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**ALUMINUM OXIDE NANOPOWDERS SINTERING AT HOT PRESSING
USING DIRECT CURRENT****СПЕКАНИЕ НАНОПОРОШКОВ ОКСИДА АЛЮМИНИЯ ПРИ ГОРЯЧЕМ
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Abstract. The article researches the regularities of aluminum oxide nanosized powders structure formation at hot pressing by direct current transmission. The kinetics of grain growth at various heating rates has been established. The main mechanisms of agglomeration influencing the process of compaction of nanosized powders of non-conductive aluminum oxide have been revealed.

Key words: dislocations, diffusion, nanosized powders, aluminum oxide, grain size, sintering.

Introduction. Electric consolidation method makes it possible to obtain high-density fine-dispersed materials not only from conductive powders, but also from non-conductive ones. We used aluminum oxide nanosized powders with a grain size of 60...80 nm, manufactured by Sumitomo Company (Japan) for the trial. The studied nanosized powders were poured into graphite molds without binding materials. Heating rate constituted 50, 250 and 500 °C/min up to 1400 °C. Curing temperature constituted 2 minutes. The samples were 19 mm in diameter and 5 mm in height.

Main text. Local heating can generate additional temperature, which allows to reach the required temperature in a short period of time and inhibit grain growth [1]. Figure 1 shows that after sintering, Al₂O₃ contains small pores in all samples, regardless of the heating rate. However, no catastrophic grain growth is observed.

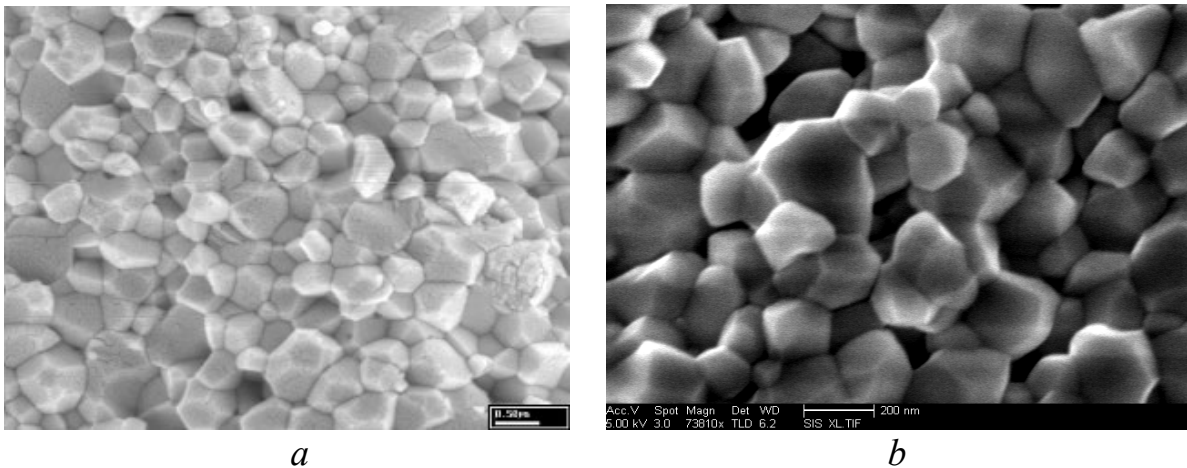


Fig. 1. The structure of sintered Al_2O_3 for 1100 °C (a) and for 1700 °C (b)

The grain size remained submicron even at not the fastest heating. At 500 °C/min, the grain size was 5...6 times larger than in initial powders. The grain size was 30...40 times larger than initial grain size when heated at a rate of 250 °C/min and 60...90 times per minute at 50 °C. The final grain size at the slowest increase constituted 6...9 microns. For comparison: in case of pure Al_2O_3 conventional agglomeration at 1850 °C, the grain size reaches up to 30 μm . It was found that in case of temperature rapid rise, the submicron grain size is retained. In this case, at heating rate increase, the pore size practically does not change. Size variation of similar pores is noticeable in each case of heating. Rapid heating is used to inhibit grain growth. To limit grain growth, sintering was performed at a high rate of temperature rise in order to inhibit diffusion transport mechanisms, which, as a rule, affect compacting. Usually, even in case of traditional agglomeration, it is difficult to identify the mechanisms responsible for compacting and grain growth [2]. For example, a thorough analysis of aluminum oxide compacting shows that diffusion at grain boundaries cannot be ignored at early stage of sintering [3].

