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Hydrothermal Synthesis of Porous Al_2O_3/Al Metal Ceramics: II. Mechanism of Formation of a Porous $Al(OH)_3$/Al Composite

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Abstract—The formation of a porous layer of aluminum hydroxide on the surface of aluminum particles and the aggregation of $Al(OH)_3$/Al composite particles were analyzed theoretically. It was found that the diffusion mass transfer of the hydroxo complexes of aluminum through the porous structure of a growing layer of aluminum hydroxide to the outer surface is a rate-limiting step in the synthesis of the porous composite. A model mechanism of formation of the porous composite was developed, and rate equations were derived for describing the growth of an aluminum hydroxide layer on the surface of an aluminum particle and changes in the degree of aluminum conversion and the contact radius between composite particles. Based on the developed mathematical model and experimental data, the diffusion coefficient of the hydroxo complexes of aluminum in the porous structure of aluminum hydroxide was calculated.

INTRODUCTION

Previously [1], we reported on the experimental studies of the oxidation of an ASD-1 aluminum powder with water at 100°C and the formation of a porous structure of an aluminum hydroxide–bayerite precipitate and $Al(OH)_3$/Al composite ceramics.

In the course of the synthesis of the porous Al_2O_3/Al metal ceramics, a precipitate of nanosized particles is formed on aluminum particles, and the morphology of these nanoparticles depends on the synthesis temperature [2]. Crystals formed at 150°C were thin fibers twisted and disordered with respect to each other. As the synthesis temperature was increased to 250°C, an ordered structure of well-crystallized platelike aggregates arranged in an ideal order was formed because of an increase in the solubility of the precipitate and a decrease in supersaturation. Tikhov *et al.* [2, 3] found an undoubted relationship between the macroscopic properties of a composite and microscopic phenomena (nanostructure formation). A quantitative theory that completely describes the nucleation and growth of nanoparticles from solution is currently unavailable [4]. However, to understand the general physicochemical behavior and to perform estimations, we shall restrict our consideration to macrokinetic models at this stage of the study.

The aggregation of aluminum particles into a porous solid is a process responsible for the mechanical strength of the porous composite; consequently, it should be considered in detail. Tikhov and coauthors [2, 3, 5–7] believed that in the course of oxidation aluminum particles were aggregated because of an increase in the volume of the resulting solid phase and the appearance of an interparticle pressure. As a result, self-packing or topochemical autoconsolidation, which is analogous to the mechanical junction of particles in the cold pressing of aluminum powder, took place. However, differences in the surface relief of contacting particles cannot disappear spontaneously because of the low mobility of molecules in a solid, and composite compaction is not the main reason for the formation of mechanical strength. Thus, for example, a powder loaded in a paper cartridge, which is not a rigid forming element, underwent aggregation, as well as in a mold of corrosion-resistant steel. Rat'ko *et al.* [8] assumed that contacts between particles in a porous composite are formed on the precipitation of aluminum hydroxide as a porous polycrystalline aggregate from solution. They performed a theoretical analysis of the process and obtained a rate equation for the formation of contacts between $Al(OH)_3$/Al composite particles at 100°C.

It is well known [9] that electrostatic repulsion forces should be overcome for the formation of a true (crystallization) contact between adjacent particles and the particles should be brought together to a distance of 10^{-9}–10^{-8} m. In the course of agglomeration or precipitation from solution, that is, on condition that structure-forming elements are mobile, a crystallization contact can only be formed because of the transfer of a substance of the same physicochemical nature from the bulk of particles to the contact region and the incorporation of this substance into the lattice of particles. In the course of cold pressing, the crystallization contact was not formed for the above reasons. In the precipitation of a substance with an incoherent lattice from solutions containing impurities [10, 11] at high supersaturations, impurity molecules can be fixed at the surface of

