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Physics of Ceramic Powder Injection Molding Technology

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Abstract

The article examines the currently existing general theoretical approaches to various stages of the process of powder injection molding of ceramics. From the point of view of physical chemistry, ceramics, as a technological object, are suspensions. Therefore, the basis of the consideration is a discussion of mutually related problems of rheology and various forms of interaction of dispersed particles both among themselves and with a continuous dispersion medium. Based on this discussion, the physical and chemical processes occurring at various stages of the

technological process of producing ceramic products by powder molding are considered.

The main object of consideration, the example of which illustrates by the physicochemical approach to the processes occurring in the technological operations, is aluminum oxide (corundum). However, the issues discussed apply to any ceramics. In conclusion, problems are formulated, the solution of which determines the prospects for the development of this area for both powder molding technology and 3D printing.

Keywords: Ceramics, Powder Casting, Suspensions, Rheology, Interparticle Interactions, Plasticity, Elasticity, Slip

Introduction

The technology of powder injection molding has long and traditionally been one of the methods for processing metals and ceramic products of complex shapes ^[1]. Traditionally, casting methods produced ceramic materials based on aluminum oxide, various aluminosilicates, and other oxides. Recently, this method has become quite actively used in the manufacture of products of complex configurations from ceramics based various composition ^[2, 3]. The development of this technological direction is closely related to the sharply growing interest in additive technology, and in particular 3D printing, as an effective method for producing products of complicated configurations. At the same time, the method of ceramics casting is actively expanding its capabilities due to the technology of 3D printing of various thermoplastic or photocurable pastes. More recently, there has been interest in the processing of polymers by casting or injection molding of polymer powders, especially infusible ones or those with extremely high viscosity, for example, ultra-high molecular weight polyethylene (UHMWPE) (see, for example, ^[4]).

When using molding technology, the main difficulty is to prepare a mixture suitable for casting, containing the highest possible concentration of powder and at the same time maintaining the ability to flow. An important issue is the molding conditions, which should ensure the production of a high-quality workpiece without defects, cracks and deformations of the product shape. The basic principles for the preparation of such a mixture and the subsequent molding process were formulated on the basis of empirical data on the stability of highly concentrated aqueous suspensions for slip casting of porcelains, earthenware and aluminas. Generalized ideas about the behavior of these mixtures were brought together into a single picture of the Deryagin-Landau-Farwell-Overbeck (DLFO) theory, which was further used to describe the fundamentals of the physical and mechanical behavior of suspensions. Then, over the next forty years, the theory was developed and included a description of the influence of dispersion interaction in non-aqueous solvents was included ^[3]. For compositions used in injection molding, it is the extended DLVO theory that turns out to be the most relevant, since organic thermoplastic compositions, which are characterized by dispersion interaction at the phase interface, are used as a binder.

Although various options for powder casting of ceramics and polymers have already entered industrial practice, the understanding of this technology remains at the level of rules of thumb and considerations. Therefore, it seems appropriate to try to formulate general principles that play a decisive role in powder technology in relation to non-metallic materials (ceramics and polymers). The general technological scheme for processing feedstock into the final product is shown in Fig 1.

