Sintering mechanism and activation energy of MgAl$_2$O$_4$ synthesized by preceramic organomagnesiumoxanealumoxan

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Abstract. A detailed study of the new method's ceramic spinel powder was carried out in the paper. A thorough analysis of the oligomer pyrolysis temperature effect on the kinetics and sintering mechanism was carried out in this work. The dependence of the change in the shrinkage and the shrinkage rate of spinel samples during non-isothermal sintering at three heating rates - 5, 10, 20 °C/min were obtained. Analyzing the obtained dependencies can be concluded that an increase in the pyrolysis temperature leads to a shift in the spinel shrinkage curves towards higher values of the sintering start temperature. The data obtained were used to determine the sintering parameter of spinel powder, which corresponds to the change in the dominant sintering mechanism from viscous flow to bulk diffusion, increasing the pyrolysis temperature.

1. Introduction

The most topical problem nowadays is searching for new transparent materials to be used in the high-temperature and defence industries. Traditional transparent glass and polymer protection has almost exhausted the possibilities of minimizing its mass. One of the competitive solutions in creating high-performance transparent armor is developing transparent ceramic materials. Such materials are necessary for bulletproof windows of armored vehicles, visors for helmets, armored shields, and bank windows. One of the leading materials is ceramics made of aluminium-magnesium spinel (MgAl2O4) [1]. Aluminum-magnesium spinel has a low density, high hardness and mechanical strength, erosive resistance, and transparency from the ultraviolet to the spectrum's IR range. Due to its high dielectric (dielectric permittivity 8.2-9.19) and electrical insulation characteristics (electrical resistance 10$^{13}$ $\Omega$·cm at 100 °C), spinel is a promising material for electrical production insulation products. With a high melting point (more than 2100 °C) and resistance to aggressive media, spinel can be used as a refractory material [2].

The most critical stage in producing transparent ceramics from aluminium-magnesium spinel is the precursor powder's preliminary synthesis. To obtain a high-quality ceramic material, the precursor powder must comply with the essential requirements: uniformity of chemical and phase composition, high dispersion, lack of aggregation of particles, lack of impurities. Methods of gas-phase synthesis, synthesis in aqueous solutions, and solid-phase synthesis have become very popular [3, 4, 5]. At SSC
RF "GNIChTEOS", a new method of synthesizing spinel powder from a ceramic-forming oligomer has been developed. The use of such compounds as precursors for the production of ceramic materials makes it possible to obtain a powder of high purity and dispersion.

One of the most critical tasks is determining the mechanism of consolidating the workpieces and the activation energy. The study of the change in the shrinkage of the material during sintering, depending on the heating rate, allows us to presumably determine the substance transfer mechanism [6]. Thus, this work aims to study the sintering kinetics, namely, to determine the sintering mechanism and the activation energy of spinel powder obtained from a ceramic-forming oligomer after pyrolysis at 700° and 1250°C.

2. Experimental part

To obtain the precursor powder, Al,Mg-oligomers were used. The general scheme of synthesis of ceramics-forming organomagnesiumoxaneyalumoxanes represented by the following equation (1):

\[
[\text{Al(OR)}_s(\text{OR}^*)_x(\text{OH})_p\text{O}_q]_m + k(\text{R**О})_2\text{Mg} \rightarrow [(\text{R**О})\text{MgO}]_k \cdot [\text{Al(OR)}_l(\text{R**О})_g(\text{OR}^*)_x(\text{OH})_z\text{O}_y]_m + (s-l) \text{ROH} \tag{1}
\]