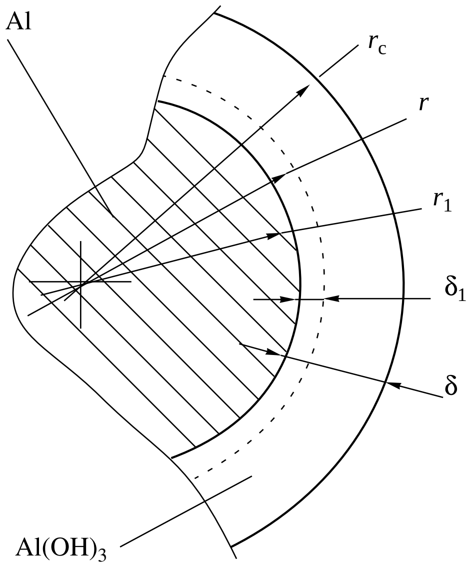

Fig. 1. Schematic diagram of the formation of a bayerite layer on an aluminum particle.

a growing particle or in the contact region between primary particles and covered with further molecular layers. However, they are not implanted into the lattice to result in mechanical stresses and impairment in the strength properties of the porous solid.

RESULTS AND DISCUSSION

Kinetics of Formation of a Porous Deposit on Aluminum Particles

Previously [1], we found that a porous $Al(OH)_3/Al$ composite results from the chemical interaction of aluminum powder with water, the probable formation of the hydroxo complexes of aluminum in the mother liquor, and the polynuclear deposition of these complexes onto the island nuclei of aluminum hydroxide formed in the course of hydrolysis of an oxide film. Because of the structural similarity of the deposit and the solid support, the growth of bayerite crystals occurs by the mechanism of secondary nucleation [12]. Crystal growth is due to the diffusion supply and sequential addition of the hydroxo complexes to the surface of an island nucleus. It includes the following steps: (a) the adsorption of a particle on the surface of a crystal accompanied by incomplete dehydration; (b) the migration of the particle on the crystal surface; (c) the adsorption (addition) of particles at the sites of growth with simultaneous dehydration; and (d) the incorporation of particles into the lattice associated with final dehydration [12]. The rate of the overall reaction depends on the slowest step—the diffusion of the hydroxo complexes of aluminum through a growing porous layer of bayerite.

Figure 1 demonstrates the schematic diagram of the formation of a bayerite deposit on an aluminum particle with radius r. The dissolution of aluminum results in a decrease in the radius of the particle to r_1, whereas the radius of the resulting $Al(OH)_3/Al$ composite particle increases to r_c because deposition occurs at the outer surface of the particle. In the course of the synthesis, the weight of the growing bayerite layer increases by

$$\Delta m_r = 4\pi r_1^2 \delta \upsilon \rho_r, \tag{1}$$

where δ is the thickness of the resulting porous layer of bayerite; υ and ρ_r are its relative and pycnometric densities, respectively. In this case, the weight of aluminum decreases by

$$\Delta m_{Al} = 4\pi r_1^2 \delta_1 \rho_{Al}, \tag{2}$$

where δ_1 is the thickness of the dissolved aluminum layer, and ρ_{Al} is the pycnometric density of aluminum. Because 1 mol of Al forms 1 mol of $Al(OH)_3$,

$$\Delta m_r = 2.89 \Delta m_{Al} \tag{3}$$

and

$$\delta_1 = 0.35 \frac{\delta \rho_r \upsilon}{\rho_{Al}}. \tag{4}$$

A porous solid is formed in the course of polynuclear precipitation from solution. Therefore, a thermodynamic criterion for the transfer of a substance from liquid state 1 to solid state 2, which is accompanied by a decrease in the Gibbs free energy and by the formation of a new interface between bayerite and solution, can be used in studying both the above process and the formation of a single solid-phase nucleus. Work should be done in order to transfer isothermally dn moles of a substance from solution to the surface of a growing bayerite layer and to form a new interface; a balance of work under thermodynamic equilibrium conditions in the case of an ideal solution can be represented by the well-known equation [12–15]

$$dnRT\ln C_2/C_1 = \sigma dS, \tag{5}$$

where R is the gas constant; T is the absolute temperature; C_2 and C_1 are the concentrations of solution at the surface of the growing solid phase and a saturated solution, respectively; σ is the surface energy at the solution–bayerite interface; and $dS = S_{Al(OH)_3} - S_{Al}$ is the change in the surface area of the solution–bayerite interface. Because $S_{Al(OH)_3} \gg S_{Al}$, $dS \approx dS_{Al(OH)_3} = S_w dm_r$, where S_w is the specific surface area of bayerite. Because

$$dn = \frac{dm_r}{M}, \tag{6}$$

where M is the molar weight of bayerite, we have

$$RT\ln C_2/C_1 = \sigma S_w M. \tag{7}$$

Thus, we obtain the equation

$$C_2 = C_1 \exp\left(\frac{\sigma S_w M}{RT}\right) \text{ or } C_2 \approx C_1\left(1 + \frac{\sigma S_w M}{RT}\right). \quad (8)$$