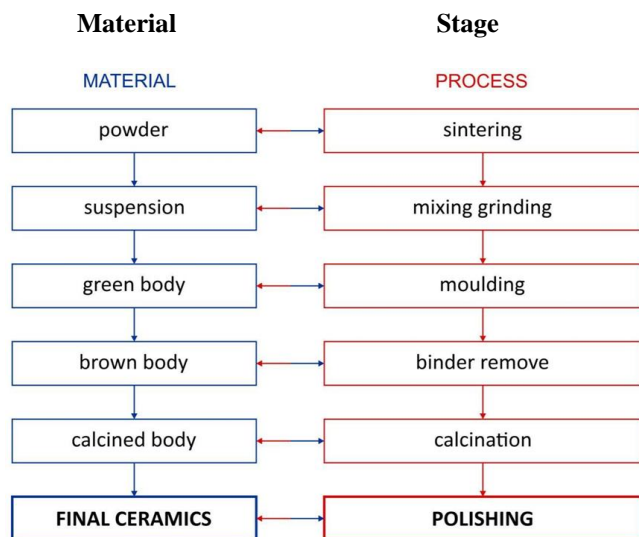


Fig 1: Circuit diagram of the technological process of ceramics molding

The purpose of this work is to examine in detail the theoretical basis for the preparation of the suspension and the process of forming the green body. We only indicate the remaining stages of processing in the general concept of the technology. Obtaining the starting powder is also not the subject of this consideration. These can be synthetic materials, products of processing waste from other industries (so-called feedstock) or powders specially prepared by one or another grinding method.

Theoretical Analysis

Ceramics in the technological process as concentrated suspensions

At the moment, we can roughly distinguish two technologies for molding ceramic products by casting. The first molding technology is based on casting from aqueous suspensions, the second is based on hot casting using a thermoplastic binder. Within the framework of this work, technology based on the use of aqueous suspensions will be considered. The DLVO theory is directly intended to describe physico-chemical phenomena in a highly concentrated suspension of oxide particles in water. From this point of view, the starting materials intended for powder molding are concentrated suspensions of the processed active material in a matrix that plays the role of a binder. Therefore, the features of the first stage of the process are the preparation of a mixture (suspension) of this material in a matrix. As a general rule, it is desirable to have the highest possible concentration of the active material in this suspension and its uniform distribution in the matrix.

The review^[5] examined in detail two issues critical for suspensions. Firstly, how and to what extent is it possible to fill the matrix volume with solid spherical particles.

Secondly, how do the rheological properties of such suspensions change during the transition from fluid dispersions (Newtonian liquid) to an extremely densely filled volume with statistically distributed particles (elastic-plastic solid). However, in that consideration, a fundamental assumption was made - no physico-chemical interactions exist between dispersed particles. In real life, this assumption becomes increasingly unacceptable when moving from dilute to concentrated suspensions. Below we consider the question of how this interaction occurs and how this affects the rheological properties of suspensions. At the same time, we will not touch upon the rheology of the suspension, since this issue is discussed in detail in publications^[6-8].

In the production of ceramics by casting from aqueous suspensions, the main tool for optimizing the water-based casting mass is changing the pH of the medium, which allows for achieving high fluidity of the suspension. This optimization is usually done “to the touch”, which results in the need to optimize the suspension composition for each powder separately. Therefore, the selected pH and composition of the mixture are suitable only for one powder from a particular manufacturer; for another it is necessary to select the conditions again. In the framework of this work, we offer a generalized consideration of this problem, based on an analysis of the physical and chemical phenomena associated with optimizing the composition of the composition for the preparation of casting mixtures from various powders. It should be recognized that such a situation is not typical for advanced technology companies in the ceramic production industry. Indeed, ideas about the relationship between the composition, structure and properties of oxide suspensions, and the requirements for controlling the granulometric composition of suspensions, the charge of particles and the influence of surfactants on the structure of suspensions is used as mandatory in the preparation of compositions^[9].

The basic theory explaining the interaction of solid particles in a suspension is the well-known Deryagin-Landau-Farwell-Overbeck (DLFO) model^[10, 11] According to this model, the particle surface is described as an idealized packing of ions, each of which interacts with solvent molecules located in a Brownian movement. In relation to the problem under consideration, the concept of the Stern layer is used, which is considered as a stationary, dense (with a density higher than the density of the solvent) layer of charged particles, described as a flat capacitor. According to this model, it was assumed that there is an additional mechanism affecting the mobility of particles and the conductivity of the suspension. This means that the electrokinetic behavior of a particle depends not only on the total charge and surface area of the particle, but also on the number and mobility of adsorbed electrolyte ions on the surface of the particle^[12].

