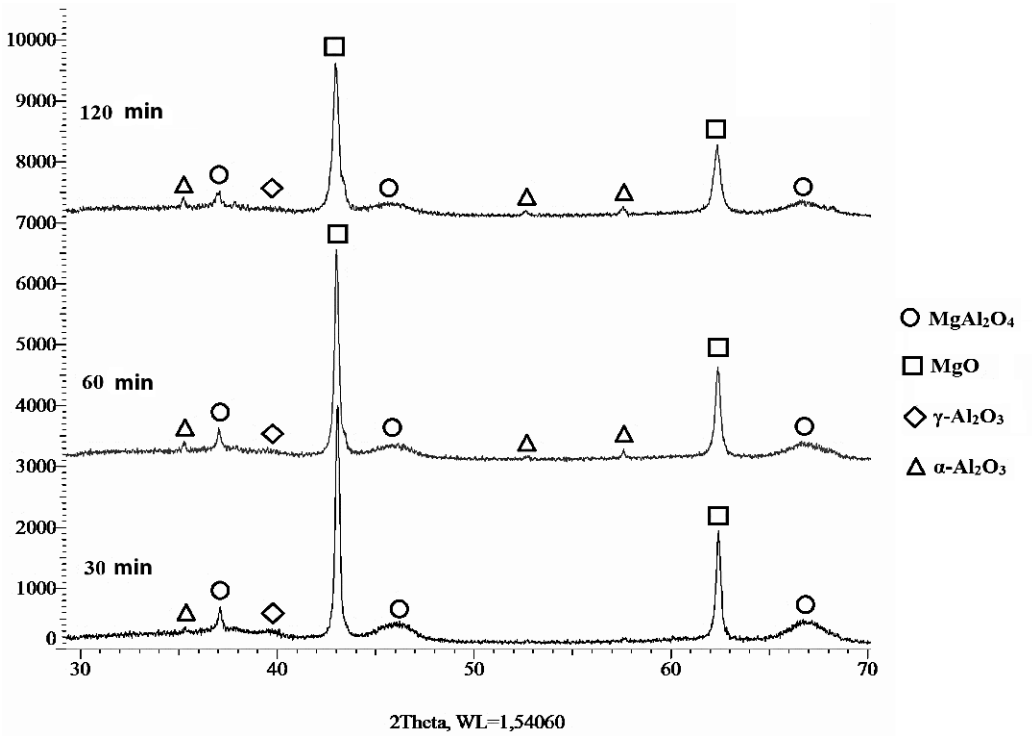

Figure 1. Radiographs of mechanically activated mixture γ-Al_2O_3: MgO in a molar ratio of 1:1 after 30, 60 and 120 minutes of grinding.

When the charge oxide is activated, structural destruction processes occur, causing amorphization of the surface layer of particles. By the nature of radiographs (Figure 1), the degree of crystallinity of the components of the mixture decreases with increasing mechanical exposure time of 30, 60, 120 minutes, respectively. The process of mechanical activation of the original nanosized powders can be described in three stages. At the first stage the initial oxide particles undergo a certain degree of amorphization during grinding, but a solid-phase reaction towards the formation of the product still does not occur. Further mechanical action, characterized as the second stage of activation, contributes to the formation of nuclei of a new phase and its crystallization. At the final stage, the grinding has a mechanical effect only on the synthesized powders, forming structural defects in the particles. Comparison of the curves of differential thermal analysis of mechanically activated powders showed the effect of mechanical activation time on the synthesis of $MgAl_2O_4$ (Figure 2). The endothermic effect observed up to 350 ºC is caused by the loss of volatile surface water, as mechanically activated magnesium oxide has a higher rate of adsorption of water molecules and, possibly, chemisorption of gas molecules on the surface of particles. The DTA curves for M60 and M120 powders exhibit an exothermic effect in the temperature range of 755–930 ° C, which is caused by the solid-phase reaction of unreacted magnesium oxide and aluminum oxide and the residual redistribution of cations between the octahedral and tetrahedral positions in the spinel structure, because the formation of the MgAl2O4 phase has occurred at the start of machining. The appearance of crystallites of alumomagnesian spinel during machining significantly reduces the subsequent temperature of heat treatment of powders. Moreover, with an increase in the time of mechanical activation, the manifestation of the exo-effect becomes more pronounced. The subsequent heat release at ~ 1000ºC, apparently, is the result of a change in the degree of defectiveness of particles towards their complete disappearance. On the derivatogram of M30 powder, there is one exothermic effect, which corresponds to the residual solid-phase reaction with the formation of defective particles of alumomagnesian spinel. Further removal of powder particle defects will either lead to an increase in the heat treatment temperature, or to an increase in the exposure time at 1000 ° C.

