Superplasticity of fine-grained alumina obtained by spark plasma sintering

A A Popov, V N Chuvil’deev, M S Boldin, A V Nokhrin, E A Lantsev and A A Murashov

Lobachevsky State University of Nizhny Novgorod, 23 Prospect Gagarina (Gagarin Avenue), Nizhny Novgorod, 603950, Russia

E-mail: popov@nifti.unn.ru

Abstract. Investigations of plastic deformation of fine-grained ceramics based on alumina obtained by the method of spark plasma sintering in the temperature range of 1150-1320 °C at an applied stress of 40-100 MPa are presented. Based on the experimental data, the parameters of rheological equations were established. It is shown that the mechanism of high-temperature deformation of alumina is superplasticity. In the process of plastic deformation, the grains of alumina do not stretch, which confirms the mechanism of superplasticity - grain boundary sliding. The activation energy for superplastic deformation was Q = 17.8 kTm at d = 6 μm and Q = 24.6 kTm at d = 1 μm, which is very close to the activation energy of grain boundary diffusion in aluminum oxide Qb = 20 kTm. For a coarse-grained material, an assumption was made about a possible mechanism for lowering the activation energy due to the generation of dislocations by the grain boundary.

1. Introduction

Spark Plasma Sintering (SPS) is a new technology for sintering ceramics and ceramic composites. A distinctive feature of SPS is the possibility of sintering micro- and nanosized ceramic materials with high mechanical properties due to ultrahigh heating rates (up to 2500 °C/min) in vacuum or inert medium with simultaneous application of pressure [1-7]. Reducing the residence time of materials at high temperatures leads to the fact that the grains do not have time to grow very much. Ceramics with a small grain size demonstrates high physical and mechanical properties at laboratory temperatures in the study of physical and mechanical properties.

The strength characteristics of structural ceramics at high temperatures and loads are determined by the grain size and phase composition of the ceramics, as well as by the structural state of grain boundaries, which depends on the type and concentration of defects in grain boundaries (micropores, microcracks, chemical composition of grain boundaries, the presence and nature of the spatial distribution of particles second phase, etc.) [8-10]. The use of ceramics as structural materials at high temperatures and loads requires a study of the mechanisms of plastic deformation to predict the service life of units and products.

Tensile tests for high-temperature deformation of materials are performed on specialized research equipment. The test is carried out using a tensile specimen to which a constant stress is applied [11]. However, it should be noted that the preparation of samples from high-strength ceramics for the standard method of tensile testing in the form of a "dumbbell" is a complex methodological and technical problem. When cutting high-strength brittle ceramics by mechanical methods, there is a high risk of
surface damage and the appearance of such surface defects characteristic of ceramics as butt micro- and nanocracks, which are practically not detected using metallographic surface control methods, but have a significant effect on the reliability and spread of test results.

In [12-14] the authors report that SPS technology can be used as a tool for studying high-temperature deformation of polycrystalline spinel magnesium aluminate and metallic materials and ceramics. Tests for high-temperature deformation of ceramics are often performed using a compressive load in order to exclude the growth of cavities and their opening and, thus, the creep rate is lower than in tension [11, 15]. For ceramics, which are inherently brittle, compression tests are preferred because the machining of the test pieces is difficult and also because of the tendency to break the clamps during tensile testing.

For materials deformation mechanisms maps have been developed. For pure aluminum oxide with grain sizes of 10 and 100 µm, the maps are presented in [16]. It is important to note that the grain size has a significant effect on the areas of implementation of the dominant mechanisms of plastic deformation [16]. Reducing the grain size both in metals and ceramics, in the required modes of plastic deformation, ensures the superplasticity of the material. Thus, the problem of studying the mechanisms of plastic deformation of aluminum oxide at high temperatures and stresses is not only of scientific interest, but also of great practical value. Mapping the deformation mechanisms of aluminum oxide is a laborious task. In this paper, we will focus on superplastic deformation processes in fine-grained aluminum oxide.