For the powder molding process, it is important to understand the physics of how this layer evolves, determining the transition from the fluid state of a concentrated suspension to the formation of a final dense product. From the point of view of material rheology, this is due to ideas about the limit of filling a suspension, transport phenomena in concentrated suspensions and interaction through Stern layers in filled suspensions^[12]. During powder molding, the aqueous suspension is in two states, the first state, fluid, allows one to fill the injection mold, the second

state, elastic and elastic-plastic, allows for holding the shape [13]. The transition from the first state to the second occurs due to the fact that part of the solvent is removed from the suspension, the concentration of particles increases, the interparticle interaction changes, and a strong but plastic mass is formed. The liquid phase is removed due to the capillary effect, which consists in the fact that the gypsum mold literally draws water from the suspension layer immediately adjacent to the wall of the mold [14]. The plasticity of the mass is determined by the nature of the interaction of particles through the Stern layers, since the diffusion layer of such a plastic mass turns out to be common.

The transition of a suspension from a fluid to a plastic state can be represented as shown in Fig 2. Therefore, the structure of the diffusion layer has a significant influence on the mobility of the suspension

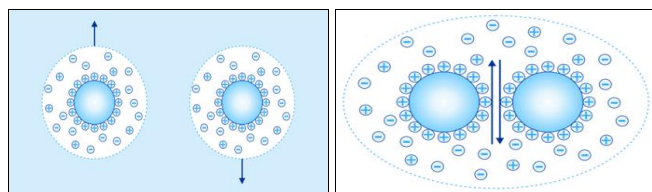


Fig 2: Fluid (particles in a liquid on the left) and plastic (interacting particles on the right) state of the suspension – transition happens due to increasing concentration of solid particles

The interaction between particles in a relatively dilute suspension comes down to the fact that in a fluid state the particles interact and repel each other through elastic diffusion layers in an excess of a continuous liquid phase. During plastic deformation, particles in a concentrated suspension interact through Stern layers, and the diffusion layer, which is characterized by an increased concentration of counterions, forms a single space. And if in the first case, counterions create the same charge of the diffusion layers of interacting particles, which do not allow the particles to form a coherent structure, then in the second case, it is the interaction between the counterions in the generalized diffusion layer and the surface charges of all particles that binds the particles into a common structure and the structure is all the more elastic -plastic, the higher the particle surface charge [15].

The composition and structure of the surface layer of the particle plays a huge role in both the fluidity and plasticity of the suspension. This role is so great that powders of the same composition, but from different manufacturers using different technologies for producing powders, can behave differently.

The most striking example is the difference in behavior between powders of ground electrofused corundum and alumina obtained by the Bauer method [16]. Both powders are aluminum oxide; in fact, the behavior of the powders in suspension is completely different. Suspensions prepared in the same way and having similar pH values have different viscosity and viscoelastic properties. Most often this is due to the concentration of impurities on the surface of particles, such as silicon and sodium, which change the structure of the Stern layer. In this regard, when producing ceramic products from these powders, it becomes necessary to treat the surface of the particles using some uniform method. That is why it is necessary to pay attention to the influence of the mobility of the Stern layer on the behavior of the

suspension and propose methods for analyzing and monitoring the composition and structure of the Stern layer. In the basic version, the Stern layer is formed from polar solvent molecules and ions that have an opposite charge relative to the surface charge of the particle itself. In classical theory, the Stern layer is considered as a stationary, dense (with a density higher than the density of the solvent) layer, described as a flat capacitor.

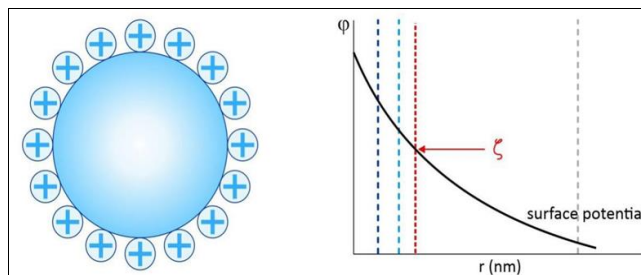


Fig 3: Stern layer. On the left positive ions are adsorbed on the surface of the particle. On the right the dependence of the electrochemical potential on the distance from the particle surface is shown. The blue dotted line is the Stern potential, the red dotted line is the electrokinetic potential (ζ), the gray dotted line is the potential of the surface of the diffusion layer.