Equation (8) is identical to the Gibbs–Kelvin equation, which describes the dependence of the critical size of a solid-phase nucleus on supersaturation or the dependence of the solubility of this nucleus on particle size [15],

$$C_2 \approx C_1\left(1 + \frac{2\sigma V_\mathrm{m}}{rRT}\right).$$

Thermodynamic relationship (8) does not describe the kinetics of formation of the bayerite layer; therefore, we use the Fick equation

$$\frac{\mathrm{d}m_\mathrm{r}}{\mathrm{d}t} = DS_\mathrm{s}\frac{\mathrm{d}C}{\mathrm{d}\delta}, \quad (9)$$

where S_s is the surface area through which diffusion transfer takes place.

As can be seen in Fig. 1,

$$S_\mathrm{s} = 4\pi r_1^2 \approx 4\pi r^2. \quad (10)$$

Substituting the values of S_s from Eq. (10) and of C_2 from Eq. (8) into Eq. (9) shows that the change in the bayerite weight is

$$\mathrm{d}m_\mathrm{r} = \rho_\mathrm{r}\upsilon \mathrm{d}V_\mathrm{r}, \quad (11)$$

where V_r is the volume of the bayerite formed:

$$V_\mathrm{r} = 4\pi r_1^2\delta \approx 4\pi r^2\delta. \quad (12)$$

Assuming stationary diffusion, that is,

$$\frac{\mathrm{d}C}{\mathrm{d}\delta} = \frac{C_2 - C_1}{\delta}, \quad (13)$$

we obtain

$$\delta \mathrm{d}\delta = \frac{DC_1\sigma S_\mathrm{w} M}{\rho_\mathrm{r}\upsilon RT}\mathrm{d}t, \quad (14)$$

where

$$\frac{M}{\rho_\mathrm{r}} = V_\mathrm{m} \quad (15)$$

is the molar volume of bayerite. After integration, we obtain the following equation for the kinetics of growth of a bayerite layer on the surface of an aluminum particle:

$$\delta^2 = \frac{2DC_1\sigma S_\mathrm{w} V_\mathrm{m}}{RT\upsilon}t. \quad (16)$$

Equation (16) corresponds to a parabolic function for oxidation processes that obey the Wagner law when the formation of a solid product in the course of reaction results in the inhibition of diffusion.

In the course of synthesis, the change in the weight of an $Al(OH)_3$/Al composite particle is

$$\Delta m = \Delta m_\mathrm{r} - \Delta m_\mathrm{Al}, \quad (17)$$

where

$$\Delta m_\mathrm{r} = 4\pi r_1^2\delta\rho_\mathrm{r}\upsilon \approx 4\pi r^2\delta\rho_\mathrm{r}\upsilon$$

$$\text{and } \Delta m_\mathrm{Al} = 4\pi r_1^2\delta_1\rho_\mathrm{Al} \approx 4\pi r^2\delta_1\rho_\mathrm{Al}.$$

Substituting the values of Δm_r, Δm_Al, and δ_1 from Eq. (4) into Eq. (17), we obtain

$$\Delta m = 2.65\pi r^2\rho_\mathrm{r}\upsilon\delta. \quad (18)$$

The powder of weight m contains

$$N = \frac{V_\mathrm{sh}}{V_\mathrm{p}} = \frac{3m}{\rho_\mathrm{sh}4\pi r^3} \quad (19)$$

powder particles, where V_sh and V_p are the volume occupied by the shaken powder of weight m and the volume of a single particle, respectively; and ρ_sh is the density of the shaken powder. Then,

$$\frac{\Delta m}{m} = \frac{2\rho_\mathrm{r}\upsilon\delta}{\rho_\mathrm{sh}r}. \quad (20)$$

