Investigation of the kinetics of spark plasma sintering of alumina. Part 2. Intermediate and final stages of sintering

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Abstract. The article presents the results of the investigation of the initial sintering stage of alumina. The authors determined the activation energy of shrinkage at the initial. The study shows that the effect of additives is observed only at the final stage of sintering.

1. Introduction
Aluminum oxide is one of the promising ceramic materials for a wide range of structural applications due to the combination of high hardness, heat and chemical resistance [1, 2].

There are a lot of articles about SPS sintering of the alumina ceramics [3–9], but none of them provides a thorough analysis of the sintering kinetics of each of the stages of the sintering process and the investigation of the role of the additives at each of that stages.

The main purpose of the second part of the article is the investigation of the intermediate and final stages of sintering of alumina ceramics during SPS.

2. Experimental
The main material used in this study is α-Al2O3 powder (d = 0.2 µm, Taimei Chemicals, Japan) and its mixtures with MgO (d ~ 0.1 µm, Alfa Aesar, Germany), TiO2 (d < 0.5 µm, UrFU RAS, Russia), ZrO2 (d = 0.03 µm, Pangea Int. Ltd., China). A detailed description of the methods which were used in the present work is provided in the first part of the article.

In the study of the kinetics of sintering under a constant heating rate, the heating rate was 100ºС/min and sintering temperature T = 1520ºС. There was no isothermal dwelling.

To study the grain growth kinetics, the samples were heated to 1320, 1420, and 1520ºС with heating rate of 100ºС/min and dwelled for 0, 3, 10, and 30 min.

3. Results and discussion

3.1. Analysis of shrinkage behavior at the intermediate stage (stage II). Sintering of ceramics under continuous heating rate mode
As was shown in Part 1 (figure 1b in Part 1), the addition of ZrO2, MgO, TiO2 additives does not affect the shrinkage kinetics of the α-Al2O3. Thus, the shrinkage curves at stage II can be considered equivalent for all studied composites. The further analysis of the shrinkage curves was made for pure Al2O3 oxide and Al2O3 + 0.5% vol MgO.
According to [10], the process of shrinkage of a powder material can be described as the process of plastic deformation of a continuous porous material.

In this case, the strain rate can be determined from experimental data by the equation:

$$\dot{\varepsilon} = \frac{S}{L_0}$$  \hspace{1cm} (1)

where $S$ is the shrinkage rate and $L_0$ is the initial height of the powder before sintering.

As experimental data, we used the sintering data of the sample obtained at a heating rate of 100°C/min, which were equal to $L_0 = 6 \times 10^{-3}$ m; $\sigma = 70$ MPa. $S = 14 \times 10^{-6}$ m/s for pure $\alpha$-$\text{Al}_2\text{O}_3$ and $S = 18 \times 10^{-6}$ m/s for $\text{Al}_2\text{O}_3 + 0.5\%$ vol MgO (at $T = 1200^\circ\text{C}$).

At this consideration, the dependence of powder shrinkage on time at a fixed temperature and applied pressure can be described using the dependence on the power creep law [11]:

$$\dot{\varepsilon} = A \left( \frac{D_V}{k^2} \right) \left( \frac{G\Omega}{kT} \right)^n \sigma^n$$  \hspace{1cm} (2)

where $\dot{\varepsilon}$ is the strain rate, $A$ is the Dorn constant, $D_V$ is the coefficient of bulk diffusion, $b$ is the Burgers vector, $G$ is the shear modulus, $\Omega$ is atomic volume, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $\sigma$ is the stress, and $n$ is the constant which determines the mechanisms of deformation and diffusion ($n = 3$).

According to [11], the following values can be used for alumina: $A = 3.38$; $b = 4.76 \times 10^{-10}$ m; $\Omega = 4.25 \times 10^{-29}$ m$^3$; $G = 126$ GPa.