Deformation of alumina at high temperatures and stresses has been extensively and thoroughly studied [8, 11]. Despite this, there are a number of discussions about the possibility of dislocation motion in the grain volume, the mechanisms of accommodation of plastic deformation, the mechanism of pore growth, the role of additives on superplastic deformation, etc. In this work, we study the high-temperature deformation of ceramic samples based on undoped aluminum oxide with a grain size of 1 µm and 6 µm, obtained by the method of spark plasma sintering (SPS). The parameters of the rheological equation (n and p) are analyzed based on the experimental dependences of the relative deformation during isothermal holding at various temperatures and stresses. The activation energies of superplastic flow are calculated based on the experimental dependences of the relative shrinkage. The microstructure of the samples before and after high-temperature deformation was studied by scanning electron microscopy.

2. Methods and materials

Dense polycrystalline samples of aluminum oxide (theoretical density> 99%, h/d = 1.25, h is the height, d is the sample diameter) with an average grain size of about 1 µm (No. 1) and 5 µm (No. 2) were obtained by the SPS method ("Dr. Sinter model SPS-625", Japan). Images of the original commercial Al₂O₃ (No. 1) nanopowders, α-phase> 99.95% and Alfa Aesar Al₂O₃ powder (No. 2), α-phase> 99.88% are shown in Figure 1. The structure of the initial ceramic samples is shown in Figure 2.

![Figure 1. Powders Alfa Aesar (a) NANOE (b)](image-url)
The sintered samples were heated in Dr. Sinter model SPS-625 *(figure 3). Shrinkage and deformation are monitored using a precision dilatometer, which is included in the installation kit, and allows on-line measurement of the value and rate of powder shrinkage under isothermal holding conditions with high accuracy. Temperature (T) is measured with a pyrometer focused on the outside of the mold. The samples were heated at a heating rate of 50 ° C / min to temperatures of isothermal holdings (1150, 1180, 1210 ° C) for series No. 1, for samples of series No. 2 to temperatures (1230, 1275, 1320 ° C) from. The experiments were carried out under compression under constant loads (initial stresses 40, 70, and 100 MPa). The deviation of the applied force was 0.05 kN during the high temperature deformation.

The microstructure of the samples before and after the experiments on high-temperature deformation was investigated using a high-resolution scanning electron microscope ("Jeol JSM-640"). The initial and final grain sizes were estimated using GoodGrains software from microstructure photographs. The density of the sintered samples was measured by the hydrostatic weighing method.

3. Results and discussion
3.1 Temperature Analysis
In this test scheme, a sintered sample of fine-grained alumina ceramic is placed in a larger graphite mold for free deformation of the sample (Figure 3). Temperature control takes place from the outside of the graphite mold. Observing the temperature of a sample by direct measurements is challenging. The study of temperature fields shows [17] that during isothermal holding, the temperature in the sample and the temperature measured by the pyrometer differ insignificantly. Based on this, we can assume that the temperature of the pyrometer and the temperature of the sample coincide.

3.2 Density Analysis
The density of the sintered samples was measured by the hydrostatic weighing method.

Figure 2. Microstructure of the original samples series No. 1 (a), series No. 2 (b)

Figure 3. Schematic of sample installation in the heating chamber (a), temperature map at isothermal exposure (b)
3.2 Stress analysis
In the process of plastic deformation of fine-grained alumina ceramics under compression, the samples undergo significant deformation, which leads to an increase in the sample cross section and, as a consequence, to a change in the effective stress.

The stress state of the sample was investigated by the method of finite element modeling in the ANSYS Workbench environment. Figure 4 shows the main stress components (Figures 4 a-d) and shear stresses (Figure 4 d). From the analysis of the stress state of the sample, it is seen that a uniaxial complex stress state is realized in the center, with a uniform distribution of stress components.

Analysis of the deformation of the sample under compression by numerical simulation methods showed that the effective stresses vary in proportion to the magnitude of the relative deformation. As a first approximation, it is permissible to take the value of the applied external stress at the beginning of stage II of plastic deformation to be approximately equal to the value of the effective stress.

![Figure 4](image)

**Figure 4.** Distribution of stress components in the sample cross section $\sigma_{11}$ (a), $\sigma_{22}$ (b), $\sigma_{33}$ (c).