where \(k=0,1–12; m=3–12; s+x+2q+p=3, \ k/m + 1 + g + x + 2y + z = 3; R - C_nH_{2n+1}, n = 2,4; R^* - C(\text{CH}_3)=\text{CHC(O)O}C\text{C}_2\text{H}_5; \) \(R^{**} - C(\text{CH}_3)=\text{CHC(O)}\text{CH}_3 \) [7]. The resulting powder was subjected to pyrolysis at 700 °C and 1250 °C for 10 hours in the air. Spinel powder was characterized by X-ray phase analysis and scanning electron microscopy. The microstructure of spinel powders was studied using a high-resolution Supra 50 VP scanning electron microscope (LEO, Germany, 2003) with an INCA Energy + Oxford microanalysis system with a local X-ray spectral analysis attachment. In both cases, the electron beam source is a cathode with field emission; the voltage at the accelerating electrode is up to 20 kV. The magnifications used are from \(\times 45\) to \(\times 20,000\). To study the sintering kinetics, the consolidated sample was placed in a horizontal graphite holder of a DIL 402 C dilatometer with a vacuum-dense furnace equipped with a graphite pusher high-precision displacement converter (measuring range 500-5000 microns). The thermo-element is located near the sample and accurately registers its temperature. The argon flow introduced into the furnace was 70 ml/min, and the heating rate was 5, 10, and 20°C/min. Heating was carried out to a temperature of 1650 °C and then cooled the sample to room temperature at a rate of 20 °C/min. Assuming the absence of anisotropy in the compaction of all samples, the relative density of the sintered sample (\(\rho_s\)) was calculated using the following equation (2) [8]:

\[
\rho_s = \left[1 + \frac{\Delta L/L_0}{\alpha(T-T_0)}\right]^3 \rho_g \tag{2}
\]

where \(\Delta L/L_0\) is the relative linear shrinkage, obtained by dilatometric study, \(L_0\) is the initial length of the sample, \(T\) is the measured temperature, \(T_0\) is the initial temperature, \(\rho_g\) – density of the original raw, \(\alpha\) is the thermal coefficient of linear expansion (CLTE). The CLTE of the samples was determined during the cooling stages of dilatometric analysis [9,10]. The average value of \(\alpha\) was determined on sintered samples from the sample's cooling curve, after sintering, using different heating rates adopted during the studies. The samples' density obtained after dilatometric studies were determined by calculating the body's saturation with liquid and subsequent hydrostatic weighing. Distilled water was used as the liquid.

The activation energy (Q), the apparent activation energy (nQ) of the initial stage of sintering and the order (n) associated with the sintering mechanism were estimated using the formulas presented in [11]. For each heating rate, the values of \(t\) and the heating rate (\(dt/dt\)) = C were determined for the same relative density of the samples. The obtained dependences plotted in the coordinates \(\ln[T(C(dp/dT))]\) from 1/T, allow us to determine the angle of inclination \(S_1\). For the same density value, the activation energy will be expressed by the following equation (3):
\[ Q = -R \cdot S_1 \]  \hspace{1cm} (3)

Using the slope angle \( S_2 \) of the dependence \( \ln[T (d (=L/L_0)/dT)] \) on \( 1/T \), the apparent activation energy was determined as follows:

\[ nQ = -R \cdot S_2 \] \hspace{1cm} (4)

\[ n = nQ/Q = S_1/S_2 \] \hspace{1cm} (5)

Calculations were performed for relative density values <76%, which corresponds to the close shrinkage range <4%. The straight-line slope determined the value of the activation energy (Q) of the sintering process at each relative density.

3. Results and discussion

XRD analysis showed that after pyrolysis at 700°C, the \( \text{MgAl}_2\text{O}_4 \) powder consists of amorphous particles without visible crystalline phase. According to the SEM results, spinel powder after pyrolysis at 700°C is large polymer-like particles. Due to the inheritance of the structure, the particles have a scaly structure (figure 2A). An increasing of the pyrolysis temperature to 1250°C leads to the crystallization of the spinel phase (figure 1). The particles are agglomerates that are no larger than 10 microns, consisting of nanoscale spinel particles. In work [12], the influence of the initial spinel powder's pyrolysis temperature on the rheological properties is considered. It was found that the powder with an amorphous structure has the highest elastic modulus because the fracture resistance is much greater. A further increase in the pyrolysis temperature leads to the formation of an organized system, and particles become more spherical. These facts lead to a significant increase in the ultimate deformation, a decreasing of the elastic modulus and a maximum compressibility coefficient.

