

# Aluminum "Core-shell" microparticles with an oxide shell - fillers of spatially strengthened composites, facilitating material digitization

*M. N. Larichev<sup>1\*</sup>, N. S. Shaitura<sup>1</sup>, O. Yu. Yurakova<sup>1</sup>, and V. V. Artemov<sup>1</sup>*

<sup>1</sup>N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, Kosygina str., 4, 119991 Moscow, Russia.

**Abstract.** The transformation of aluminum "Core-shell" microparticles formed by low-temperature oxidation with water during their heating in a controlled atmosphere has been studied. Spherical particles with an oxide shell, convenient for mathematical modeling of the structure and properties of the developed composites, are planned to be used as fillers for metal and polymer oxide composites, as well as for 3D printing.

## 1 Introduction

Dispersion-strengthened metal and polymer composites [1], in particular particulate-reinforced aluminum matrix composites (PAMCs) [2], are promising structural materials. Their operational properties can significantly exceed the properties of the material used to form the matrix, due to the enhancement of the properties of this material. What's more, they can be custom designed and manufactured with properties optimized for that particular use. The use of such materials shows steady growth. Their properties are widely studied, methods of their production are being improved. In practice, composites are often used that have an aluminum or polymer matrix reinforced with a filler (framework) of aluminum oxide particles of various shapes and sizes. In the development and manufacture of such composites, several scientific and engineering problems have to be solved at once in order to provide the material with the performance properties necessary for a specific intended use. Such tasks, in particular, are:

- selection of the optimal size and shape of oxide filler particles;
- organization of a given spatial distribution of aluminum oxide particles over the volume of the composite matrix (products from it);
- creation of an adhesive bond between the oxide filler and the matrix material having the required value.

In this work, it is proposed to use oxide shells of pre-oxidized spherical aluminum particles (POSAP) as reinforcing oxide fillers. The spherical shape of the particles is chosen based on the convenience of reproducing both the Al particles themselves of a given diameter and the convenience of forming oxide shells of the required thickness on their surface. The latter is determined, in particular, by the fact that the surface reactivity of

---

\* Corresponding author: [mlarichev@chph.ras.ru](mailto:mlarichev@chph.ras.ru)

particles of various shapes differ [3]. POSAP coated with an oxide shell are usually referred to in the literature as "Core-shell particles". They can be made by additional oxidation from commercially available aluminum particles of a given diameter. Usually, the surface of Al particles in the delivered state is covered with an oxide film with a thickness of approximately 2–4 nm [4], which is formed on the freshly formed aluminum surface upon contact with air. This oxide coating protects the particle metal from further oxidation by atmospheric oxygen and atmospheric moisture during particle storage and allows various aluminum products, including structural ones, to be successfully operated under normal conditions. However, by special additional oxidation of the particle surface, the thickness of the oxide shell can be increased. Depending on the type of oxidation method used, it is possible to obtain oxide shells of one thickness or another, which have different physicochemical properties.

When using POSAP as a reinforcing filler:

- the diameter of the particles will be one of the determining factors that ensure the regularity of the distribution of oxide shells (filler particles) over the volume in the formed composite;
- the thickness of the shell will determine the characteristic minimum particle size of the oxide filler, as well as the limiting stresses, under the influence of which the shell of particles in the composition of the composite material will be destroyed;
- the spherical shape and the known diameter of the particles will allow the use of the filler as “bricks” for building the structure of the reinforcing frame that is optimal for this application;
- physico-chemical properties of the POSAP surface will determine the adhesive bond of the filler with the matrix.

At the same time, when using POSAP as a filler, it becomes possible to provide:

- convenient mathematical modeling of the behavior of the planned structure of the composite under the expected conditions of its operation due to the relative simplicity of creating digital models for a similar structure of the material. Digital models will make it possible to predict the behavior of a material under expected operating conditions. This will affect the duration and cost of the material development stage and will speed up the determination of the optimal structure, which is preferable for the conditions of its intended use;
- high reproducibility of the structure of the strengthening matrix in the formed composite materials (parts) during their replication in the production process.

## **2 Materials and methods**

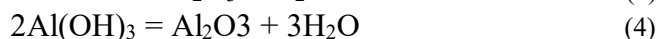
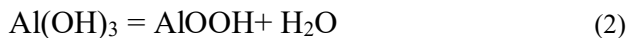
For the manufacture of POSAP, various methods of particle surface oxidation are used, including oxygen [5, 6] and water. Oxidation of particles with oxygen forms smooth oxide coatings on their surface, the specific surface of which, as a rule, is close to geometric (Fig. 1b). On the contrary, the oxidation of the aluminum surface with water molecules allows the formation of hydroxide coatings with a high specific surface area (Figure 1 c, d, e). Such oxidation is a convenient method that makes it possible to controllably form particles with the necessary parameters, among which are the thickness of the hydroxide shell, its specific surface area, and its physicochemical properties. It can be carried out, for example, by the hydrothermal method described in [7, 8]. However, the flexible control of the hydrothermal oxidation process seems to be problematic, which makes it difficult to control the shell formation on-line. From this point of view, the method of controlled oxidation of the surface of Al particles with water at atmospheric pressure [9, 10], in which liquid-phase oxidation is carried out at temperatures not exceeding the boiling point of water, seems to

be a more preferable method used in this work. For particles of micron size and above, the process proceeds, as a rule, according to equation (1):



