Rheological properties of MgAl$_2$O$_4$ obtained from preceramic organomagnesiumoxanealumoxanes

E A Gumennikova$^{1,2}$, D D Titov$^1$, A S Lysenkov$^1$, M G Frolova$^1$, Yu F Kargin$^1$, G I Shcherbakova$^3$ and E A Novokovskaya$^3$

$^1$A.A. Baykov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, 119334, Russia, Moscow, Leninskiy prospect, 49
$^2$Mendeleev University of chemical technology of Russia, 125047, Moscow, Miusskaya sq., 9
$^3$State Research Institute for Chemistry and Technology of Organoelement Compounds, 105118, Russia, Moscow, sh Entuziastov 38

Abstract. In this study, a detailed study of ceramic spinel powder obtained by the new method was carried out. Namely, the study of the influence of the pyrolysis temperature of the oligomer and grinding time on the microstructure, phase composition and rheological properties of spinel during pressing. Graphs of the dependences “stress-strain” and “stress – relative density” were obtained, which characterize the rheological properties of aluminium-magnesium spinel obtained in a new way. Analyzing the obtained dependences, we can conclude that with an increase in the pyrolysis temperature, spinel is more natural to deform, which is associated with a change in structure. According to the data obtained, a dependence on the growth of the elastic modulus after grinding is also observed.

1. Introduction

In the modern world, materials with high physical and mechanical properties are in great demand. A special place among such materials is occupied by optically transparent ceramics from aluminium-magnesium spinel MgAl$_2$O$_4$ (spinel), which is capable of transmitting in various spectral regions without losing other valuable properties. Binary ceramics made of magnesium-aluminium spinel is widely used to create heat-resistant, catalytically active, optically transparent, electrotechnical, chemical, corrosion and radiation-resistant products [1].

The properties of optically transparent ceramic products strongly depend on the composition, structure, dispersion of powdery precursors and especially the presence of impurities. Therefore, great attention should be paid to the synthesis of initial powders in the preparation of optically transparent ceramic materials [2]. The synthesis and manufacture of MgAl2O4 spinel have long been known. Many methods, such as conventional solid-state reaction (SSR), sol-gel, spray drying (spraying), and citrate complexation with an organic gel, have been widely used [1, 3-15]. A few years ago, a new method of synthesis from a ceramic-forming oligomer was introduced at the GNIIKhTEOS. The first synthesized hydrolytically stable in air soluble in organic solvents ceramic-forming organomagnesium oxanalumoxanes are alkyl magnesium oxanalumoxanes, i.e. had Mg – C and Al – C bonds; therefore, they actively interacted with air moisture and oxygen. The use of such compounds as precursors for the preparation of components (binders, coatings, fibres, powders) of high-purity ceramic composites based on aluminium and magnesium oxides is practically impossible. In contrast to alkyl magnesium oxanalumoxanes, organomagnesium oxanalumoxanes synthesized in GNIIKhTEOS...
are ceramic-forming oligomers that can be used as precursors of components of high-purity ceramics based on aluminium and magnesium oxides, in particular, magnesium aluminate of the composition MgAl₂O₄ (spinel) [17].

Thus, the goal of this work is a detailed study of ceramic spinel powder obtained by the original new method. Namely, the study of the effect of the pyrolysis temperature of the oligomer and grinding time on the microstructure, phase composition and rheological properties of spinel during pressing.

2. Experimental part

2.1. Materials

The general scheme for the synthesis of ceramic-forming organomagnesium oxanaluminoxanes can be represented by the following equation:

\[ \text{[Al(OR)}_2 \text{(OR*) (OH) O]} + k\text{[R**(O)}_2 \text{Mg)} \rightarrow \text{[(R**(O)}_2 \text{MgO)}_k \cdot \text{[Al(OR)}_l \text{(R**O)}_g \cdot \text{(OR*)} \text{(OH)O]} + + (s-l) \text{ROH}, \]

where \( k = 0,1−12, m = 3−12, s+x+2q+p = 3, k/m + 1 + g + x + 2y + z = 3; R = \text{C}_n \text{H}_{2n+1} , \)
\( n = 2,4; R^* = \text{C} (\text{CH}_3) = \text{CHC}(\text{O}) \text{OC}_2 \text{H}_5 ; R^{**} = \text{C}(\text{CH}_3) = \text{CHC}(\text{O}) \text{CH}_3 \) [17].