Let us take the expressions (1) and (2) and substitute the above values of constants and experimental values. This way we can obtain $D_V = 3.5 \times 10^{-15}$ m$^2$/s for pure $\alpha$-$\text{Al}_2\text{O}_3$ and $D_V = 4.5 \times 10^{-15}$ m$^2$/s for $\alpha$-$\text{Al}_2\text{O}_3 + 0.5\%$ vol MgO.

The expression for the coefficient $D_V$ is the following:

$$D_V = D_{V0}\exp\left(\frac{-Q_V}{kT}\right)$$  \hspace{1cm} (3)

where $D_V$ is the coefficient of bulk diffusion, $D_{V0}$ is the pre-exponential factor, $Q_V$ is the activation energy of bulk diffusion, $k$ is the Boltzmann constant, and $T$ is the absolute temperature.

By substituting $D_{V0} = 0.19$ m$^2$/s [11] (for bulk diffusion of oxygen ions), we obtained the value of the activation energy of diffusion at stage II. For pure $\alpha$-$\text{Al}_2\text{O}_3$ ceramic $Q_V = 31.6$ kTm, and for the composite $\text{Al}_2\text{O}_3 + 0.5\%$ vol MgO $Q_V = 31.4$ kTm. Similar values of sintering activation energy ($Q_{V \sim 31}$ kTm, which corresponds to $Q_{V \sim 530}$ kJ/mol) at stage II were obtained for all considered systems.

Thus, the studied additives do not affect the sintering kinetics of alumina at the intermediate stage of the SPS process under conditions of constant heating rate.

Analysis of the experimental results shows that the rapid shrinkage of alumina at stage II is caused by plastic deformation carried out under the applied mechanical pressure, controlled by bulk diffusion (power creep). In this case, the activation energy of the shrinkage process at the intermediate stage $Q = \sim 31$ kTm.

To eliminate the possible effect of residual pores on the kinetics of grain growth, further studies were carried out on samples that have reached the density of more than $\rho = 99.5\%$. The study of grain growth kinetics was carried out at the heating rate of 50°C/min and temperatures of 1320, 1420, and 1520°C with subsequent isothermal dwelling for 0, 3, 10, and 30 min. The dependences of the grain size ($d$) on the duration of isothermal dwelling ($t$) at various temperatures of the SPS are shown in figure 1.

Figure 1 shows that magnesium oxide has a significant impact on the grain growth kinetics at the final stage (stage III). The grain size of ceramic with the addition of MgO is about 10 times smaller than in pure alumina ceramics. Zirconium oxide particles inhibit grain growth less effectively than magnesium oxide. Addition of the titanium oxide leads to a slight increase in the average grain size.
Figure 1. Dependence of grain size on isothermal dwelling time: (a) pure $\alpha$-$\text{Al}_2\text{O}_3$, (b) $\text{Al}_2\text{O}_3 + 0.5\%$ vol $\text{MgO}$, (c) $\text{Al}_2\text{O}_3 + 0.5\%$ vol $\text{TiO}_2$, (d) $\text{Al}_2\text{O}_3 + 0.5\%$ vol $\text{ZrO}_2$.

3.2. Analysis of shrinkage behavior and grain growth at stage III. Sintering of ceramics in isothermal conditions.

3.2.1. Estimation of the grain growth activation energy for pure $\alpha$-$\text{Al}_2\text{O}_3$. The expression describing the grain growth during isothermal dwelling has the following form [12]:

$$d^n - d^n_0 = D_b t = D_{b0} \exp(-\frac{Q_b}{kT_m}) t$$

where $d_0$ is the initial grain size, $d$ is the grain size at time $t$, $D_b$ is the coefficient of grain-boundary diffusion, $D_{b0}$ is the pre-exponential factor, $Q_b$ is the activation energy of grain-boundary diffusion, $k$ is the Boltzmann constant, $T_m$ is the melting temperature, and $n$ is the growth rate constant.

According to [12, 13], the growth rate constant for a homogeneous system, which does not contain second phase particles, $n = 2$.