Reaction (1) makes it possible, due to the oxidation of surface layers, to form a shell of amorphous aluminum hydroxide, which has a structure commonly referred to in the literature as “Nanowalls” [9, 10], which is characterized by a high specific surface area, reaching 80 m<sup>2</sup>/g in our experiments [11]. In this case, the surface of Al particles before oxidation was only 1–2 m<sup>2</sup>/g. For the objects under consideration, reaction (1) seems to be a convenient alternative to chemical etching [12] for obtaining “Nanowalls” structures. The thickness of the oxidized aluminum layer and, consequently, the resulting hydroxide layer can be estimated from the amount of hydrogen released during the oxidation of the particle surface. The proposed oxidation method is the most flexible and makes it possible to conveniently control the parameters of the formed POSAP (the thickness of the hydroxide shell, the value of its specific surface area). In particular, for the studied micron particles, the shell thickness can be from ten to several hundred (500) nm. Methods for activating reaction (1) can be used to accelerate the process of particle surface oxidation. In particular, thermal activation, ultrasonic (US) activation, chemical activation using calcium oxide CaO, described in detail in [9, 10], can be used.

POSAP with a shell of aluminum hydroxide have their own specific properties, determined by the properties of aluminum hydroxide containing a large number of OH groups and, as a result, water molecules. They can be used as fillers for some types of matrices in the production of composites. However, these same particles can be easily transformed into oxide-coated POSAP, the scope of which seems to be much wider. To do this, particles oxidized with water must be subjected to heat treatment at temperatures exceeding the temperature of the chain of phase transitions: aluminum hydroxide - aluminum oxide aluminum hydroxide - aluminum oxide (up to 350 °C):



The features of the occurrence of such a transformation for spherical particles were studied and described in [13]. As a rule, POSAP coated with an amorphous hydroxide shell of the “Nanowalls” type are transformed into an amorphous oxide shell of the same type. The resulting Al particles coated with an amorphous oxide shell can be used to strengthen metal (aluminum) or polymer matrices. Such a developed surface makes it possible to ensure reliable adhesion of the filler particles in the matrix material, and at high degrees of filling, the POSAP will provide the composite with the effect of a "sandbag" i.e. the ability to effectively detain objects penetrating it. The thickness of the oxide shell will determine the threshold of its destruction as a result of external influence. This will allow turning on an additional channel for the dissipation of the energy of the external action, leading to the destruction of the shells. This will increase the efficiency of the composite application. The implementation of this option implies the need to optimize the strength and surface properties of the formed oxide shells and additional control of their reproducibility.

It should be noted that the oxide-shell POSAP obtained by the method proposed above can also be used for 3D printing of composite materials, both by selective laser melting (SLM) and selective laser welding (SLW) [14, 15]. After heat treatment and phase transition, particles coated with an oxide shell will be characterized by a minimum gas

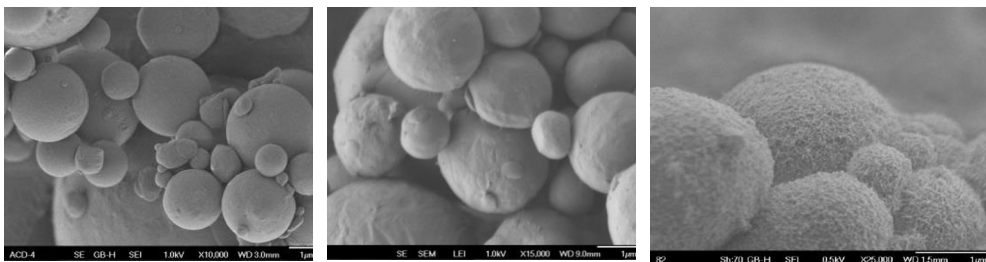
evolution in subsequent stages associated with heating. However, the algorithms that ensure their efficient use in the SLM and SLW methods appear to be quite different due to the significant difference in operating temperatures used in each of these methods.

The results of the experiments show that if the heating of POSAP coated with a hydroxyl shell is carried out in a gas atmosphere of a controlled composition, then it becomes possible to change the surface physicochemical properties of the formed oxide shell due to chemical modification of its surface layers [16].