High-speed sintering reduces vacancy flow and reduces large pores as well as limits grain growth. The rapid decrease in porosity at grain boundaries increases mobility at grain boundaries. This makes the sintering of fine, clean powders sensitive to heat. This process leads to formation of a significant number of small pores. Small pores create small interferences at grain boundaries, which favors rapid grain growth. It is also necessary to take into account that below Debye temperature, quantum effects in the material become important [4]:

$$\Theta = \frac{h \cdot \nu_{\max}}{k}, \quad (1)$$

where Θ is Debye temperature; h is Planck's constant; ν_{\max} is the highest frequency of atoms elastic vibrations in the crystal lattice of the material; k is Boltzmann's constant.

In case of nanosized powders temperature increase, the frequency of atoms elastic vibrations in the crystal lattice increases faster than for ordinary powders. Simplified formula (1) can be represented in the form [4]:

$$\Theta = 4,79 \cdot 10^{-11} \cdot \nu_{\max}. \quad (2)$$



It is seen from formula (2) that increase in the frequency of atoms elastic vibrations leads to increase in Debye temperature, below which quantum effects begin to act, which also activate powder sintering process.

Trials of aluminum oxide nanopowders sintering kinetics showed that the compaction rate depends on temperature and applied pressure and, in comparison with wolframium monocarbide powders, weakly depends on the rate of temperature rise (Fig. 2).