3.3 Relative deformation curves
When the mold is heated in SPS unit, the dilatometer additively registers the expansion of the press column (electrodes) and the deformation of the sample. To calculate the true deformation curve, it is required to subtract the mold expansion curve from the experimental deformation curve in the same heating modes (Figure 5).

![Figure 5](image)

**Figure 5.** A typical form of graphs of deformation versus time.

Relative deformation ($\varepsilon$) and rate of relative deformation ($\dot{\varepsilon}$) are calculated by the formulas:

$$\varepsilon = \frac{\Delta L}{L_0}$$

(1)

$$\dot{\varepsilon} = \frac{\Delta \varepsilon}{\Delta t}$$

(2)
where $\Delta L$ is the shrinkage, $L_0^*$ is the initial height of the sample, at the moment of entering isothermal exposure, $\Delta \varepsilon$ is the relative change in the linear dimensions of the sample during the time $\Delta t$.

Figure 6 shows graphs of the relative deformation of the samples in the process of isothermal holding for samples of series No. 1 and No. 2.

### 3.4 Analysis of the mechanism of high-temperature deformation of aluminum oxide

Within the framework of traditional concepts of high-temperature deformation, the rheological equation connecting the material flow rate $\dot{\varepsilon}$ with the flow stress $\sigma$ by the deformation temperature $T$ has the form [18]:

$$\dot{\varepsilon} = A \frac{D}{b^2} \left( \frac{b}{d} \right)^p \frac{\sigma^n}{G} \exp \left( - \frac{Q}{kT_m} \frac{T_m}{T} \right)$$

where $\dot{\varepsilon}$ - strain rate, $A$ - material constant, $D$ - diffusion coefficient, $b$ - Burgers vector, $d$ - grain size, $\sigma$ - stress, $G$ - shear modulus, $Q$ - activation energy, $k$ - Boltzmann constant, $T_m$ - melting point in Kelvin. The parameters $p$ and $n$ depend on the material deformation mechanism.

The values of the creep rates obtained as a function of the true stress at given temperatures are shown in Figure 7. The stress index $n$ obtained from the construction (figure 8a) is close to 2. The stress index $p$ obtained from the construction (Figure 7b) is close to 2 too.

From the calculated parameters $p$ and $n$ in equation (4.1), it follows that alumina in the high-temperature deformation scheme in these temperature and stress ranges is described by the
superplasticity equation. The obtained result is confirmed by works [8, 11]. The rheological equation of superplastic deformation of a material for aluminum oxide looks like [18]:

\[
\dot{\epsilon} = A \left( \frac{G \Omega}{kT} \right) \left( \frac{b}{d} \right)^2 \left( \frac{\sigma}{G} \right)^2 \frac{D_{b0} \delta}{b^3} \exp \left( - \frac{Q}{kT_m} \frac{T_m}{T} \right)
\]

(4)

where \( A \) - numerical coefficient (≈100), \( G \) - shear modulus (150 GPa), \( D_{b0} \) - pre-exponential coefficient, \( \Omega \) - atomic volume (4.25x10^{-11} m^3), \( b \) - Burgers vector (4.79x10^{-10} m), \( \delta \) - width of the boundary (\( \delta = 2b \)), \( D_{b0} \) - pre-exponential coefficient of grain boundary diffusion, \( Q \) - activation energy of superplastic flow.

To calculate the activation energy, we transform expression (4) and obtain the dependence of \( \ln \dot{\epsilon} \) on \( T_m/T \), where the slope will be an estimate of the activation energy. The calculation of the values of the factors of equation (4) is given in Table 1. Figure 8 shows the curves for calculating the activation energy in the coordinates \( \ln \dot{\epsilon} \) from \( T_m/T \).

| \( d, \mu m \) | A | \( \frac{G \Omega}{kT} \) \((T=0.5T_m)\) | \( \left( \frac{b}{d} \right)^2 \) | \( \left( \frac{\sigma}{G} \right)^2 \) | \( \frac{D_{b0} \delta}{b^3} \) | \( Q, kT_m \) | \( Q, kJ/mol \) |
|---|---|---|---|---|---|---|---|
| 1 | 100 | 394 | 6.4 x 10^{-9} | 2.2 x 10^{-7} | 5.9 x 10^{8} | 22.8±1.5 | 479±29 |
| 6 | 100 | 394 | 2.3 x 10^{-7} | 2.2 x 10^{-7} | 5.9 x 10^{8} | 17.6±1.5 | 340±29 |

Figure 8. Calculation of the activation energy of superplastic flow.