Substituting the value of δ in Eq. (20), we obtain

$$\frac{\Delta m}{m} = \frac{2\rho_\mathrm{r}\upsilon}{\rho_\mathrm{sh}r}\sqrt{\frac{2DC_1\sigma S_\mathrm{w}V_\mathrm{m}t}{RT\upsilon}} \quad (21)$$

or

$$\left(\frac{\Delta m}{m}\right)^2 = \frac{8\rho_\mathrm{r}^2\upsilon DC_1\sigma S_\mathrm{w}V_\mathrm{m}}{RT\rho_\mathrm{sh}^2 r^2}t. \quad (22)$$

The aluminum conversion (α) in the course of chemical reaction with water is equal to

$$\alpha = \frac{\Delta m_\mathrm{r} - \Delta m_\mathrm{Al}}{m_\mathrm{r} - m}, \quad (23)$$

where m_r is the weight of the hydroxide formed on the complete conversion of aluminum of weight m. With the use of Eq. (3), we obtain

$$\frac{\Delta m}{m} = 1.89\alpha. \quad (24)$$

Thus,

$$\alpha^2 = \frac{2.24\rho_\mathrm{r}^2\upsilon DC_1\sigma S_\mathrm{w}V_\mathrm{m}}{RT\rho_\mathrm{sh}^2 r^2}t. \quad (25)$$

The diffusion coefficient of the hydroxo complexes of aluminum in a porous bayerite layer can be calculated with the use of the experimental function $\alpha = f(t)$, which was obtained previously [1], substituting known constants and values ($R = 8.31$ J K^{-1} mol^{-1}; $T = 373$ K; $\rho_\mathrm{sh} = 1.56 \times 10^3$ kg/m^3; $r = 10^{-5}$ m; $\rho_\mathrm{r} = 2.42 \times 10^3$ kg/m^3 [10]; $\upsilon \approx 0.5$; $C_1 = 0.027$ kg/m^3 is the concentration of aluminum in solution at which a hydrolytic polymerization reaction begins [16]; $\sigma = 773 \times 10^{-3}$ J/m^2 [17]; $S_\mathrm{w} = 53 \times 10^3$ m^2/kg [1]; and $V_\mathrm{m} = 23 \times 10^{-6}$ m^3/mol) in Eq. (25).

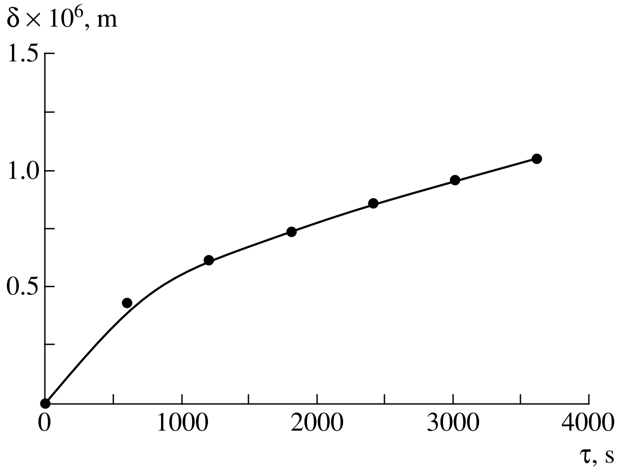

Fig. 2. Calculated kinetic function for the thickness of a bayerite layer on an aluminum particle.

Over the range $t = (1.5–18) \times 10^3$ s, the calculated values of the diffusion coefficient are $(0.067–0.13) \times 10^{-10}$ m^2/s, and the average value is 0.096×10^{-10} m^2/s. Substituting the average value of the diffusion coefficient in Eq. (16), we can calculate the kinetics of growth of the bayerite layer on aluminum particles. The calculated value of δ after the synthesis for 1 h is ~1 μm (Fig. 2), which is consistent with the experimental value obtained with the use of electron microscopy [1]. Taking into account that this calculation is rough, the above value suggests that the diffusion model developed is correct and the calculated value of the diffusion coefficient is reliable.