The liquid-phase oxidation method can also form hydroxide coatings of mixed elemental composition on the POSAP surface [17], which, in turn, can be transformed into oxide coatings of mixed composition upon heating. As an example of such a mixed oxide coating, one can cite POSAP, which are formed using a chemical activator [10] calcium oxide (CaO), also having the “Nanowalls” structure, the images of which are shown in Fig. 1e. This also makes it possible to widely vary the physicochemical properties of the PSACH surface, in particular, to control its adhesive properties.

Micron spherical particles with an average diameter of 4  $\mu\text{m}$  (ASD-4 powder, commercially produced by the Russian industry (TU 48-5-226-87)) were chosen as the initial aluminum particles, the surface of which was subjected to oxidation. The initial particles, as well as particles subjected to the necessary chemical and physical effects (heat treatment, oxidation, drying) were studied by scanning electron microscopy (SEM) on a JSM-7401F instrument, X-ray phase analysis (XRD) on a DRON-3 instrument (CuK $\alpha$  - radiation). Elemental analysis of the surface of the samples (EDS elemental analysis) was performed on a Quanta 200 3D instrument with EDAX Genesis energy dispersive microanalysis.

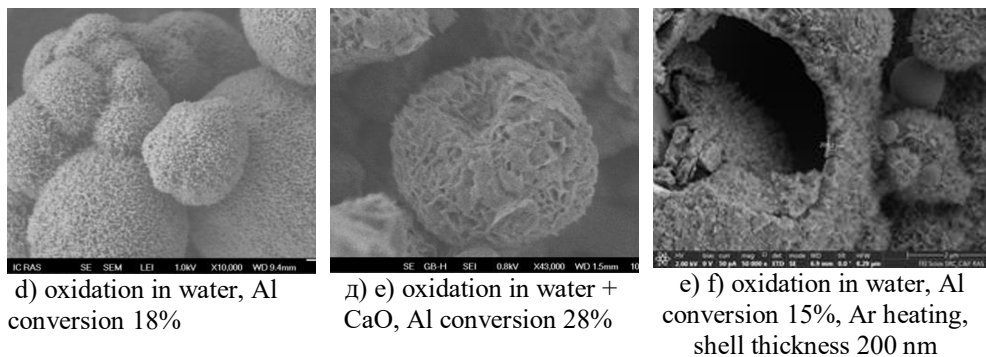
A photograph of the surface of ASD-4 particles in the delivered state is shown in Fig. 1 a. Particles were oxidized with water using installations and according to the procedures described in [9]. Micron powder particles oxidized in distilled water were obtained with a metal conversion degree of 8%, 18%, and 33%, which corresponds to the average thicknesses of the oxidized aluminum layer of 120, 270, and 500 nm. After reaching the required degree of aluminum conversion, the oxidation process was forcibly stopped, and the oxidized particles were subjected to rapid drying with dry air until a constant weight was reached. After drying, hydroxyl-coated POSAP were stored in closed glass containers, which were opened to the atmosphere only for a short time when particles were collected for experiments and analyses.



a) ASD-4 - initial state

b) oxidation in oxygen at 630°C

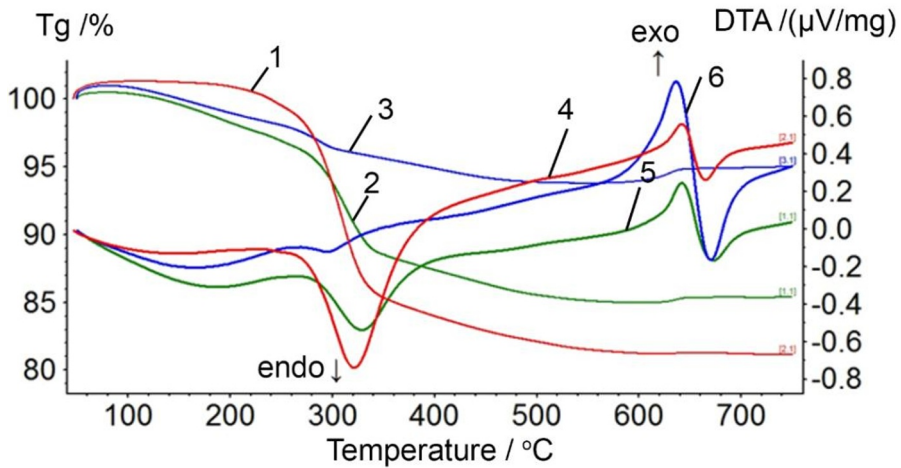
c) oxidation in water, Al conversion 8%



**Fig. 1.** Micrographs of ASD-4 powder particles: a) in the initial state; b) oxidized in oxygen; c), d) oxidized by water without activation with different degrees of metal conversion; e) oxidized by water with CaO activation; f) oxidized with water after heating in Ar at 750°C. The shell thickness is 200 nm. Particles a), b), f) are covered with an oxide shell. Particles c) - e) are covered with a hydroxide shell.