However, more recent study indicates the presence of layer mobility. Thus, it is argued that there is a mechanism that affects the mobility of particles and the conductivity of the suspension, which helps explain the change in liquid viscosity and dielectric constant near the phase interface [12]. Transport within the Stern layer occurs due to diffusion due to the ion concentration gradient and conductivity in the layer in response to the tangential electric field. Therefore, the electrokinetic behavior of a particle depends not only on the total charge and surface of the particle, but also on the amount and mobility of adsorbed electrolyte ions. It is also necessary to take into account the individual contribution of several ions. In the classical theory, the Stern adsorption isotherm is described by the following expression

$$\theta_i = \frac{c_{0i} K_{Hi} \exp\left[-\frac{\phi_i + z_i e \phi_d}{k_B T}\right]}{1 + \sum_i c_{0i} \exp\left[-\frac{\phi_i + z_i e \phi_d}{k_B T}\right]} \quad (1)$$

Where ϕ_d is the potential of interaction of the ion in the plane of closest approach to the surface of the particle, ϕ_i is the energy of non-electrostatic interaction of the ion with the surface, K_{Hi} is the reduced Henry constant.

In the proposed model, the ion concentrations in the Stern layer are in local equilibrium with the diffuse double layer, so the polarization of the diffuse layer affects the Stern layer and, conversely, changes in the Stern layer affect the polarization of the diffusion layer [12]. The interaction in a fluid suspension consists of Born repulsion and van der Waals attraction. It was noted that in suspensions of large particles, the DLVO theory does not fully describe the behavior of particles if polyvalent microions are present in the system [17]. As for nanoparticles, the cited work pointed to the role of charge distribution and polarizability, which enhanced the influence of attraction, as well as other possible reasons for deviations from the predictions of the DLVO theory.

To assess the interaction of solid particles in suspensions, interaction potentials of various types are used. So, when

analyzing the behavior of nanoparticles in the range of the Peclet numbers Pe from 0.1 to 100, i.e. in situations where there was an overlap of Brownian motion and hydrodynamic interaction, the well-known Yukawa potential was used [18]:

$$W \propto \frac{e^{-\kappa r}}{r} \quad (2)$$

The Peclet number was expressed as

$$Pe = \frac{6\pi\eta\dot{\gamma}a^3}{k_B T} \quad (3)$$

where η is the viscosity of a continuous medium (matrix), $\dot{\gamma}$ is the shear rate, a is the radius of particles, k_B is Boltzmann's constant and T is the absolute temperature.

Thus, an assessment was made of the role of repulsive forces in Brownian filler particles. In a more general case, the standard Lenard-Jones potential was used to represent long-range attractive forces. For larger particles, which are usually used in powder casting technology, the particle interaction potential is described based on the idea that large particles are considered as polyions, and charged associates of solvent molecules are represented as microions [19]. The electrical properties of a fluid suspension are characterized by ζ -potential, which is proportional to the electrokinetic potential of particle interaction. An example of the dependence of the electrokinetic potential on the pH of the medium for pure aluminum oxide (often used in powder casting of ceramic products) is shown in Fig 4 [14]. For powder casting technology, measuring the electrokinetic potential allows one to determine the limits of suspension stability. Stability means the absence of segregation of suspension components, i.e. separation into thicker and more liquid parts. It is also important to define the so-called point of zero surface charge, which corresponds to the transition of the electrokinetic charge through zero, at which the suspension abruptly and completely precipitates, and all the liquid is almost completely separated from the powder. Thus, the residual concentration for aerosil in water at an electrokinetic potential close to zero is 0.1 vol.% [20]. Such a suspension is subsequently very difficult to revive and homogenize again. The pH range of this state in Fig 4 is 8-10. For concentrated, filled suspensions, one can observe a stable state at a high (in absolute value) electrokinetic potential, and irreversible separation at a potential tending to zero.