By substituting the value $n = 2$ into equation (4), which describes the kinetics of grain growth of pure $\alpha$-$\text{Al}_2\text{O}_3$, and by taking a logarithm we can find the value of the diffusion activation energy by the slope of the straight line in the coordinates $\ln (D) - T_m/T$ (figure 2).
As shown in figure 2 for Al₂O₃, the activation energy of grain growth at the final sintering stage $Q = Q_b = 22 \text{kTm}$. The found value of the energy corresponds to the data of [14] ($Q = 19.8 \text{kTm}$) which is approximately $Q = 340 \text{kJ/mol}$).

3.2.2. Estimation of the grain growth activation energy for $\text{Al}_2\text{O}_3 + 0.5\% \text{ vol ZrO}_2$. According to the phase diagram, zirconium oxide is not soluble in alumina and does not form any phases with alumina. In ceramics obtained by sintering powder mixtures, zirconium ions are predominantly detected along the grain boundaries of $\text{Al}_2\text{O}_3$ [15].

The analysis of the microstructure carried out using SEM showed that the size of ZrO₂ particles in sintered samples is approximately 10–100 nm.

Analysis of the sample microstructure parameters at $T = 1520^\circ \text{C}$ and $t = 30 \text{ min}$ shows that the ratio $d_{\text{ZrO}_2} \approx d_{\text{Al}_2\text{O}_3 + \text{ZrO}_2} \cdot f_v$ is met. This means that the growth rate of alumina grains is determined by the growth rate of zirconium oxide particles. In this case, the growth rate constant in equation (4) can be 3 when the process of the second phase particles growth is controlled by bulk diffusion (diffusion of Zr ions in the $\text{Al}_2\text{O}_3$ lattice), or 4 when the process of the second phase particles growth is controlled by grain boundary diffusion (diffusion of Zr ions along $\text{Al}_2\text{O}_3$ grain boundaries). At $n = 3$, the activation energy $Q = 38 \text{kTm}$, which is $Q_v \sim 650 \text{kJ/mol}$.

Thus, the addition of 0.5 vol % ZrO₂ leads to the increase of the activation energy of grain boundary diffusion from $Q_b = 22 \text{kTm}$ to $Q_b = 37 \text{kTm}$. This increase corresponds to the data [15, 16]. In [16], the values of the activation energy for $\text{Al}_2\text{O}_3 + \text{ZrO}_2$ systems are equal to $Q = 700–100 \text{kJ/mol}$, which are approximately 31–41 kTm.

3.2.3. Estimation of the grain growth activation energy for $\text{Al}_2\text{O}_3 + 0.5\% \text{ vol MgO}$. The results of X-ray phase analysis show that $\text{Al}_2\text{O}_3 + 0.5\% \text{ MgO}$ samples, sintered at a temperature of 1520°C, contain about 2% wt MgAl₂O₄ phase. The volume of the unit cell of the MgAl₂O₄ phase is 7 times higher than the volume of MgO phase. Therefore, it can be concluded that approximately 0.2% vol MgO was dissolved in the $\text{Al}_2\text{O}_3$ lattice and 0.3% vol MgO remained in the form of particles, which formed the MgAl₂O₄ phase. The average particle size of the MgAl₂O₄ phase is about 0.7 μm.

Analysis of the sample microstructure parameters at $T = 1520^\circ \text{C}$ and $t = 30 \text{ min}$ shows that the ratio $d_{\text{MgAl}_2\text{O}_4} \geq d_{\text{Al}_2\text{O}_3 + \text{MgO}} \cdot f_v_{\text{MgAl}_2\text{O}_4}$ is met. This means that particles of MgAl₂O₄ may inhibit the growth of alumina grains due to the action of Zener force.

However, the ratio of the volume fraction of particles to their size for all the above temperatures is $(f_v_{\text{MgAl}_2\text{O}_4}/d_{\text{MgAl}_2\text{O}_4}) \geq 10^{-2} \cdot (1/d_{\text{Al}_2\text{O}_3 + \text{MgO}})$. The Zener effect caused by MgAl₂O₄ particles is insignificant and can be neglected. Thus, the growth rate constant in equation (4) for $\text{Al}_2\text{O}_3 + 0.5\% \text{ MgO}$ can be set at $n = 2$. 