![Figure 1. XRD of MgAl2O4 powder at pyrolysis temperature of 1250°C](image)

Figure 3 shows the change in the shrinkage and shrinkage rate of spinel samples during non-isothermal sintering at three heating rates-5, 10, and 20 °C/min, respectively. Regions of normal linear expansion of the spinel are observed for each heating rate, and then the shrinkage process occurs. Comparative data of sintering process are shown in table 1. It was found that pyrolysis at 1250°C leads
to a shift in the spinel shrinkage curves towards higher values of the sintering start temperature from $T_{700} = 1068^\circ\text{C}$ to $T_{1250} = 1546^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$. Pyrolysis temperature also affects the value of the maximum shrinkage. At $1650^\circ\text{C}$, with increasing heating rate, shrinkage decreases by 2% with an increase in the rate from $5^\circ\text{C}/\text{min}$ to $20^\circ\text{C}/\text{min}$. It is established that the maximum shrinkage rate depends on the heating rate, and more than higher the heating rate, the instantaneous shrinkage rate is higher regardless of temperature.

**Figure 2.** SEM analysis of MgAl$_2$O$_4$ after pyrolysis: A – 700°C; B – 1250°C
Figure 3. Curves of continuous shrinkage and spinel shrinkage rate after pyrolysis: A-at 700°C; B-1250°C

Table 1. Data of dilatometric analysis of spinel and composite at 3 heating rates

| Heating rate, °C/min | \( T_{\text{start of shrinkage 700°C}} \) | \( T_{\text{max shrinkage 700°C}} \) | \( \Delta l/l_0 \), % | \( T_{\text{start of shrinkage 1250°C}} \) | \( T_{\text{max shrinkage 1250°C}} \) | \( \Delta l/l_0 \), % |
|----------------------|------------------------------------------|---------------------------------|-----------------|------------------------------------------|---------------------------------|-----------------|
| 5                    | 1061                                     | 1123                           | 25,5            | 1491                                     | 1565                           | 4,37            |
| 10                   | 1068                                     | 1117                           | 23,9            | 1546                                     | 1629                           | 3,55            |
| 20                   | 1076                                     | 1126                           | 23,8            | 1607                                     | 1649                           | 2,86            |

The sintering parameter and the sintering activation energy were calculated to confirm that the pyrolysis temperature and spinel formation lead to a change in the sintering mechanism. The obtained data are shown in Table 2. Following the model of sintering of two spherical particles, the values of the parameter \( n = 0.31-0.33 \) correspond to the grain boundary diffusion, \( 0.40-0.50 \) for the volume diffusion only from the grain boundary, and more than 0.53 for the volume diffusion from the grain boundary and the surfaces of the spheres [13].

Table 2. Activation energy, apparent activation energy, and an order of the diffusion mechanism at the initial stage of spinel sintering after pyrolysis at 700° and 1250°C.

| Sample | n   | Q       | nQ      | Sintering mech        |
|--------|-----|---------|---------|-----------------------|
| 700 °C | 2,92| 147±82  | 430±86  | Viscous flow          |
| 1250 °C| 0,98| 481±103 | 470±21  | Volume diffusion      |

4. Conclusion
The paper presents a detailed study of the sintering kinetics of MgAl\(_2\)O\(_4\) powder obtained from a ceramic-forming oligomer. The influence of the oligomer's pyrolysis temperature on the activation energy of the sintering process and the spinel sintering mechanism is considered. After analyzing the obtained data, it can be concluded that an increase of the pyrolysis temperature leads to a shift in the spinel shrinkage curves towards higher values of the sintering start temperature from \( T_{700} = 1068°C \) to
\[ T_{1250} = 1546°C \] at a heating rate of 10°C/min. It is established that the maximum shrinkage rate depends on the heating rate, and the higher heating rate leads to a higher instantaneous shrinkage rate regardless of temperature. The character of the change in the sintering parameter \( n \) from 2.92 to 0.98 is determined, which corresponds to the difference in the dominant sintering mechanism from viscous flow to volume diffusion.

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