The effect additives of magnesium, titanium and zirconium oxides additives on the densification kinetics and structure of alumina during spark plasma sintering

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Abstract. The results of an experimental study of the effect of metal oxide additives on the sintering kinetics of systems based on alumina by the method of spark plasma sintering (SPS) are presented. The influence of additives at the stage of intensive compaction of powder pressing and at the stage of intensive growth of ceramic grains is analyzed. A qualitative explanation of the mechanism of the effect of magnesium oxide additives on the stabilization of the grain structure of aluminum oxide is given.

1. Introduction
Ceramics based on aluminum oxide have high physical and mechanical properties, low cost and availability. This makes alumina the most promising ceramic material for a wide range of structural applications [1]. An increase in the physical and mechanical properties of this ceramics can be expected when a homogeneous fine-grained structure is formed [2]. SPS technology is able to provide materials with small grain size [1].

Research results [1, 3, 4] show that composite ceramics based on aluminum oxide are suitable for creating modern wear-resistant metalworking tools, making armor protection elements, angular contact bearings, etc.

One of the tools for influencing the sintering kinetics, grain size, and physical and mechanical properties of ceramics is the introduction of a small amount of different additives, for example: MgO, TiO$_2$, Y$_2$O$_3$, SiC, ZrO$_2$ and others. The aim of this work is to study the effect of such additions on the sintering kinetics, the evolution of the grain structure of alumina ceramics during spark plasma sintering.

2. Experimental and materials
Ceramic samples made of pure α-Al$_2$O$_3$ (Taimei Chemicals Co., Ltd, d = 200 nm) and composites based on it with MgO additives (Alfa Aesar - A Johnson Matthey Company, d = 100 nm), TiO$_2$ (Institute of Electrophysics, UB RAS, d = 100 nm) and ZrO$_2$ (Pangea Int., Ltd, d = 100 nm).

Spark plasma sintering of powders was carried out on the installation Dr. Sinter SPS-625 "SPS SYNTEX, INC." Heating rate $V = 10 \pm 700 \, ^\circ C/min$, mechanical stress during sintering $P = 6 \pm 70 \, MPa$. Sintering was carried out in a vacuum of 5 Pa. The temperature of the sintering process was monitored with an optical pyrometer focused on the surface of a graphite mold with an inner diameter of 12 mm.
The maximum temperature - sintering temperature (T) lay in the range 1150 ÷ 1300°C. Isothermal holding at T was τ = 0 ÷ 30 min. The density of the sintered samples was measured by hydrostatic weighing in distilled water using a Sartorius CPA analytical balance. The average grain size in sintered ceramics was calculated using the Good Grains software package from micrographs obtained with a Jeol JSM-6490 scanning electron microscope.

3. Results and discussion

The dilatometer measures the change in linear dimensions. During sintering, it integrally measures the shrinkage of the powder compact and the thermal expansion of the materials of the molds and press plungers. The shrinkage graph of the powder was obtained by subtracting from the overall shrinkage graph the thermal expansion graph obtained by repeating the sintering regime with an empty mold. Conversion of shrinkage to compaction value ρ/ρth was carried out on the basis of the procedure described in [5].

3.1 Analysis of the effect of additives at the stage of intensive compaction.

Let us calculate the activation energy of grain boundary diffusion at the second stage. According to [5], the value of the activation energy of grain-boundary diffusion Qb can be calculated from the experimental dependence ρ/ρth(T), presented in double logarithmic coordinates on the reciprocal temperature Tm/T:

\[
\frac{Q_b}{kT_m} = \frac{\partial \ln \left( \frac{V_p^{\text{max}}}{V_{\text{theor}}} \cdot \left( \frac{\rho(T)/\rho_{\text{theor}}}{1 - (\rho(T)/\rho_{\text{theor}})} \right) \right)}{\partial (T_m/T)}
\]

where Qb - activation energy of grain boundary diffusion, Vp^{\text{max}} - maximum pore volume, V_{\text{theor}} - theoretical pore volume, ρ(T) - density versus temperature, ρ_{\text{theor}} - theoretical density, Tm - melting temperature, k - Boltzmann constant.

Table 1 shows the calculations of the activation energy of sintering at the II stage. For the systems Al2O3 + 0.5% MgO, Al2O3 + 0.5% vol. TiO2, and Al2O3 + 0.5% ZrO2, the activation energy is Qb = 30 ± 2 kTm and coincides with the activation energy of sintering of pure Al2O3 in the entire range of the studied heating rates (from 10 °C/min to 700 °C/min). Thus, it can be concluded that particles of MgO, TiO2, and ZrO2 do not affect the kinetics of sintering of aluminum oxide at the stage of intense shrinkage. It should be noted that the found value of the activation energy for sintering is in agreement with the experimental values of the activation energy for grain-boundary diffusion of oxygen in aluminum oxide (Qb ~ 16–40 kTm) given in the review [6].

| Systems:             | stage of intensive compaction | the stage of isothermal holding |
|----------------------|------------------------------|-------------------------------|
|                      | 10 °C/min        | 100 °C/min       | 700 °C/min      | Qb, kTm      |
| Al2O3                | 30±1.5           | 30±1.5           | 30±1.5          | 29±1.5       |
| Al2O3+0.5%vol.MgO    | 31±1.5           | 31±1.5           | 31±1.5          | 30±1.5       |
| Al2O3+0.5%vol.TiO2   | 29±1.5           | 29±1.5           | 29±1.5          | 30±1.5       |
| Al2O3+0.5%vol.ZrO2   | 31±1.5           | 31±1.5           | 31±1.5          | 24.5±1.5     |

Thus, the analysis of the influence of modifier additives on the stage of intense shrinkage showed that the introduced additives do not affect the activation energy of grain boundary diffusion. The activation energy of grain boundary diffusion is Qb ~ 30 kTm
In other words, the change in the sintering kinetics of aluminum oxide caused by the segregation of Mg$^{2+}$ and Ti$^{4+}$ ions at the grain boundaries of the sintered ceramics, widely described in the literature [7-10], is not observed.