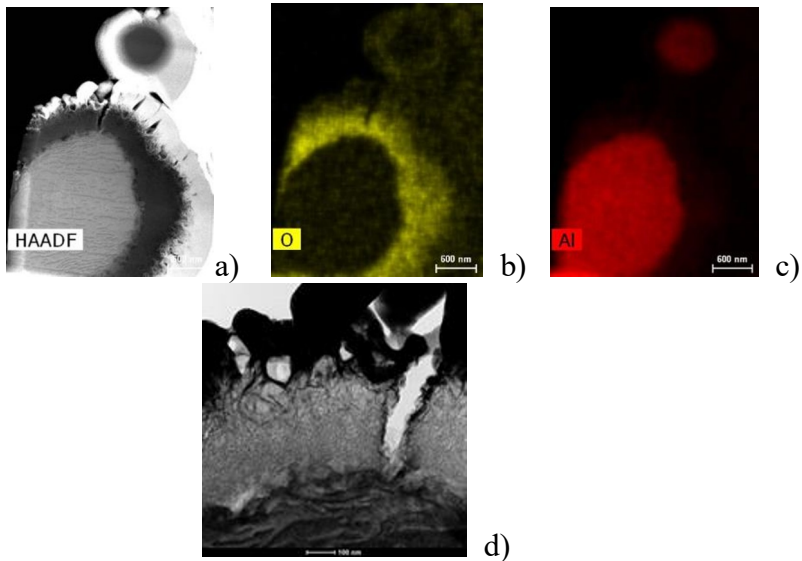
### 3 Results and discussion

Figure 1c, d, e shows micrographs of POSAP surfaces with various degrees of metal conversion, coated with a hydroxide shell, the subsequent heat treatment of which was carried out in order to form oxide shells. The results of electron microscopy show that at a degree of metal conversion less than 30%, “Nanowalls” structures are formed on the surface, which, according to XRD analysis, are formed from amorphous  $\text{Al}(\text{OH})_3$ . The cellular structure of this type of coating is well represented in Fig. 1c, d, e, f. The characteristic cell size is about 100 nm, and the thickness of the walls forming the cells is up to 20 nm. Fig. 1f shows that for a sample with a metal conversion of 15%, the thickness of the Nanowalls shell after the transformation of the hydroxide shell into an oxide shell is about 200 nm. The thermophysical properties of POSAP samples coated with hydroxide and oxide shells were studied using a NETZSCH STA 449 F1 Jupiter thermal analysis instrument equipped with a QMS Aeolos 3 mass spectrometer. mass-spectrum analysis of the composition of gas-phase compounds released into the environment. STA 449 F1 analysis of samples coated with hydroxide shells (linear heating to 750°C at a rate of up to 20°C/min in an oxidizing (artificial air (75%  $\text{O}_2$  + 25% Ar)) (Fig. 2) and neutral atmosphere (Ar) shows that in the temperature range of 260–400°C, the  $\text{Al}(\text{OH})_3$  surface layer undergoes a chain of phase transitions (2) – (4), dehydrates, and transforms into the  $\text{Al}_2\text{O}_3$  surface layer [13]. (release of water and hydrogen), the DTA curve shows the endothermic effect (phase transition), and mass spectral analysis registers the release of water and hydrogen molecules into the surrounding space.



**Fig. 2.** Thermoanalytical curves DTA (1, 2, 3) and TG (4, 5, 6) obtained for POSAP heated in an atmosphere of artificial air with different degrees of conversion of aluminum oxidized by water at temperatures below 100°C. The degree of aluminum conversion in the samples: 1 - 33%; 2 - 18%; 3 - 8%.

The SEM data demonstrate that the oxide coatings formed as a result of the phase transition also belong to the “Nanowalls” type structures. According to XRD analysis, the formed structures of oxide shells are also amorphous. Fig. 3 shows the structure and construction of an oxide-shell POSAP cut by a high-energy atomic beam. The boundary between the metal core and the oxide shell is clearly defined. The structure of the oxide shell is clearly visible, including thickness unevenness, density inhomogeneity, and through defects.



**Fig. 3.** Micrographs of POSAP with an oxide shell, cut by a high-energy beam: a – in transmission; b - in the characteristic radiation of oxygen; c - in the characteristic radiation of aluminum; d - the structure of the metal-oxide shell boundary, a crack in the oxide shell

Analysis of the thermoanalytical curves shown in Fig. 2 shows that at temperatures above 550°C, the oxide coating formed on the surface of the Al particle core as a result of phase transitions (2-4) is broken. This leads to an increase in the mass of the sample due to the oxidation of the surface layer of the aluminum core by the oxygen of the atmosphere surrounding the particle, which is accompanied by the observed exothermic effect.