The synthesized ceramic-forming oligomer was then subjected to pyrolysis for 2 hours in a muffle furnace at 700 °C, 800 °C and 900 °C in air. Next, the resulting powder was crushed.

The grinding of the initial powder was carried out in a planetary mill for two hours at 250 rpm in a solution of isopropyl alcohol. The powder was ground before and after pyrolysis to compare rheological properties. After grinding, the powder was dried in an oven at 130 °C until the alcohol was completely removed. The resulting spinel powder was characterized by particle size analysis, x-ray phase analysis, and using scanning electron microscopy.

Granulometric analysis of powders after pyrolysis was carried out on a Fritsch Particle Sizer ‘analysette 22’ laser diffraction analyzer. The dispersion was carried out in a liquid (laser wavelength 655 nm, incident beam diffraction 0.01–1000 μm, sample amount 0.1–2 cm³, measured particle size of the powder 0.16–1160 μm); the Fraunhofer optical method was used for calculation. Grain composition was presented on a differential particle distribution curve.

The microstructure of spinel powders was studied on a Supra 50 VP high-resolution scanning electron microscope (LEO, Germany, 2003) with an INCA Energy + Oxford microanalysis system with an attachment for local X-ray spectral analysis. In both cases, the electron beam source is a cathode with a field emission, the voltage at the accelerating electrode - up to 20 kV. Used magnifications - from × 45 to × 20,000.

2.2. Rheology

Rheological properties were tested on the mechanical testing machine (Instron 5581, Great Britain). The stain velocity was 1 mm/min. A sample of the test sample weighing 0.15 g was placed in a steel mould. At least 5 measurements were carried out for each composition, then the values were averaged, and calculations were made using the formulas below.

The deformation was calculated by the equation (1):

\[ \Delta h = \frac{h_0}{\varepsilon} \]

where Δh is the change in the height of the bulk layer over time; h₀ is the initial height of the bulk layer.

The compressibility modulus is numerically equal to the tangent of the linear section slope angle of the diagram strain against deformation, and is calculated by the equation (2):

\[ G = \frac{\Delta p'}{\varepsilon^*} \]

where \( \Delta p' \) is the limiting change in the linear section pressure value; \( \varepsilon^* \) is the final value of the linear section deformation.

The compressibility coefficient \( k_c \) characterises the reversible decrease in the sample height (volume) under the pressure action and is quantitatively determined by equation (3):

\[ k_c = \frac{-1}{h_0} \cdot \frac{\Delta h}{\Delta p'} \]
where $\Delta h'$ and $\Delta p'$ are the limiting values of the height and the linear section pressure variation, $h_0$ is the initial height of the backfill.

The physical meaning of the compressibility coefficient is characterisation the material ability to compact at the initial (linear) stage, during which the compaction intensity is maximal.

3. Discussion of results

Kinetic curves were obtained, representing the pressure versus time for spinel powder. These values were rearranged in the stress-strain curve. To study the effect of powder grinding on rheological properties, the obtained data were used to plot the strain dependences of the strain before and after grinding (figure 1A). On the stress-strain diagram before grinding, the dependence of the rheological properties on the pyrolysis temperature can be traced. With an increase in the pyrolysis temperature, the limiting value of the strain increases markedly.

![Figure 1](image)

**Figure 1.** The stress-strain curve of MgAl$_2$O$_4$ after pyrolysis at 700 °, 800 °, and 900 ° C A — before grinding, B — after grinding

Analyzing the obtained stress-strain graph after grinding (figure 1B), it is seen that for the initial powder after pyrolysis at 700 ° C, the limiting value of the linear section deformation is approximately equal to the value after pyrolysis at 800 ° C, and the value after pyrolysis at 900 ° C is much higher. This behaviour of the powder during deformation is associated with the microstructure of the powders.