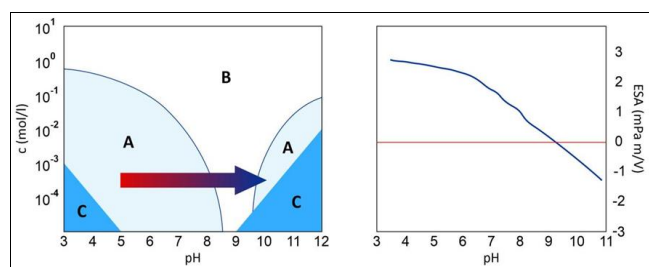


Fig 4: Diagram of stability of an aluminum oxide suspension (left) where A is the region of a stable suspension, B is the region of sedimentation of the suspension, C is the region with an unrealizable composition and the dependence of the electrokinetic potential on pH (right).

When working with thick pastes, one can judge their stability and homogeneity based on rotational rheometry methods, since there is a correlation between the elastic modulus and the electrokinetic potential. Models describing this correlation were proposed in [21-24]. According to model concepts, the elastic modulus decreases linearly with increasing ζ^2/λ_D where λ_D is the Debye length – the distance over which the particle charge field extends. In a suspension, this distance depends on the degree of shielding of the particle surface by the charge of the Stern layer. Both ζ and λ_D vary depending on pH and electrolyte concentration, which leads to a non-monotonic change in elastic (storage) modulus G' as shown in Fig 5a. Fig 5b presents the maximum value of the interaction potential as a function of the concentration of ions Ca^{2+} .

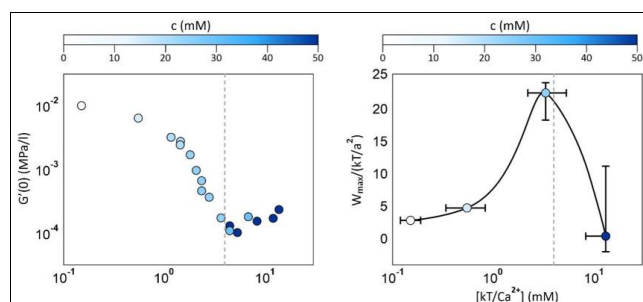


Fig 5: (a) Initial value of the storage modulus G' as a function of initial calcium ion concentration $[Ca^{2+}]$. Different data points correspond to different values of concentration shown by the color scale. (b) Parameter $W_{max}/(k_B T = a^2)$ shown as a function of $[Ca^{2+}]$.

The points correspond to actual measurements ζ , while the continuous line drawn by interpolating (according [21], with permission)

The models discussed above are valid only for systems with weak particle repulsion. To go beyond the linear regime of small electrostatic repulsion, one should take into account the dependence of the ζ -potential of suspensions on the concentration of electrolyte ions and its ionic strength. The influence of these factors on the interaction potential is opposite. The former enhances electrostatic repulsion, while the latter enhances electrostatic shielding. To assess the change in the nature of the interaction, the value of the maximum interaction potential W_{max} is calculated depending on the concentration of electrolyte ions, as shown in Fig 5b. The positions of the minimum value of the elastic modulus G' and the maximum value W_{max} coincide at the concentration of electrolyte ions ≈ 4 mM. Below this value, the role of the ζ -potential dominates, and the repulsion increases with the concentration of calcium ions. Above this threshold, the shielding of the surface charge by the Debye layer predominates and causes the repulsion to decrease with the electrolyte ion concentration.

Physico-chemical Processes at the Main Technological Stages

Forming the workpiece:

In the production of ceramic articles, it is customary to call a fluid suspension of ceramic powder particles a slip. Preparation of slip to produce ceramics based on pure aluminum oxide is a process of mixing and dispersing the prepared powder of ground electrofused corundum in water. In this case, it is often recommended to use corundum of

two fractions $D[4.3] = 5-10 \mu\text{m}$ in an amount of 80-90 wt.% and $D[4.3] = 0.7-1.0 \mu\text{m}$ in an amount of 10-20 wt. % [25]. The size of the fractions can vary, but a size ratio of 1:10 with a fraction mass ratio of 10% fine fraction to 90% coarse fraction is considered preferable due to the fact that such the powder is more densely packed during molding [25]. The powder must first be calcined to a constant mass. This requirement is fundamental. It is due to the fact that the powder actively adsorbs water from the air onto the surface of the particles. As a result, shell of water molecules is formed around the particles. This shell partially screens the surface charge of the particles, resulting in a dispersion with an already formed Stern layer and a diffusion layer consisting of condensed moisture. For some time, ions migrate from the liquid to the Stern layer according to the mechanism described above, which leads to a change in the properties of the suspension and, most often, to precipitation of the suspension.

In the case when pre-calcined powder is dispersed, a Stern layer and a diffusion layer are formed containing polymer binder molecules and a fixed concentration of electrolyte ions, which leads to a stable suspension that does not change over time. The amount of water in the slip varies from 40 to 50 vol. %. This allows for preparing a composition with the required fluidity. The latter is achieved due to the fact that a polymer polyion is added to the dispersion, for example ammonium polyacrylate, which at the stage of suspension formation acts as a source of positively charged ammonium ions for the diffusion layer. They are counterions to the negatively charged surface of the aluminum oxide particle. These counterions form a positively charged diffusion layer, which in this case has a high charge and small thickness, which ensures the formation of hard and compact isolated spheres inside which there are aluminum oxide particles (Fig 6).

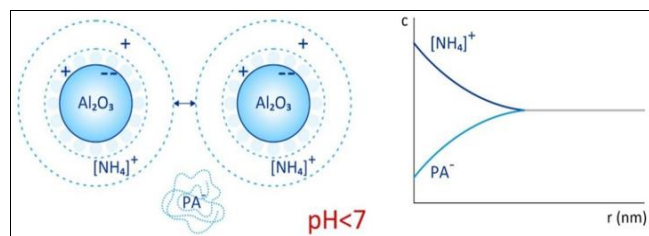


Fig 6: Formation of aluminum oxide spheres in a fluid suspension (left); distribution of polyelectrolyte ions and changes in ion concentration with distance from the surface of the Stern layer into the medium (right.)

The liquid slip is poured into a gypsum mold, which, through the mechanism of capillary pressure, draws water from the surface layer of the suspension. As a result, a dense plastic layer of ceramic powder is formed along the plaster mold. The excess slip mass is poured out and a hollow blank with a wall thickness of 0.5 to 1.5 mm remains in the mold, which, after drying, is easily separated from the gypsum and has sufficient strength so that it can be transferred to a drying cabinet and then to a kiln. The description of the

process of removing liquid from the surface layer of the suspension should be divided into two stages. Fig 7.

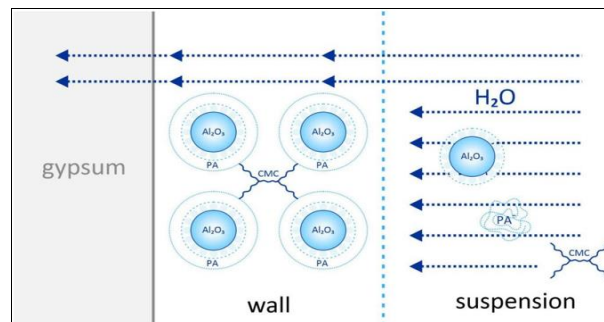


Fig 7: Flow of a liquid phase through a layer of suspension particles

Upon contact with the gypsum material, the suspension on the surface quickly hardens, and then only the wall thickness increases. The curing of the suspension is well illustrated in Fig 4 shows a diagram of the stability of a suspension of aluminum oxide in water. Due to the removal of water, the composition of the suspension changes and it transitions from a viscous-flowing state to an elastic-plastic one, which already turns out to be quite resistant to external deformations. Further, under the action of capillary forces, the liquid flow first passes through a dense and solid layer of suspension, and then diffuses through the porous body of the gypsum mold. This means that a difference in hydrostatic pressure occurs between the casting and the mold and separation of components occurs at the boundary between the suspension layer and the mold.