It is well known that the diffusion coefficients of the components of aqueous solutions under normal conditions are $\approx 10^{-9}$ m^2/s; at the same time, the diffusion coefficients of liquids in porous solids largely depend on their nature and structure characteristics [18]. Thus, Khozina *et al.* [19] experimentally found that the diffusion coefficient of water in FAS active carbon is $(5.84–9.3) \times 10^{-10}$ m^2/s. The diffusion of water in vermiculite was studied, and the value of $D = 10^{-10}$ m^2/s (in the bulk phase, $D = 2.3 \times 10^{-9}$ m^2/s) was determined [20]. In fine pores, the structure of water hydrogen bonds is distorted so that the molecules become orientationally ordered, and the plane of water molecules is arranged parallel to the solid–water interface. Because of this, the diffusion coefficient decreases from 4.2×10^{-9} m^2/s (in the bulk phase) to 1.8×10^{-9} m^2/s (in a thin film) [21]. Churaev [22] found that in a solid the value of D increases from 5×10^{-10} to 1.5×10^{-9} m^2/s as the effective pore radius increases from 3 nm to 3 μm, whereas $D = 2.95 \times 10^{-9}$ m^2/s in the bulk phase. Prokhorov [23] theoretically and experimentally studied the effect of adsorption on the diffusion coefficient of water in soils and found that D depends on the adsorption of water and is on the order of 10^{-9} m^2/s. Voloshina *et al.* [24] studied the dependence of the diffusion coefficient of a sodium chloride solution on the pore radius of a porous glass membrane and observed a dramatic decrease in D from $(6–7) \times 10^{-10}$ to 2×10^{-10} m^2/s at $r < 15$ nm ($D = 1.25 \times 10^{-9}$ m^2/s in the bulk of solution at 25°C [25]). According to Voloshina *et al.* [24], the formation of structured liquid layers at the solid surface and an increase in the viscosity of water in fine pores are responsible for the decrease in the integral value of D. The orders of magnitude of the effective pore size in a bayerite layer on aluminum particles (≈2 nm [1]) and the above values are consistent; however, the calculated value of D is lower by one order of magnitude. Consequently, particles coarser than water molecules or ions in an aqueous solution of sodium chloride (i.e., the hydroxo complexes of aluminum) diffuse in a bayerite layer.

Kinetics of Aggregation of Al(OH)$_3$/Al Composite Particles

In the course of synthesis, the porous layer of bayerite, as well as a portion of "old" contacts, underwent partial degradation under the action of mechanical stresses as the solid-phase volume increased. Simultaneously, new interfaces were formed because of the dissolution of aluminum and the precipitation of the hydroxo complexes of aluminum. The kinetics of contact formation on the intense consolidation of particles is difficult to analyze theoretically because contacts with an uncertain geometry are formed at the stage of particle degradation. Moreover, the competing processes of the degradation of "old" contacts and the formation of new contacts cannot be taken into account. Physically, the initial stage of aggregation in the course of synthesis is much more certain. In this case, changes in the contact radius (x) and ultimate strength (σ_u) are associated only with changes in the geometry of contacts due to the precipitation of the hydroxo complexes of aluminum, and a model of two contacting spheres can be used as an adequate approximation for the theoretical study of aggregation.

The aggregation of Al(OH)$_3$/Al composite particles results from processes that occur near a contact between two spherical aluminum particles. Initially, these particles are in contact at a point to form a dihedral angle, where heterogeneous precipitation occurs much more easily than at a smooth surface. The hydroxo complexes of aluminum are transferred to the contact region through diffusion from solution due to a concentration gradient because concentration at a concave surface is lower that in the bulk. As a result, as the volume is filled with a solid substance, the radius of a contact and its radius of curvature increase; a crystallization layer is formed between the contacting composite particles, and this layer is responsible for the high mechanical strength of the material synthesized.