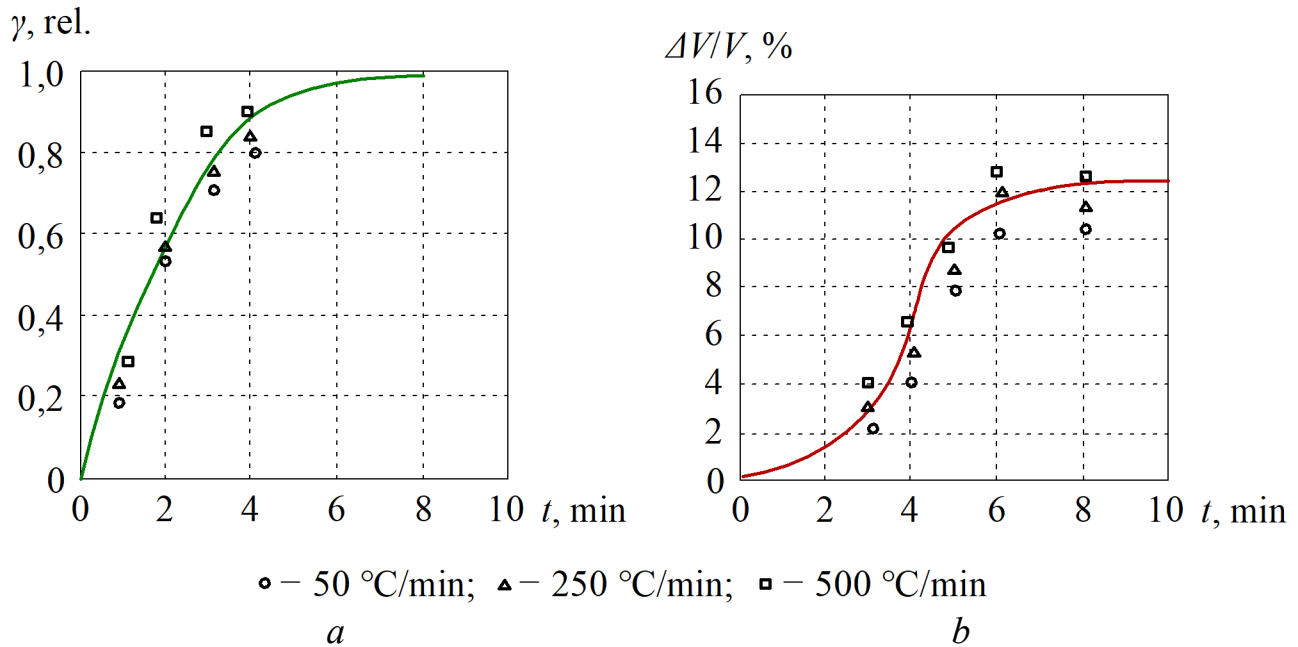


Fig. 2. The change of relative density of Al₂O₃ (a) and shrinkage (b) at different heating rates

It is known that one of the driving forces of the blending process, in addition to excess surface energy, is the energy of grain boundaries, which separates different areas from each other [5]. When heated, a physical contact is formed between the particles in the sample, and subsequently a branched system of boundaries, which means, that free surface energy is spent on boundaries formation, and excess energy is the driving force of sintering. As a result of rapid heating, the sliding process along the grain boundaries is activated and the sample is quickly compacted. Sintering process is also activated due to the energy of the crystal lattice imperfections, which is not a small value in plasma-chemical synthesis nanosized powders [6]. In the process of sintering, there are formation and growth of contact between the particles.

The stress in the neck of the sintered particles depends on the particle size according to the following relation [7]:

$$\sigma = 4 \cdot \gamma \cdot x + \frac{12 \cdot \pi \cdot r \cdot \gamma}{x^2} + 4 \cdot \pi \cdot r \cdot \gamma, \tag{3}$$

where σ is surface tension; γ is free surface energy; r is grain radius; x is contact area of particle isthmus.

Since the free surface energy is greater than the energy of the boundaries, the energy of vacancies formation on these surfaces is different. Supersaturation with vacancies is different on free surface of the neck and contact boundary between



particles. Due to the gradient of vacancy concentration, diffusion transfer of mass to the neck is caused. Kinetics of growth of the contact area between particles is described by equation [8]:

$$x^\omega = A(T) \cdot \tau, \quad (4)$$

where x is contact area of particle isthmus; $A(T)$ is a function that depends on temperature, particle geometry and the mechanism of mass transfer; ω is exponent.

In case of mass transfer by the surface self-diffusion mechanism, the equation is as follows [8]:

$$x^7 = \frac{28 \cdot \gamma \cdot \Omega \cdot D_s \cdot \delta_s \cdot r^3}{R \cdot T \cdot \tau}, \quad (5)$$

where x is contact area of particle isthmus; γ is free surface energy; Ω is volume of vacancies; D_s is surface diffusion coefficient; δ_s is surface diffusion layer thickness; r is grain radius.

In fact, the growth of the boundary occurs simultaneously due to bulk diffusion, surface diffusion and along grain boundaries [9]. The technique developed by Johnson for description of compacting taking into account volume, boundary and surface diffusions [10] makes it possible to determine corresponding diffusion coefficients using experimental data. Mechanism of diffusion-viscous flow assumes that grain boundaries are vacancy sinks. The role of linear defects in this mass transfer mechanism is not taken into account. In dispersed particles, dislocations are usually fixed on the surface.

Currently existing theoretical and experimental material confirms the possibility of dislocations nucleation and generation during sintering. This allows us to assume that nanoparticles contain linear defects in significant quantities, limiting the dislocations reproduction in each small particle does not exclude such possibility for a group of particles, where the source of dislocations generation is in the contact plane [11], dislocations are formed during sintering in particles contact zone of [12].