The influence of suspension permeability and mold porosity on the fluid flow rate through them is described in [25, 26]. The main interest here is how the physical and mechanical properties of the suspension will change. It should be emphasized that this is a transition from one stable state to another stable state of suspension. With a sharp decrease in the concentration of the liquid phase, particles settle. As a result, the thickness of the diffusion layer should increase as the space charge of the layer decreases. This is due to the fact that with a slightly changing pH of the environment, the proportion of particles increases and the energy of attraction of particles begins to play a larger role than repulsion because additionally, the compacting force of capillary pressure appears. However, this is not enough to form a plastic and durable wall. The action of capillary forces of particle compaction leads to the formation of a brittle, dense wall that will crumble in layers. The plasticity of the entire composition is imparted by the introduced polyanions, specifically polyacrylates, which are present in the Stern layer, adsorbed as polymer molecules and in the liquid phase. When the liquid phase is removed, these polyanions remain and accumulate in suspension. In addition, additional polymers are introduced into the slip, acting as a binder. In the case of aluminum oxide, for example, carboxymethylcellulose or carboxyethylcellulose can be considered as a binder (Fig 8).

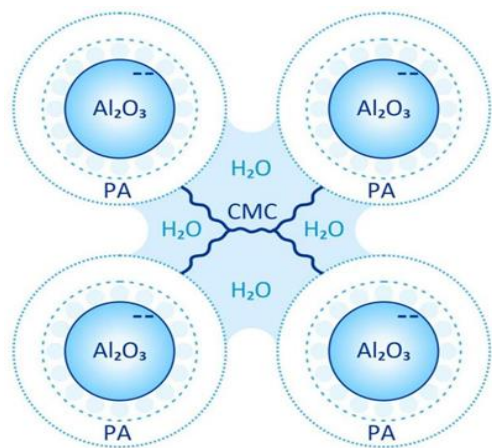


Fig 8: Structure of the cured suspension

These are branched polymer molecules that form a three-dimensional network with polyacrylate macromolecules adsorbed on the surface of aluminum oxide particles. The binder concentration usually does not exceed 1 vol.%, but when the liquid is removed, the volume fraction of the binder approximately doubles. This means that the initially small amount of binder may be excessive for the molded preform. In addition, the binder molecules retain some of the water in their free volume, so that an excess of binder leads to a decrease in the packing density of the particles, and hence the density of the entire molded mass. It should be separately noted that the particles are held together not due to the formation of chemical bonds between the binder molecules and the surface of the particles, but through capillary contraction of the particles by the liquid, which in turn is held in volume as a result of interaction with a branched polysaccharide molecule. Thus, excess binder is detrimental to the molding of the product, both because excess water will be retained and because it will lead to increased shrinkage of the product during drying and firing. To control the density of molded workpieces, methods similar to determining water absorption are used, based on the method of kerosene absorption of newly molded ceramics, which makes it possible to determine what the density of the molded workpiece is.

Thus, the behavior of a suspension based on pure aluminum oxide with a corundum structure, when there is no lyotropic adsorption of electrolyte ions, the elasticity of the formed mass is determined by the elastic interaction of the binder molecules between the particles and the repulsive forces of the Stern layers. The plasticity is determined by the intermolecular interaction of polyacrylate adsorbed on the surface of the particles and capillary forces contraction by the liquid remaining between the particles. Plasticity should be directly proportional to the concentration of water adsorbed by the binder and polyanion - polyacrylate in the concentration range up to 3 vol. % and is proportional to the surface area of the aluminum oxide particles.

Sintering and obtaining the final product:

This work does not discuss the mechanisms of particle sintering to obtain a complete ceramic product. This is due to the fact that issues related to sintering represent a separate area that requires independent, full consideration. However, the nature of the change in particle packing during green body molding has a direct impact on the quality of the resulting product, so the main problems associated with

sintering cannot be circumvented. During sintering, compaction occurs, the so-called shrinkage of the product, which leads to the appearance of internal stresses in the structure of the ceramic product and its deformation. When manufacturing products of complex shape, it turns out that it is necessary to select molding conditions in such a way that deformation during shrinkage occurs evenly, and cracks and other defects caused by internal stresses do not appear in the product.