The reason for the discontinuity of shells at temperatures in the region of 570°C is thermal stresses arising in the core-shell system. Due to the fact that the thermal expansion coefficient (TEC) of metallic aluminum ( $34.55 \cdot 10^{-6}$ ) [18] significantly exceeds the TEC of its oxides ( $6.58 \cdot 10^{-6}$  - for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) [19] (the values of the TEC correspond to a temperature of 600°C and are obtained by extrapolating data from the relevant articles), the expansion of the aluminum core during heating of the particles should occur faster than the oxide shell, however, the shell prevents the core from expanding due to its slower growth, as a result of which pressure arises in the system under consideration, which acts on the shell from the side of the more rapidly growing core, which in turn causes stress in the shell, leading to its rupture when a certain critical deformation is reached, corresponding under the given conditions to the ultimate tensile strength of aluminum oxide ( $\sigma_{(Al_2O_3, ext)} = 551$  MPa [20]). The metal core expanding more rapidly with increasing temperature destroys the oxide shell, disrupts its continuity, providing contact of the core metal with the atmosphere surrounding the particle and, if the latter contains an oxidizing agent (oxygen, water vapor), it leads to oxidation of the surface of the metal core.

To obtain an estimate of the destruction temperature of oxide shells, a model can be considered that describes the interaction between the shell and the metal core of a particle, when each particle can be modeled by an aluminum ball placed in a thin spherical oxide shell weakly bonded to it. When heated, independent volumetric expansion of the sphere and the shell are considered.

Upon reaching the tensile strength - that maximum force applied to the sample, at which the critical value of deformation is reached, the sample is destroyed. Since aluminum oxide is a brittle material, it does not have a region of plastic deformations and, in the model used, Hooke's law for linear deformations is valid up to sample failure. The force applied to the sample is related to the resulting elongation through the coefficient of proportionality - Young's modulus, and for the stress  $\sigma$  we have:

$$\sigma = E\varepsilon, \quad (5)$$

where  $E$  – modulus of normal elasticity (Young's modulus),  $\varepsilon$  – relative strain.

For the oxide shell, expression (5) takes the form:

$$\sigma_{Al_2O_3} = \varepsilon_{Al_2O_3} E_{Al_2O_3}, \quad (6)$$

where  $E_{Al_2O_3}$  – modulus of normal elasticity (Young's modulus) of aluminum oxide,  $\varepsilon_{Al_2O_3}$  – relative deformation of aluminum oxide. Hence the value of relative deformation for aluminum oxide:

$$\varepsilon_{Al_2O_3} = \frac{\sigma_{Al_2O_3}}{E_{Al_2O_3}} = \frac{\Delta l_{crit}}{l_0}, \quad (7)$$

where  $\Delta l_{crit}$  – is the value of the critical deformation at which the shell is destroyed,  $l_0$  – circumference of the large diameter of the oxide shell. From expression (7) for the critical strain, we have

$$\Delta l_{crit} = \frac{l_0 \sigma_{Al_2O_3}}{E_{Al_2O_3}} \quad (8)$$

For the initial circumference of the original aluminum ring, we write:

$$l_0 = 2\pi R_0, \quad (9)$$

where  $R_0$  – the radius of the aluminum core of the initial particles. Then, for the critical strain, taking into account (9), we have:

$$\Delta l_{crit} = \frac{2\pi R_0 \sigma_{Al_2O_3}}{E_{Al_2O_3}}. \quad (10)$$

At the same time, the magnitude of the absolute deformation is determined by the temperature of the heated particle. An increase in the linear dimensions of an aluminum spherical core in accordance with the theory of thermal expansion corresponds to the following increase in the radius of spherical aluminum:

$$R_{Al} = R_0(1 + \alpha_{Al}\Delta T), \quad (11)$$

where  $R_0$  – radius of the aluminum core of the initial particles,  $\alpha_{Al}$  – coefficient of thermal expansion of metallic aluminum,  $\Delta T$  – the temperature to which the initial oxide-coated particles were heated. The magnitude of the absolute deformation of the circumference of the oxide shell, which first causes stress in the shell, and then its destruction, is equal to the difference between the elongation resulting from the thermal expansion of the aluminum core and the elongation associated with the thermal expansion of aluminum oxide:

$$\Delta l_{crit} = (2\pi R_0(1 + \alpha_{Al}\Delta T) - 2\pi R_0) - \frac{(2\pi R_0(1 + \alpha_{Al_2O_3}\Delta T) - 2\pi R_0)}{2\pi R_0\Delta T(\alpha_{Al} - \alpha_{Al_2O_3})} \quad (12)$$

where  $\alpha_{Al_2O_3}$  – coefficient of thermal expansion of aluminum oxide,  $\alpha_{Al}$  – TEC of aluminum.