Calculations show the possibility of dislocations nucleation and generation in particles contact. The difference in pressure on the convex surface of the particle and the concave one creates a shear stress, which must exceed the stresses required for dislocations sliding [13]:

$$\tau_\kappa = \frac{2 \cdot \gamma}{r} + \gamma \left(\frac{1}{\rho} - \frac{1}{x} \right), \quad (6)$$

where τ_κ is shear stress; γ is free surface energy; ρ is the radius of curvature of the particle contact surface; x is contact area of particle isthmus.

The motion of dislocations underlies the grain boundary sliding of particles. In [14], an equation was obtained for the slip rate due to grain boundary dislocations motion.

For the first time, the mechanism of sliding along grain boundaries with diffusion accommodation was considered in [15], where structural equation for the flow was derived under assumption that the speed with which work is performed under stress is equal to the interaction energy of boundaries and sliding along boundaries, which are ideal vacancy sinks:



$$\varepsilon'_c = \frac{25 \cdot \Omega}{R \cdot T \cdot r^2 \cdot \left(\gamma - 0,72 \cdot \Omega \cdot \frac{\delta}{2 \cdot r} \right) \cdot D \cdot \left(1 + \frac{3,3 \cdot \delta \cdot D_e}{2 \cdot r \cdot D} \right)}, \quad (7)$$

where ε'_c is flow rate; Ω is vacancies volume; r is the grain size; δ is grain boundary; D_e is gas diffusion coefficient; D is diffusion coefficient.

This equation is similar to the diffusion-viscous flow equation, but the rate of deformation, determined by it is higher by order. Experimental studies confirm the possibility of shape change due to sliding of grains along the boundaries.

Diffusion of vacancies into lattice and their interaction with dislocations create a flow of atoms into the contact zone between particles. In addition, interaction between vacancies and dislocations leads to vacancy annihilation and dislocation climb. The creep of dislocations parallel to the boundary leads to grain shift parallel to the boundary. General deformation is caused by boundary sliding [16].

The dislocation creep mechanism can compete with grain boundary sliding or occur simultaneously. The equation, describing the deformation by the dislocation creep mechanism has the form:

$$\varepsilon'_\delta = \frac{A \cdot G \cdot b}{R \cdot T \cdot \left(\frac{\sigma}{G \cdot b} \right) \exp\left(\frac{-E_\delta}{R \cdot T} \right)}, \quad (8)$$

where ε'_δ is flow rate; G is shear modulus; b is Burgers vector; R is gas constant; T is temperature; E_δ is activation energy of dislocation creep.

The total strain rate by the mechanism of activated sliding and dislocation creep is determined by the sum:

$$\varepsilon' = \varepsilon'_c + \varepsilon'_\delta, \quad (9)$$

where ε' is deformation rate; ε'_c is activated sliding speed; ε'_δ is the rate of dislocation creep.

Conclusions and findings. The regularities of aluminum oxide nanosized powders structure formation at hot pressing by direct current transmission have been studied. The kinetics of grain growth at various heating rates has been established. The main mechanisms of sintering influencing the process of compaction of nanosized powders of non-conductive aluminum oxide have been revealed.

So, in the low-stress mode, activated sliding with diffusion accommodation prevails, in the high-stress mode, dislocation creep prevails. In case of Al_2O_3 nanosized powders high-speed sintering, most likely, both mechanisms operate, which makes it possible to obtain density, close to the theoretical one already at a temperature of 1400°C.

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Аннотация. В статье исследованы закономерности структурообразования при горячем прессовании прямым пропусканием тока нанопорошков оксида алюминия. Установлена кинетика роста зёрен при различных скоростях нагрева. Выявлены основные механизмы спекания, влияющие на процесс уплотнения нанопорошков непроводящего электрический ток оксида алюминия.

Ключевые слова: дислокации, диффузия, нанопорошки, оксид алюминия, размер зерна, спекание.