The calculated values of the activation energy correspond to the grain-boundary activation energy in aluminum oxide, which is 20 kT_m (400 kJ/mol) for pure aluminum oxide [19-21]. Literature data for the activation energy calculated according to equation (4) (with parameters \( p = 2 \) and \( n = 2 \)) give a range of values. Thus, aluminum oxide in the studied temperature and stress ranges is deformed as a superplastic material.

From the analysis of the activation energy for ceramics with different grain sizes, it follows that the material with \( d = 6 \mu m \) has a lower energy than the energy of grain boundary diffusion in aluminum oxide. Our hypothesis is that a decrease in the activation energy is associated with the processes of accommodation of dislocations in grain boundaries upon activation of sliding [22, 23]. In this case, the sources of dislocations are grain boundaries under conditions of high shear stresses. It can be assumed that in a coarse-grained material, dislocation glide is more favorable than in a fine-grained material.

The deformed specimens remained intact at the end of the test and exhibited symmetrical barrels deforming over the total strain. The microstructures of both sintered alumina and creep-deformed samples are shown in Figure 9.
Sintered alumina series No. 2 (Figure 9a) was substantially completely dense and had an initial grain size of about 6 microns. The morphology of the grain shape remained equiaxed in all deformed samples. In the deformed samples, grain boundaries and triple point cavities were observed (figure 9 b, c). In this case, grain growth was observed from 6 microns (in the original) to 7 and 7.5 microns. Figure 9 shows the grains of aluminum oxide do not stretch under these deformation modes. It is important to emphasize that plastic deformation leads to the formation and growth of pores in ceramics.

Figure 9. Microstructure of samples: (a) $\dot{\varepsilon} = 0$ s$^{-1}$, (b) $\dot{\varepsilon} = 5.0 \times 10^{-5}$ s$^{-1}$, (c) $\dot{\varepsilon} = 3.3 \times 10^{-4}$ s$^{-1}$

4. Conclusion
High-temperature deformation of fine-grained alumina-based ceramics under compression was successfully performed by the SPS method in the temperature range of 1150–1320 °C at an applied stress of 40–100 MPa. The use of numerical simulation methods for calculating temperatures in the SPS mode makes it possible to estimate the true temperatures of deformation. Using the method of numerical simulation, it allows you to correctly calculate the effective stresses in the sample cross section.

The experimental rates of relative deformation were determined, and the parameters of the rheological equation were calculated: $n = 2$, $p = 2$. It was found that the mechanism of high-temperature deformation of aluminum oxide is superplasticity. The calculated values of the activation energy of superplastic flow for a microcrystalline material ($d = 1$ μm) $Q = 24.6$ kT$_m$($Q = 479$ kJ / mol), for coarse-crystalline aluminum oxide ($d = 5$ μm) $Q = 17.8$ kT$_m$($Q = 340$ kJ / mol). The obtained values are close to the activation energy of grain boundary diffusion in pure aluminum oxide $Q_b = 24.6$ kT$_m$, ($Q_b = 386$ kJ / mol). Comparison with published data on high-temperature creep deformation for fine-grained alumina showed that our experimental data are in good agreement with the values found in the literature for similar temperature and stress conditions.

The microstructure of the deformed samples shows that in the process of high-temperature deformation, grain growth occurs from 6 μm to 7.5 μm (increases by 1.5 times) under the selected deformation modes. Alumina grains do not stretch in these high-temperature deformation modes. It is important to note that pore growth is observed in fine-grained aluminum oxide ceramics in the process of superplasticity.

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