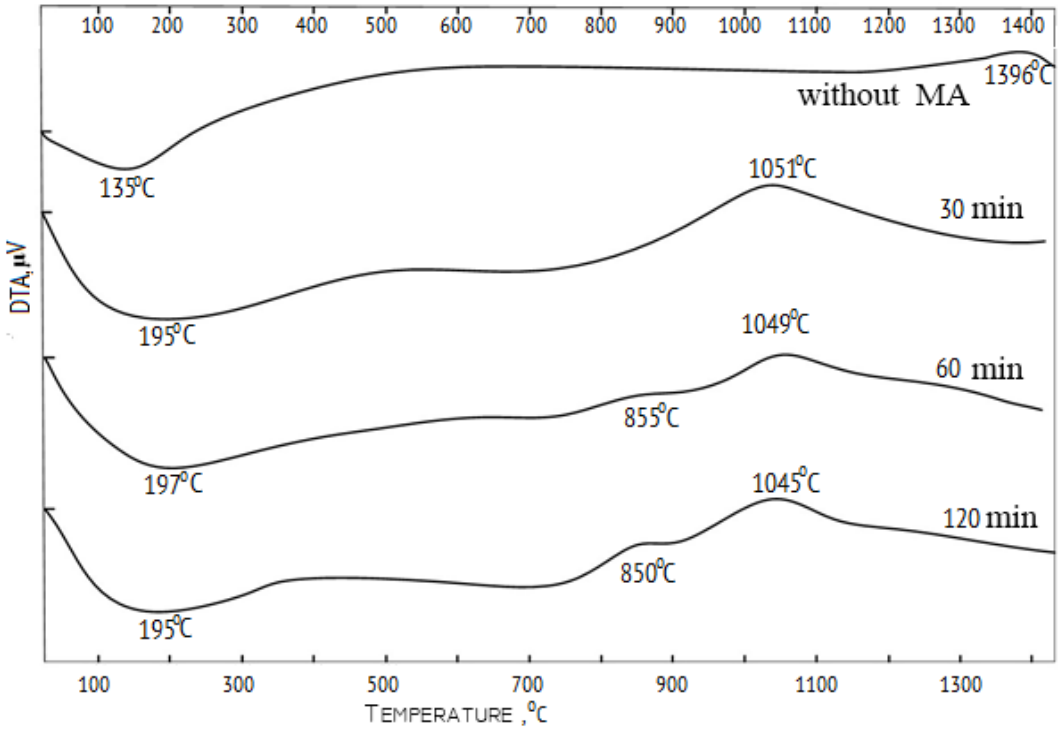

Figure 2. DTA curves of the studied powders.

In order to identify the effectiveness of mechanical activation on the powder, the composition of magnesium oxide and aluminum oxide was prepared, also taken in a 1: 1 molar ratio. The grinding of this composition was carried out on a roller mill for 6 hours. The speed of rotation of the mill was 48-50 revolutions per minute. The result of the DTA revealed the temperature of the synthesis of alumomagnesian spinel for the composition, not subjected to mechanical activation, as 1400 °C (Figure 2). Mechanical activation promotes subsequent thermal activation, reducing the heat treatment temperature of the powder by 400 ° C. The dependence of crystallite size (CSR) and the crystallization of alumomagnesian spinel on temperature was studied on the composition of M30 to exclude the contribution of free corundum to the process of formation of MgAl2O4. With an increase in the synthesis temperature, the crystals grow (Figure 3 (a)), which can be seen in the diffraction patterns as a decrease in the width of the peaks and an increase in their intensity (Figure 3 (b)).

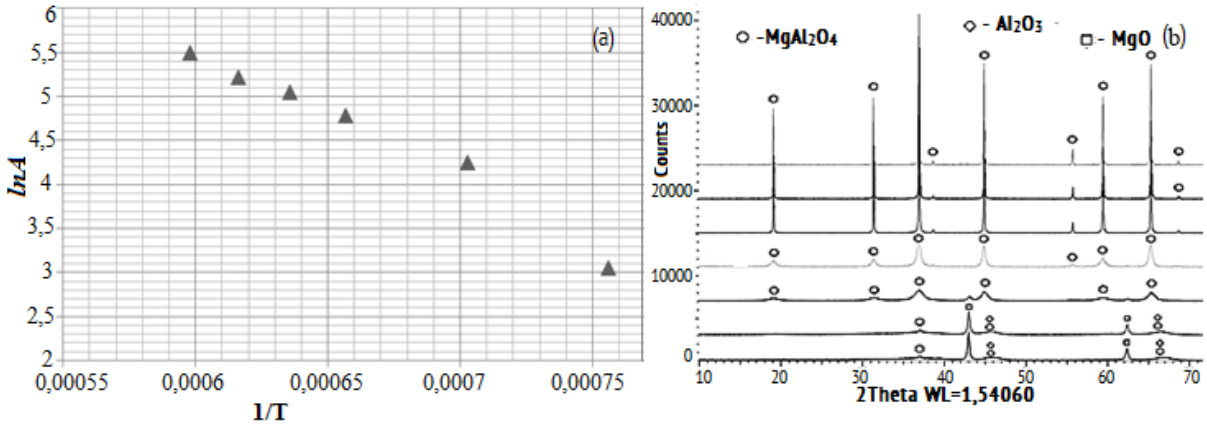

Figure 3. (a) Dependence of the average crystallite size on the synthesis temperature, (b) Radiographs of the heat-treated composition M30.