The initial powder after pyrolysis at 700 ° C after grinding consists of large particles without a visible crystalline phase, which is confirmed by X-ray phase analysis (figure 2), and some particles retain their shape like a polymer (figure 3A). Due to the amorphous structure, the elastic modulus of such a powder is the largest, therefore, to create an ordered structure, it is necessary to exert a greater force since the fracture resistance is more significant. After pyrolysis at 800 ° C, according to the XRD data, primary spinel crystallization occurs, the powder ceases to be amorphous. Particles are agglomerates 5–10 µm in size consisting of spinel nanoparticles 30–40 nm in size (figure 3B). For this powder, the elastic modulus is maximum, since the particles have a rounded shape, fit well during pressing (table 1). A further increase in the pyrolysis temperature to 900 ° C leads to the growth of crystals on the surface of the agglomerate. Thus, the powder particles are 5–10 µm agglomerate, consisting of 30–40 nm spinel nanoparticles, and the entire surface of this agglomerate is covered with crystals up to 500 nm in diameter (figure 3C). Such a powder structure is looser concerning different pyrolysis temperatures. As a result, agglomerates of powder particles are more easily deformed. We assume that it is this particle roughness that leads to a significant increase in the ultimate strain value, a decrease in the elastic modulus, and a maximum compressibility coefficient (Table 1).
Figure 2. XRD of MgAl₂O₄ powder after pyrolysis at 700 °, 800 °, and 900 ° C.

Figure 3. SEM analysis of MgAl₂O₄ powder after pyrolysis of a - 700 ° C, b - 800 ° C, c - 900 ° C

Table 1. The rheological parameters of MgAl₂O₄ powder

|       | G, MPa | Kc, E⁺ | ε⁺, % |
|-------|--------|--------|-------|
| 700 after | 45,33  | 1,72   | 12,08 |
| 800 before | 43,87  | 1,68   | 10,46 |
| 800 after  | 49,80  | 1,59   | 11,59 |
| 900 before | 36,78  | 2,16   | 16,51 |
| 900 after  | 42,36  | 1,88   | 15,13 |

The data presented indicate the effect of grinding on the growth of the elastic modulus. This may be due to the destruction of particle agglomerates that form after pyrolysis. This once again proves that the particles created during the recrystallization process are brittle.

4. Conclusion
In the presented work, a detailed study of ceramic spinel powder obtained by the original new method was carried out. Namely, the study of the influence of the pyrolysis temperature of the oligomer and grinding time on the microstructure, phase composition and rheological properties of spinel during pressing. Based on the results of the experiments, graphs of the dependences “stress-strain” and “stress – relative density” were obtained, which characterize the rheological properties of aluminium-
magnesium spinel obtained in a new way. Analyzing the obtained dependences, we can conclude that with an increase in the pyrolysis temperature, spinel is more natural to deform, which is associated with a change in structure. According to the data obtained, a dependence on the growth of the elastic modulus after grinding is also observed.

Acknowledgements
The work was financially supported by the Grant of the President of the Russian Federation No. MK-39.2019.3

References
[1] Ma Y & Liu X 2019 Molecules 24 1704–25
[2] Senina M O, D O Lemeshev 2017 Successes in chemistry and chemical technology 31 1 182
[3] E Ryshekewitch 1960 Oxide Ceramics (Academic Press, New York) p 257
[4] W W Kriegel, H Palmer, D M Choi 1964 Special Ceramics 3 167
[5] W T Bakker, L G Lindsay 1967 Am. Ceram. Soc. Bull. 46 1094
[6] J T Bailey, R Russell 1968 Am. Ceram. Soc. Bull. 47 1025
[7] K Hamono, S Kanzaki 1977 J. Ceram. Soc. Jpn. 85 225
[8] E Kostic, L Momcilovic 1977 Ceramurgia International 3 57
[9] I Teoreanu, N Ciocea 1987 Interceram. 4 19
[10] H C Park, Y B Lee, K D Oh, F L Riley 1997 J. Mater. Sci. Lett. 16 1841
[11] R Sarkar, S K Das, G Banerjee 1999 Ceram. Int. 25 485
[12] R Sarkar, G Banerjee 1999 J. Europ. Ceram. Soc. 19 2893
[13] C Zografou, P Reynen, D Van Mallinckrodt 1983 Interceram. 38 37
[14] C Zografou, P Reynen, D Van Mallinckrodt 1983 Interceram. 38 40
[15] M A Serry, S M Hammad, M F Zawrah 1998 Br. Ceram. Trans. 97 275
[16] Shcherbakov G I, Krivtsova N, Kudinov N B, Apukhtina T L, Varfolomeyev M S, Storozhenko P A 2017 A Method of producing organosiloxane of alumoxanes, binders and impregnating materials (Pat. Of the Russian Federation 2615147.2017)
[17] Shcherbakova G, and Ashmarin A 2017 Inorganic materials 123 3-9