Then, equating expressions (10) and (12), we obtain for the value  $\Delta T$ :

$$\Delta T = \frac{\sigma_{Al_2O_3}}{E_{Al_2O_3}(\alpha_{Al} - \alpha_{Al_2O_3})}. \quad (13)$$

For  $\alpha$ -aluminum oxide  $E_{Al_2O_3} = 400$  GPa [20], for alumina ceramics  $E_{Al_2O_3} = [220 - 350]$  GPa [21]. To carry out calculations, it is necessary to determine the starting temperature of heating particles with an already formed oxide shell. The initial particles are covered with a layer of amorphous  $Al(OH)_3$ ; from the results of TGA and DTA, it follows that the temperature range of 250–380°C corresponds to a first-order phase transition corresponding to the transition of aluminum hydroxide  $Al(OH)_3$  to oxide hydroxide  $AlOOH$  (called boehmite), which proceeds according to the reaction (2). On the water release rate curve, this transition corresponds to a pronounced maximum in the given temperature range. A further increase in temperature to 500°C transforms aluminum oxide hydroxide into oxide and is also accompanied by the release of water. The transition occurs according to reaction (3). Thus, the formation of the oxide shell ends at temperatures of about 500°C, and at higher temperatures, the oxide shell is already subjected to heating. Then for the cracking temperature  $T_{damage}$  we have:

$$T_{damage} - 500 = \frac{\sigma_{Al_2O_3}}{E_{Al_2O_3}(\alpha_{Al} - \alpha_{Al_2O_3})}, \quad (14)$$

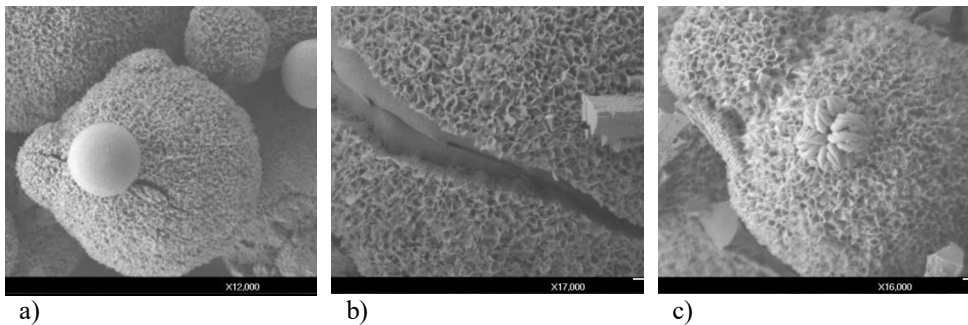
Substituting into formula (14) the values of the coefficients obtained from the literature, characterizing various forms of alumina, we obtain: - for particles with a shell of  $\alpha$ -



aluminum oxide, the temperature of crack formation  $T_{\text{damage}} = 549.2^{\circ}\text{C}$ ; - for particles, the coating of which corresponds to alumina ceramics, the temperature of crack formation, which lies within the limits  $T_{\text{damage}} = [556.3 - 589.5]^{\circ}\text{C}$ .

Thus, the estimates show the destruction temperatures of oxide shells close to those observed in our experiments. Note that for the case of a shell made of the  $\alpha$ -modification of aluminum oxide, lower values were obtained. This suggests that amorphous alumina with a “Nanowalls” type structure, which is formed under the conditions of the described experiments, is more resistant to thermal action.

Due to the difference in the values of the thermal expansion coefficients of aluminum and aluminum oxide at temperatures close to the melting temperature of the metal, it is possible for the metal to reach the surface of the PSACH through the formed through defects of the oxide shell.



**Fig. 4.** a – images of aluminum droplets extruded onto the POSAP surface; b - a crack in the coating with metal drawn in during cooling; c - metal extruded to the surface through through pores, not merged into a single drop.

Micrographs of various options for the release of aluminum core of the particle on its surface, depending on the conditions under which the particles are heated, are shown in Fig.4. Thus, one can see images of aluminum droplets extruded onto the surface of the POSAP, which are balls, and sometimes even hollow bubbles [22]. Fig. 4b shows a crack into which, when the particle cools, molten metal is drawn in after the particle cools down (end of heat treatment), and Fig. 4c shows the metal extruded to the surface through the through pores, which has not merged into a single drop. Such different results were obtained due to the different conditions under which the PSACH with the hydroxide shell (precursors) was heated in order to transform it into an oxide one. It can be stated that the release of metal to the surface of the oxide shell of the particle is determined by the heating conditions and can be organized in various forms (drops, spreading a thin layer over the surface of the metal) and used to connect individual particles into a connected structure (framework) for further use in the production of composites or highly porous materials.

## 4 Conclusions

Spherical aluminum particles with an oxidized surface (“Core-shell particles”) of various diameters and oxide coating thicknesses seem to be a convenient filler for the production of volume-strengthened metal-oxide and oxide-polymer composites. The use of such particles as composite fillers will facilitate the creation of mathematical models of the structure and structure of specific composite materials and the prediction of their behavior under conditions that simulate real operating conditions, thus facilitating the use of mathematical

modeling methods in the design of composites designed to solve specific engineering problems.

