Investigation of the kinetics of spark plasma sintering of alumina ceramics. Part 1. The initial stage of sintering

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1. Introduction
Aluminum oxide is one of the promising ceramic materials for a wide range of structural applications due to the combination of its high hardness, heat and chemical resistance [1, 2]. These properties of alumina can be used only with a fine-grained structure of this compound. The long-term isothermal dwelling applied in the traditional sintering methods (such as vacuum sintering or hot pressing) leads to the production of a coarse-grained structure with low quality.

The quality of alumina-based ceramics can be substantially improved through the reduction of grain growth by using some additives (for example, MgO, CaO, ZrO$_2$, SiC, TiC, etc.) [3–8].

One of the most effective methods for obtaining a fine-grained structure in alumina ceramics is the method of Spark Plasma Sintering (SPS) [9–13]. This method is based on the controlled heating of the powder material in a graphite mold via a sequence of DC pulses. Sintering is usually carried out in a controlled environment with simultaneous application of uniaxial mechanical stress [13–16].

There are a lot of articles about SPS of the alumina ceramics [11, 17–21], 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 these stages.

The main purpose of the first part of the article is the investigation of the initial stage of sintering of alumina ceramics during SPS.

2. Experimental
The main material used in this study is α-Al$_2$O$_3$ powder ($d = 0.2$ µm, Taimei Chemicals, Japan) and its mixtures with MgO ($d \sim 0.1$ µm, Alfa Aesar, Germany), TiO$_2$ ($d < 0.5$ µm, UrFU RAS, Russia), ZrO$_2$ ($d = 0.03$ µm, Pangea Int. Ltd., China).

The additives were selected in accordance with the way they interact with alumina:
- ZrO$_2$ is not soluble in Al$_2$O$_3$ and does not form new phases with it;
- MgO is soluble in Al$_2$O$_3$ at low temperature and may form the Al$_2$MgO$_4$ phase at $T < 600^\circ$C;

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- TiO₂ is not soluble in Al₂O₃ and does not form new phases with it up to 7 = 1200°C. At temperatures higher than 1200°C this compound forms the Al₂TiO₅ phase.

Powder mixtures were obtained by mixing the initial powders in the “FRITSCH-Pulverisette 6” planetary mill. Grinding media and bodies were made of stabilized zirconia. The rotational speed of the grinding cup was 200 rpm. Mixing was done in isopropyl alcohol for 5 h. The removal of alcohol was carried out at a temperature of 70°C for 12 h. The selected mixing modes ensured homogeneity and the absence of impurities in the grinding media.

Sintering of samples with a diameter of 12 mm and a height \( h = 3 \) mm was carried out by the SPS method in the “DR. SINTER model SPS-625 Spark Plasma Sintering System” (SPS SYNTEX INC. Ltd., Japan). The temperature of the sintering process was measured using Chino IR-AHS2 pyrometer focused on the outer surface of the graphite die with the outer diameter of 30 mm. The actual temperature inside the mold was calculated using the calibration curves of the temperature difference measured by a pyrometer on the outer surface of the graphite mold and temperatures measured by a thermocouple in the central part of the sintered powder compact (for all heating rates used).

The applied uniaxial pressure was 70 MPa. The pressure was applied before the onset of the intense shrinkage stage and maintained at a constant level throughout the entire process. The accuracy of the pressure measurement was ±5 MPa. Sintering was carried out in a vacuum at 6 Pa.

The study of the kinetics of sintering with constant heating rate was carried out at the maximum sintering temperature \( T = 1520°C \). The heating rate up to 600°C was 100°C/min; further heating to the sintering temperature was carried out at the heating rate of 10, 50, 100, 250, 350, and 700°C/min. There was no isothermal dwelling at the sintering temperature.

To study the kinetics of sintering under isothermal conditions, we chose the temperature range from 1010 to 1120°C. Samples were heated up to 600°C at the heating rate of 100°C/min, the further heating rate to sintering temperature was carried out at a rate of 25°C/min, after which the samples were dwelled for 60 min.

The shrinkage of the samples during the sintering process was controlled using a precision dilatometer, which is part of the “DR. SINTER model SPS-625”. The accuracy of the measurement of shrinkage was ±0.05 mm.

The density (\( \rho \)) of sintered samples was measured using the Archimedes' Principle in distilled water using Sartorius CPA scales. The accuracy of density calculations was ±0.005 g/cm³. The theoretical density of alumina (\( \rho_{th} \)) was taken as 3.99 g/cm³.

Vickers hardness (\( H_V \)) was measured using the automated microhardness tester "Struers Duramin-5" under a load of 19N. Crack resistance (\( K_{IC} \)) was calculated using the Palmqvist method. Measuring accuracy of \( H_V \) and \( K_{IC} \) was ±1.5 GPa and ±0.5 MPa·m¹/², respectively.