Mechanical action provides a sufficiently rigid impact on the structure of the initial oxides, which leads to excessive defects (disorder) in the crystal lattice and, accordingly, the longer the particles are exposed to the higher rate of formation of the new compound. The morphology of alumomagnesia spinel powders after mechanical activation is shown in Figure 4.

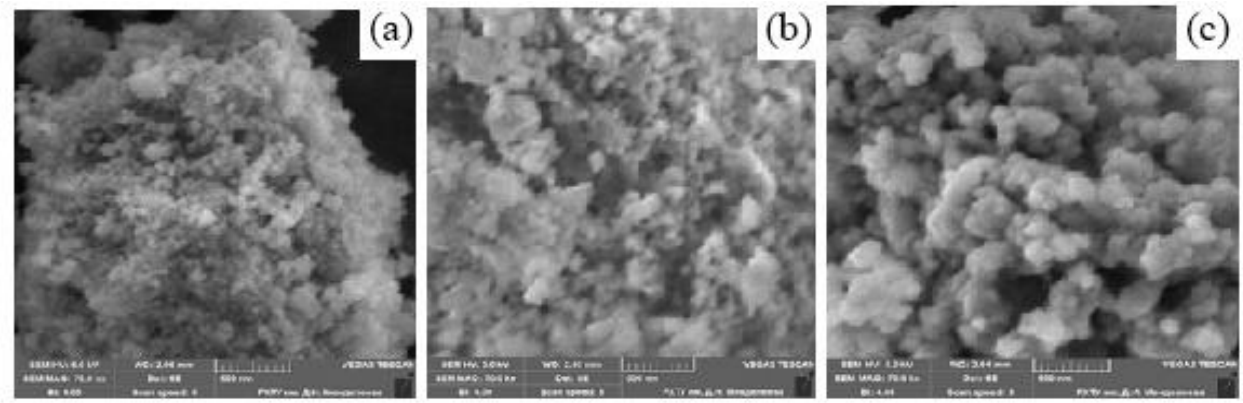

Figure 4. (a) Photographs of the microstructure of the powders (a) M30; (b) M60; (c) M120.

The powders are subject to a sufficiently strong agglomeration, increasing with an increase in the duration of the mechanical action. Regardless of the shape of the agglomerates, nanoparticles of the powder are clearly visible in the images. The average size of the aggregates for 30 minutes of grinding

was ~ 50 nm, for 60 minutes ~ 120 nm, for 120 minutes ~ 150 nm. With an increase in the time of mechanical action on the powder, the density and size of the aggregates increases, in the SEM image (Fig. 4 (c)). For 120 minutes of mechanical activation, the morphology of the rounded agglomerates is characterized by a tighter fit of the particles to each other.

4. Conclusions

Thus, it can be concluded that the use of mechanical activation of the initial γ-alumina and magnesium oxide powders accelerates the formation of alumomagnesian spinel, significantly reducing the temperature of the subsequent heat treatment. Mechanical activation increases the surface of the reacting phases (the reaction zone) and thus facilitates the course of reactions towards the formation of the product. An increase in the time of mechanical action leads to a decrease in the particle size and the degree of crystallinity of the starting oxides.

References

[1] R.J. Bratton, Sintering and grain-growth kinetics of MgAl2O4 *// J. Am. Ceram. Soc.,* 2008**, 52. № 8**. P.141-143.

[2] W. Bakkar, J.G. Lindsay, Reactive magnesia spinel, preparation and properties // *Am. Ceram. Soc. Bull.,* 2010, **46. № 11**. P. 1094 – 1097.

[3] Carmen Baudin, Rafael Martinez, and Pilar Pena, High-Temperature Mechanical Behavior of Stoichiometric Magnesium Spinel *// J. Am. Ceram. Soc.*, 2009, **42. № 4**. P.235-242.

[4] W. Bakkar, J.G. Lindsay, Combustion synthesis, characterization and sintering behavior of magnesium aluminate ($MgAl_2O_4$) powders// *J. Am. Ceram. Soc.*, 2011, **46. № 4**. P.111-123.

[5] Huang ZC, Zhang L, Pan W., Mechanochemical synthesis of barium titanate// *J. Eur. Ceram Soc.* 2012, **34**. P.783–790.