The precursors of these fillers, spherical Al particles with an oxidized surface (“Core-shell particles”), which have the specified parameters: particle diameter, hydroxide shell thickness, and specific surface area, can be successfully produced by controlled liquid-phase oxidation of spherical aluminum particles with water at atmospheric pressure.

Subsequent heating of the precursor particles in a controlled atmosphere makes it possible to transform their hydroxide shell into an oxide shell, thus forming “Core-shell particles” with parameters that satisfy the parameter values (shell thickness, adhesion to the matrix material, particle specific surface area) obtained by mathematical modeling optimal structure of the material, optimal for given specific conditions of use of the composite material strengthened by particles.

The release of the metal of the particle core to the surface of the oxide shell is determined by the heating conditions and can be organized in various forms (droplets, metal spread over the surface) and used to combine individual particles into a connected structure (3D framework) for further use in the production of composites or highly porous materials.

In this paper, an attempt is made to propose a concept of a digital approach to the creation of composite materials dispersion-strengthened with aluminum oxide, the structure, structure and operational properties of which are developed by mathematical modeling methods directly for the specific application of the created material (parts from it). It is proposed to use aluminum "Core-shell particles" as reinforcing fillers, with parameters calculated by mathematical modeling methods: particle diameter, thickness, specific surface area and physicochemical properties of the oxide shell. As precursors of such fillers, it is proposed to use spherical Al particles with a surface oxidized by the method of controlled liquid-phase oxidation of aluminum with water at atmospheric pressure. Such hydroxide-coated POSAP having the required particle diameter, as well as the thickness and specific surface area of the shells, can be easily fabricated and transformed into composite filler particles coated with oxide shells (“Core-shell particles”). Thus, a system can be created that allows designing composites with desired properties.

## 5 Acknowledgment

The work was carried out within the framework of the state task of the Ministry of Science and Higher Education of the Russian Federation and has budget funding. SEM and EDRA measurements were carried out at the Center for Collective Use of the Federal Research Center "Crystallography and Photonics" (project RFMEFI62119X0035).

## References

1. P. Wang, J. Eckert, K. Prashanth, M. WU, I. Kaban, XI L, S. Scudino, A review of particulate-reinforced aluminum matrix composites fabricated by selective laser melting *Trans. Nonferrous Met. Soc. China*, **30(8)**, 2001–2034 (2020) DOI: 10.1016/S1003-6326(20)65357-2
2. S. Lokesh, S. Shankar, K. S. Kuldeep, *Behaviour of Al<sub>2</sub>O<sub>3</sub> in aluminium matrix composites*, An overview E3S Web of Conferences, **309**, 01028 (2021) DOI: 10.1051/e3sconf/202130901028
3. A. A. Gromov, A. P. Il'in, U. Foerter-Barth, et al., Effect of the passivating coating type, particle size, and storage time on oxidation and nitridation of aluminum powders