![Figure 2. The dependence of $\ln (D)$–$T_m/T$ for pure $\alpha$-$\text{Al}_2\text{O}_3$ ceramic under isothermal dwelling during SPS](image-url)
The obtained value of the activation energy of grain-boundary diffusion is $Q_b = 26 \text{kTm (440 kJ/mol)}$. Thus, at a dissolution of 0.2\% vol MgO in alumina, the activation energy of grain boundary diffusion increases by 4 kTm, which leads to a decrease of a grain growth rate.

During the interaction between Al$_2$O$_3$ and MgO, Al ions are replaced by Mg ions, with the increase in the concentration of Al interstitial ions [13] and the decrease in the diffusion coefficient of oxygen within the boundaries [17–19].

3.2.4. Estimation of the grain growth activation energy for Al$_2$O$_3$ + 0.5\% vol TiO$_2$. According to [20], the solubility limit of TiO$_2$ in Al$_2$O$_3$ at temperatures above 1300°C does not exceed 0.25\% vol. Thus, in the temperature range used in the experiment, 0.5\% vol TiO$_2$ exists in a form of dissolved Ti ions and particles of Al$_2$TiO$_5$.

In the process of isothermal dwelling for 30 min, the particle size of Al$_2$TiO$_5$ increases significantly from initial $d \sim 0.1 \mu$m to $d \sim 0.4 \mu$m at $T = 1320^\circ$C, $d \sim 1.6 \mu$m at $T = 1420^\circ$C and $d \sim 10 \mu$m at $T = 1520^\circ$C.

Analysis of the sample microstructure parameters at $T = 1420^\circ$C and $t = 30$ min shows that the ratio $d_{\text{Al}_2\text{TiO}_5} \geq d_{\text{Al}_2\text{O}_3+\text{TiO}_2}$, $f_0$ is met. This means that particles of Al$_2$TiO$_5$ may also inhibit the growth of alumina grains due to the action of Zener force.

However, the ratio of the volume fraction of particles to their size for all the above temperatures is $(f_{\text{Al}_2\text{TiO}_5}/d_{\text{Al}_2\text{TiO}_5}) \geq 10^{-3} \cdot (1/d_{\text{Al}_2\text{O}_3+\text{TiO}_2})$. The Zener effect, which is caused by Al$_2$TiO$_5$ particles, is insignificant and also can be neglected.

In this case, the grain growth kinetics of alumina grains should be controlled only by the diffusion of Al and O ions in the Al$_2$O$_3$ lattice; therefore, the growth rate constant should be $n = 2$.

The rapid growth of Al$_2$TiO$_5$ particles is due to the fact that the diffusion coefficient of Ti ions in the Al$_2$O$_3$ lattice is more than 10 times higher than the diffusion coefficient of Al ions [21].

The obtained value of the activation energy is $Q = 21 \text{kTm}$. Thus, after the dissolution of 0.25\% vol TiO$_2$ in alumina lattice, the diffusion activation energy decreases by 1.2 kTm, which accelerates the growth of grains.

During the interaction between Al$_2$O$_3$ and TiO$_2$, Al ions are replaced by Ti ions with the formation of additional Al vacancies. This vacancies increase the bulk diffusion of Al [13] and accelerate grain growth [22–23].

4. Conclusion

The authors estimated the activation energy of shrinkage processes at the intermediate and final stages of sintering.

The study shows that rapid densification of alumina at stage II is caused by plastic deformation carried out under the action of the applied mechanical pressure, controlled by bulk diffusion (power creep law). The activation energy of the shrinkage process at the intermediate stage is $\sim 31 \text{kTm (530 kJ/mol)}$.

The effect of additions of MgO, ZrO$_2$, and TiO$_2$ (at a concentration of up to 0.5\% vol) was observed only at the final stage of sintering of alumina - the stage of grain growth.

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