### 3.2 Analysis of the effect of additives on grain growth.

Let us consider the effect of the introduced additives at the stage of grain growth. In this case, let us consider the evolution of the grain structure for three systems: Al$_2$O$_3$, Al$_2$O$_3$ + 0.5%vol.MgO, Al$_2$O$_3$ + 0.5%vol.TiO$_2$, Al$_2$O$_3$ + 0.5%vol.ZrO$_2$, under conditions of isothermal holding. Let us estimate the activation energy of sintering of the systems under study.

As shown in [11, 12], recrystallization processes are carried out by the diffusion of single atoms and their groups. Thus, the mobility of the boundary is determined by a parameter that has the physical meaning of the diffusion coefficient.

Let us analyze the effect of the addition of zirconium oxide and magnesium oxide on the activation energy of grain growth in aluminum oxide under SPS conditions. The expression [11, 12] can be used to describe the kinetics of grain growth during sintering of aluminum oxide:

\[
d^n - d_0^n = \frac{2\gamma_b b \delta t}{kT} D_0 \exp\left(-\frac{Q_b}{kT_m}\right)
\]

where \( d \) - grain size, \( d_0 \) - initial grain size, \( n \) - exponent, \( t \) - sintering time, \( k \) - Boltzmann coefficient, \( \gamma_b \) - surface energy, \( b \) - Burgers vector, \( \delta \) - grain boundary width.

It can be seen from table 1 that the activation energy of grain-boundary diffusion at the third stage, the stage of grain growth, does not change with the introduction of magnesium and zirconium modifier particles and is \( Q_b = 30 \pm 1.5 \) kT$_m$. Adding to aluminum oxide 0.5% vol. titanium oxide leads to a decrease in the activation energy of grain growth to \( Q_b = 24.5 \) kT$_m$.

As shown above, the additives do not change the activation energy of grain boundary diffusion during grain growth. However, the introduced additives of magnesium oxide and zirconium slow down the growth of grains (2.75 μm and 3 μm, respectively) in relation to pure aluminum oxide. So, the samples which sintered at 1300°C with 30 min holding time have the average grain size 16 μm for pure alumina oxide, and 2.75 and 3 μm for alumina with magnesium and zirconium additions, respectively.

In this case, the most probable stabilization mechanism seems to be the Zener fixation mechanism. When used as additives MgO and ZrO$_2$ powders with the same initial particle size (d ~ 100 nm), the stabilized grain size of ceramics Al$_2$O$_3$ + 0.5%vol.MgO and Al$_2$O$_3$ + 0.5%vol.ZrO$_2$ must match. However, this contradicts the experimental data obtained, since at high temperatures and long holding times, the average grain size of ceramics Al$_2$O$_3$ + 0.5%vol.MgO is approximately two times smaller than the average grain size of the ceramic Al$_2$O$_3$ + 0.5%vol.ZrO$_2$.

It should be noted that the structure of the Al$_2$O$_3$ + 5%vol.ZrO$_2$ is characterized by a comparable average grain size with ceramics Al$_2$O$_3$ + 0.5%vol.MgO. This means that the rate of grain growth in these composites was the same:

\[
d = \alpha \cdot \left(\frac{d_{MgO}}{f_{MgO}}\right) = \alpha \cdot \left(\frac{d_{ZrO2}}{f_{ZrO2}}\right)
\]

where \( d_{MgO} \) is the diameter of MgO particles, \( f_{MgO} = 0.005 \) is the volume fraction of MgO particles, \( d_{ZrO2} = 50–100 \) nm is the diameter of ZrO$_2$ particles, \( f_{ZrO2} = 0.05 \) is the volume fraction of ZrO$_2$ particles.

Substituting into expression (5) the volume fractions of the additives used and the average particle size of ZrO$_2$, we obtain \( d_{MgO} = 5 \pm 10 \) nm.

It should be noted here that in reality we are not talking about MgO particles, but about dispersed particles of spinel MgAl$_2$O$_4$. Since the reaction of its formation during the interaction of MgO and Al$_2$O$_3$ lies below the temperature of the onset of sintering [13].
4. Conclusions
The influence of MgO, TiO$_2$ and ZrO$_2$ particles on the sintering kinetics and grain growth of Al$_2$O$_3$ has been studied. It is shown that MgO, TiO$_2$ and ZrO$_2$ have no effect on the kinetics of the stage of intensive compaction of Al$_2$O$_3$ at heating rates $V = 10$ °C/min, 100 °C/min, 700 °C/min. The activation energy of grain boundary diffusion at stage II is $Q_b = 30kT_m$. It is shown that MgO and ZrO$_2$ do not change the diffusion activation energy at the stage of Al$_2$O$_3$ grain growth. The activation energy of grain boundary diffusion at stage III is $Q_b = 30 \pm 1.5 kT_m$. Adding to aluminum oxide 0.5% vol. titanium oxide leads to a decrease in the activation energy of grain growth to $Q_b = 24.5 kT_m$.

It is shown that the grain structure of composites containing 5% ZrO$_2$ and 0.5% MgO is equivalent.

The size of the MgO particles in the sintered sample was estimated. The size of the magnesium oxide particles in the sintered ceramics is 5 ÷ 10 nm. A qualitative explanation of the mechanism of the effect of the addition of MgO on the stabilization of the grain structure of Al$_2$O$_3$ is given. The small size of dispersed particles and the uniformity of their distribution determines the effective action of the Zener force even with the introduction of a small amount of additive.

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