- Combustion, Explosion, and Shock Waves, **42(2)**, 177–184 (2006)  
DOI:10.1007/S10573-006-0036-4
4. A. Fernandez, J. C. Sanchez-Lopez, A. Caballero, et. all., Characterization of nanophase Al-oxide/Al powders by electron energy-loss spectroscopy, *J. Microscopy*, **191(2)**, 212-220 (1998) DOI: 10.1046/j.1365-2818.1998.00355.x
  5. D. A. Firmansyah, K. Sullivan, K. S. Lee, Y. H. Kim, R. Zahaf, M. R. Zachariah, D. Lee Microstructural behavior of the alumina shell and aluminum core before and after melting of aluminum nanoparticles *Journal of Physical Chemistry C*, **116(1)**, 404-411 (2012) DOI: 10.1021/Jp2095483
  6. L. P. H. Jeurgens, W. G. Sloof, F. D. Tichelaar, E. J. Mittemeijer, Growth kinetics and mechanisms of aluminum-oxide films formed by thermal oxidation of aluminum *Journal of Applied Physics*, **92(3)**, 1649-1656 (2002) DOI: 10.1063/1.1491591
  7. A. Nalivaiko, A. N. Arnautov, S. Zmanovsky, D. Ozherelkov, P. Shurkin, A. Gromov, Al–Al<sub>2</sub>O<sub>3</sub> powder composites obtained by hydrothermal oxidation method: Powders and sintered samples characterization *Journal of Alloys and Compounds*, **825**, 154024 (2020) DOI: 10.1016/j.jallcom.2020.154024
  8. K. Trowell, S. Goroshin, D. Frosta, J. Bergthorsona, Hydrogen production rates of aluminum reacting with varying densities of supercritical water *RSC Adv.*, **12(20)**, 12335-12343 (2022) DOI: 10.1039/D2RA01231F
  9. M. N. Larichev, *Metal Nanopowders: Production, Characterization, and Energetic Applications* (Wiley CH Verlag GmbH & Co. KGaA), 163 (2014) DOI: 10.1002/9783527680696.ch8
  10. N. S. Shaitura, O. O. Laricheva, M. N. Larichev, Studying the mechanism of the low-temperature oxidation of microsized aluminum powder by water *Russian Journal of Physical Chemistry B.*, **13(2)**, 231-244 (2019) DOI: 10.1134/S1990793119020088
  11. N. S. Shaytura, M. N. Laritchev, O. O. Laritcheva, E. I. Shkol'nikov, Study of texture of hydroxides formed by aluminum oxidation with liquid water at various activation techniques *Current Applied Physics*, **10(2)**, 66-68 (2010) DOI: 10.1016/j.cap.2009.11.044
  12. X. X. Sun, J. Liang, J. F. Zhao, et al., Preparation of alumina nanowires, nanorods, and nanowalls by chemical etching *Appl. Phys. A*, **98(2)**, 263-267 (2010) DOI: org/10.1007/s00339-009-5417-6
  13. N. S. Shaitura, V. V. Artemov, M. N. Larichev, Aluminum-aluminum hydroxide core-shell particles heating *Protection of Metals and Physical Chemistry of Surfaces 2* (2023)
  14. J. Deckers, S. Meyers, J. P. Kruth, J. Vleugels, *Direct Selective Laser Sintering, Melting of High Density Alumina Powder Layers at Elevated Temperatures* *Physics Procedia*, **56**, 117-124 (2014) DOI: 10.1016/j.phpro.2014.08.154
  15. Z. Fan, M. Lu, H. Huang, Selective laser melting of alumina: A single track study *Ceramics International*, **44(8)**, 9484-9493 (2018) DOI: 10.1016/j.ceramint.2018.02.166
  16. M. Larichev, I. O. Leipunsky, O. O. Laricheva, P. A. Pshechenkov, New reactive surface coatings for Al metal nanoparticles 36th Annual Conference of ICT & 32nd International Pyrotechnics Seminar (2005)
  17. A. Packer, L. F. Khaw, The coprecipitation of calcium aluminium hydroxide (calcium hydroxoaluminate hydrate) powders from aqueous solution with sodium hydroxide: Precipitate compositions and precipitation mechanisms *Crystal Research and Technology*, **20**, 1325-1331 (1985) DOI: 10.1002/crat.2170201006

18. A. Shrivastava, V. Lambade, P. Chaudhuri, Measurement of Thermal Expansion for Stainless Steel 304, Copper, Aluminium & Brass by Push Rod Dilatometry (2020) DOI: 10.13140/RG.2.2.16279.29604
19. [https://www.researchgate.net/profile/Aroh-Shrivastava/publication/349945037\\_Measurement\\_of\\_Thermal\\_Expansion\\_for\\_Stainless\\_Steel\\_304\\_Copper\\_Aluminium\\_Brass\\_by\\_Push\\_Rod\\_Dilatometry/links/6048663e92851c077f2b23f7/Measurement-of-Thermal-Expansion-for-Stainless-Steel-304-Copper-Aluminium-Brass-by-Push-Rod-Dilatometry.pdf](https://www.researchgate.net/profile/Aroh-Shrivastava/publication/349945037_Measurement_of_Thermal_Expansion_for_Stainless_Steel_304_Copper_Aluminium_Brass_by_Push_Rod_Dilatometry/links/6048663e92851c077f2b23f7/Measurement-of-Thermal-Expansion-for-Stainless-Steel-304-Copper-Aluminium-Brass-by-Push-Rod-Dilatometry.pdf) (Last accessed 21.05.2023)
20. J. Zygmuntowicz, et al., Dilatometric sintering study and characterization of alumina-nickel composites, Processing and Application of Ceramics, **12(2)**, 111-117 (2018) DOI: 10.2298/PAC1802111Z
21. R. Narayan, Encyclopedia of Biomedical Engineering (Elsevier), 572 (2018) DOI: 10.1016/B978-0-12-801238-3.10999-7
22. A. M. Abyzov, Aluminum oxide and alumina ceramics. Properties of Al<sub>2</sub>O<sub>3</sub> and commercial production of dispersed Al<sub>2</sub>O<sub>3</sub> Refractories and industrial ceramics, **60(1)**, 24-32 (2019) DOI: 10.1007/s11148-019-00304-2
23. M. N. Larichev, N. S. Shaitura, V. V. Artemov, Spherical Aluminum Shells (Bubbles) with Nanodimensional Wall Thickness: a New Class of 2D Nanoobjects Technical Physics Letters, **47(4)**, 379-382 (2021) DOI: 10.1134/S1063785021040222
24. D. Klimyuk, M. Serezhkin, A. Plokhikh, Application of 3D printing in sheet metal forming, Materials Today: Proceedings, **38(4)**, 1579-1583 (2021) <https://doi.org/10.1016/j.matpr.2020.08.155>