The microstructure of samples was studied using a Jeol JSM-6490 scanning electron microscope. The average grain size in sintered ceramics was calculated after analyzing at least 400 grains.

3. Results and discussion

3.1. Shrinkage behavior at a constant heating rate during SPS

Shrinkage behavior has three stages. This behavior is typical for solid state sintering [22], therefore the processes occurring during SPS sintering can be described as a sequence of initial (I), intermediate (II) and final (III) sintering stages [23].

Let us consider the sintering stages using the samples obtained at a heating rate of 10°C/min. In accordance with [23], the initial stage of sintering — (stage I) is characterized by the formation of contacts between powder particles and fit is observed at temperatures below 1120°C (figure 1). The transition between stages I and II occurs at \( \rho/\rho_{th} \sim 0.7 \). Stage II (\( T \sim 1120–1230°C \)) is characterized by the increase in the contact area between the particles and intensive compaction of the powder. Stage III (\( T \) higher than 1230°C) is characterized by the formation of closed porosity (\( \rho/\rho_{th} \sim 0.9 \)), diffusion-controlled dissolution of isolated pores and the growth of grains.
3.2. Analysis of shrinkage behavior at the initial stage (stage I). Dependence of shrinkage on isothermal dwelling time during SPS. Sintering of ceramics in isothermal conditions

The analysis of shrinkage behavior under the heating temperature in figure 1 shows that stage I occurs at a temperature lower than 1120°C. In this regard, the study of stage I was carried out at temperatures of 1010, 1070, and 1120°C.

A typical view of shrinkage behavior during the isothermal dwelling, shown in figure 2. The value $L_0$, equal to the initial height of the sintered powder compact, was 4.5 mm.

Figure 2 shows that at the initial stage of sintering under isothermal conditions (dwelling step), the addition of MgO, TiO2, and ZrO2 leads to the decrease in the absolute value of shrinkage compared to pure alumina, while the inclination of the shrinkage curve for the studied compositions is the same within the experimental error.
The dependence of shrinkage on the time of isothermal dwelling can be described using the expression [24]:

\[ \frac{L_1}{L_0} = B t^q \]  

(1)

where \( B \) and \( q \) are constants which depend on the temperature and characteristics of the sintered material.

In the case where the sintering mechanism is determined by diffusion, the constants are related by the following equation [24]:

\[ B = \frac{B'}{T^q} D^b = \frac{B''}{T^q} \exp \left( -\frac{qQ}{kT_m} \frac{T_m}{T} \right) \]  

(2)

where \( B' \) and \( B'' \) are the constants which are independent of temperature, \( T_m = 2323 \text{ K} \) (melting point for alumina), and \( Q \) is the activation energy of a diffusion-controlled process, the intensity of which limits the sintering rate.

From equations (1) and (2), the value of the coefficient \( q \) can be found from the slope of the relative shrinkage versus time in logarithmic coordinates \( \ln \left( \frac{L_1}{L_0} \right) - \ln \left( t \right) \) (figure 3a). The free coefficient in relation \( \ln \left( \frac{L_1}{L_0} \right) - \ln \left( t \right) \) will determine the value of \( \ln \left( B \right) \). The magnitude of the activation energy of sintering \( qQ \) at stage I can be found from the slope of the relation \( \ln \left( B \right) - \frac{T_m}{T} \) (figure 3b).

Figure 3 shows that for pure \( \text{Al}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 + 0.5\% \text{ vol MgO} \) the value of the coefficient \( \frac{1}{q} \) approximately equals to 0.3, and the value \( qQ = 6.5 \text{ kTm} \) (figure 3b). Thus, the activation energy of the initial stage of sintering (stage I) for pure \( \text{Al}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 + 0.5\% \text{ MgO} \) \( Q = 19.5 \text{ kTm} \). The determined value of the energy corresponds to the data of [25] \( Q = 19.8 \text{ kTm} \) and agrees with the activation energy of grain boundary diffusion of alumina \( Q = Q_b \sim 20 \text{ kTm} \), which is \( Q = 340 \text{ kJ/mol} \).

Thus, the addition of magnesium oxide in the amount of 0.5% vol does not affect the diffusion properties of alumina at the initial stage of sintering.

Slowing down of the shrinkage process at the initial stage of sintering of alumina with the addition of 0.5% vol \( \text{ZrO}_2 \), MgO, and \( \text{TiO}_2 \) may be explained by the fact that the particles of additive powders inhibit the neck growth between the particles of alumina powder due to the action of the Zener force.
4. Conclusions
The authors determined the stages of sintering and their temperature ranges under SPS conditions for alumina-based ceramics and estimated the activation energy of shrinkage processes at the initial stage of sintering. The study shows that the additives do not change the kinetics of shrinkage at the initial stage. The study also determined that the shrinkage process is controlled by grain-boundary diffusion of alumina ($Q_b = 340$ kJ/mol).

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