The formation of contacts between the particles of aluminum powder in the course of synthesis of a porous Al(OH)$_3$/Al composite, as well as the growth of a bay-

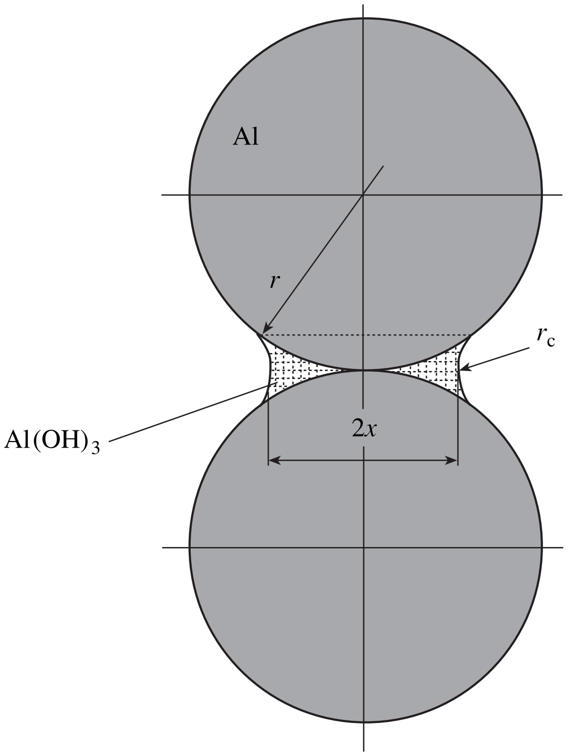

Fig. 3. Schematic diagram of the formation of a contact between aluminum particles in the course of synthesis.

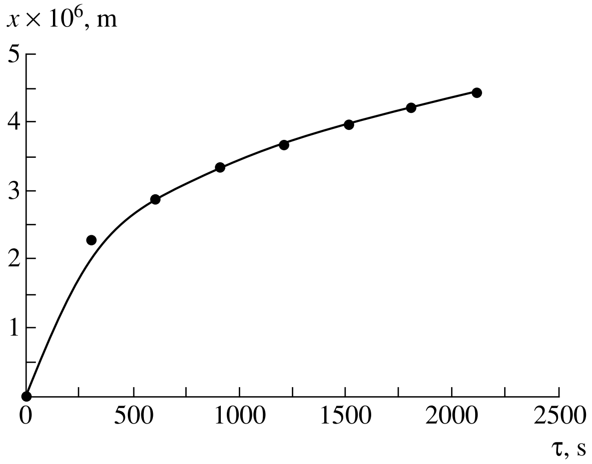

Fig. 4. Calculated kinetic function for the radius of a contact between $Al(OH)_3$/Al composite particles.

erite layer on aluminum particles, is accompanied by a decrease in the Gibbs free energy and the formation of a new interface between the contact substance and the solution. The rate of aggregation can be calculated based on model approximations associated with the effect of the convolution of surfaces on the processes of aggregation in diffusion mass transfer from the solution to the contact region without the participation of significant mechanical stresses and assuming that dissolution–precipitation processes serve as a controlling mechanism. Let us assume that a contact of radius x with a concave surface of radius r_1 between aluminum particles of radius r (Fig. 3) is formed as bayerite with the same pore-structure characteristics because of the polynuclear precipitation of the hydroxo complexes of aluminum from solution. The formation of a bayerite layer on aluminum particles occurs simultaneously with the aggregation of $Al(OH)_3$/Al composite particles. However, because 1 mol of Al forms 1 mol of $Al(OH)_3$, $\delta = 6.45\delta_1$ (Fig. 1). It is easy to show that, in the formation of a bayerite layer 1 μm in thickness, the initial diameter of an aluminum particle equal to 20 μm increases by 1.56 μm. Without introducing considerable errors into the subsequent calculations, we can ignore the formation of a bayerite layer on aluminum particles and assume that the radius of contacting particles remained unchanged in the course of aggregation. As in the formation of a bayerite layer, the growth of a contact is accompanied by the formation of a new interface, and the solution concentration at the formed surface of a porous contact is determined from the condition that changes in the Gibbs energy (Eqs. (5) and (8)) are equal to zero. The kinetics of growth of the contact weight is also determined by the Fick equation

$$\frac{\mathrm{d}m_\mathrm{c}}{\mathrm{d}t} = DS_\mathrm{c}\frac{\mathrm{d}C}{\mathrm{d}r_1}, \tag{26}$$

where S_c is the surface area through which diffusion transfer takes place. The diffusion of a substance takes place from the bulk of the solution adjacent to the growing contact surface. However, because the diffusion of the hydroxo complexes of aluminum through a bayerite layer is the rate-limiting step of the synthesis, the above-calculated value of the diffusion coefficient should be used in Eq. (26). Taking into account that

$$\mathrm{d}m_\mathrm{c} = \rho_\mathrm{r}\upsilon\mathrm{d}V_\mathrm{c}, \quad S_\mathrm{c} = \frac{2\pi x^3}{r},$$

$$V_\mathrm{c} = \frac{\pi x^4}{r} \quad \text{and} \quad r_1 = \frac{x^2}{2r}$$

under conditions of stationary diffusion, we obtain

$$x^2dx = \frac{DC_1\sigma S_\mathrm{w}V_\mathrm{m}r}{RT\upsilon}dt. \tag{27}$$

After integrating Eq. (27), the rate equation for the growth of an interparticle contact has the following form:

$$x^3 = \frac{3DC_1\sigma S_\mathrm{w}V_\mathrm{m}r}{RT\upsilon}t \tag{28}$$

or

$$\left(\frac{x}{r}\right)^3 = \frac{3DC_1\sigma S_\mathrm{w}V_\mathrm{m}}{RT\upsilon r^2}t. \tag{29}$$

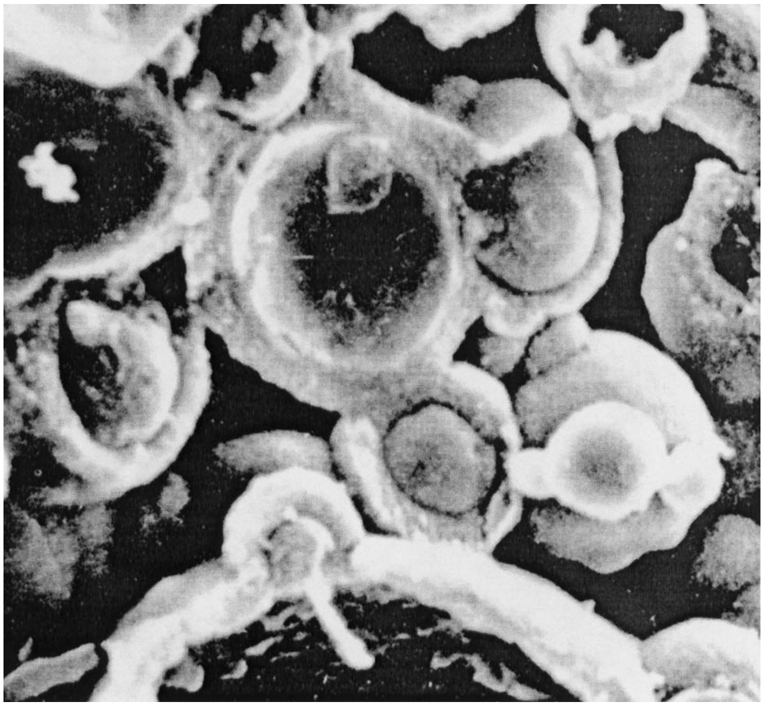

Fig. 5. Microstructure of a porous $Al(OH)_3/Al$ composite (×2500).

These equations are analogous to the equations that characterize the growth of contacts in the sintering of powder materials when a substance is transferred through a gas or solid phase [26]:

$$x^n = At.$$

Initial data for plotting the kinetic curves of changes in x and x/R in the course of the synthesis of the porous composite (Fig. 4) were obtained by introducing known quantitative values into Eqs. (28) and (29) (on the assumption that $D = 0.096 \times 10^{-10}$ m^2/s). The calculated value of x after the 1-h synthesis was ~3.8 μm, which is consistent with experimental results [1], whereas the ratio x/R ~0.38 is characteristic of contacts formed in the sintering of powder materials [26]. Figure 5 demonstrates an electron micrograph of the microstructure of the material synthesized. The fractured surface exhibits isolated aluminum particles coated with a bayerite cover, and a formed contact is observed between $Al(OH)_3/Al$ composite particles.

Thus, based on theoretical and experimental studies, we proposed a controlling mechanism for the synthesis of a porous $Al(OH)_3/Al$ composite. This mechanism includes colloid-chemical and diffusion processes in the formation of a porous solid; these processes are responsible for the formation of the "building material" (the hydroxo complexes of aluminum) and its transport to the growing surfaces of bayerite nanoparticles.

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