The solution of the corresponding problems belongs to the field of solid state physics and has no relation to the behavior of disperse systems. However, the influence on the processes of deformation during sintering is possibly due, first of all, to varying the structure of the molded green body and, secondly, the drying conditions of the green body, removal of the binder and the choice of sintering modes. The structure of the green body is influenced by the ratio of particle sizes of powder fractions and the packaging of these particles, which is determined by the amount of temporary technological binder (this is the same case when its excess worsens the quality of the packaging due to a decrease in its density) and its molecular structure, which retains a small amount of moisture and determines the magnitude of the capillary pressure forces that tighten and additionally compact the particles of the green body during its molding and drying [14, 25].

Product examples:

The technology for producing liquid water slip described above is actively used in the manufacture of a number of ceramic products for various purposes. Earthenware, dishes and sanitary ware are made from aluminosilicates using the powder casting method. It should be noted, however, that for such products the quality of molding of the original green body is not subject to serious requirements, since most of the deformations and inhomogeneities that arise during sintering are "healed" by the viscous flow of free silicon oxide, the so-called. glass phases at high temperatures. The presence of the glass phase makes it possible to eliminate a number of flaws and defects in the molding of the product and significantly simplify the process of quality control in ceramic production. When molding porcelains, i.e. products with a low concentration of silicon oxide, the quality issue is resolved by increasing the sintering temperature and the appearance of an intermediate stage of glazing, the so-called. glaze and underglaze, which allows not only to create a waterproof layer, but also to artistically design the product. When it comes to high-density refractory corundum ceramics based on aluminum oxide for technical purposes, one no longer has to rely on the fact that molding flaws will be eliminated by the flow of the glass phase during sintering. Therefore, in this case, it turns out that it is necessary to work out the conditions for molding the green body much more carefully and optimize the composition and structure of the slip for molding. In this regard, the production of vacuum-dense high-temperature corundum ceramics turns out to be a much more complex technology than the production of earthenware or porcelain and requires more complex techniques, higher firing temperatures and higher quality kilns. To improve the quality of cast corundum ceramics, additives based on magnesium oxide and periclase are also used, which during sintering interacts with aluminum oxide to form spinel $MgAl_2O_4$. This reaction accelerates and simplifies diffusion over the particle

surface and facilitates the process of exit and collapse of pores in the ceramic during sintering. This complicates the slip manufacturing process because... requires stabilization of particles of different composition, therefore, for the production of slip, additives based on magnesium salts or magnesium hydroxide are used, which also affects the stability of the suspension, which should be the object of special attention of the production technologist.

The most complex industrial ceramics made from aqueous slip are ceramics based on yttrium or calcium stabilized zirconium oxide. Here it is necessary to prepare suspensions taking into account the presence of 10–15% doping agent, which can be introduced either from a salt solution or in the form of an additional suspension of oxide or hydroxide [14, 25].

Conclusion

This work examines modern theoretical ideas about the structure, physicochemical and rheological properties of suspensions used in the molding of industrial ceramics for engineering and biotechnological applications. An attempt has been made to generalize information about the relationship between the structure of the suspension and its physical and mechanical properties, and how these properties change when the composition and structure of the suspension changes. A critical analysis of ideas about technological stages in the molding of cast ceramics was carried out, and the role of the components of liquid aqueous slip in the formation of a fluid suspension and a plastic green body was investigated. Based on the discussion of modern approaches to the theoretical foundations of the technological process of powder casting of ceramic products, it seems important to understand what issues remain unclear in the area under consideration and require further in-depth theoretical and experimental research. These questions can be formulated as follows:

How to experimentally separate the elastic and plastic components in highly filled suspensions?

How do the elastic and plastic components of deformation depend on the total surface area of particles in suspensions?

How does the ratio of elasticity and plasticity change when going from aqueous media to polar non-aqueous solvents and when going to non-polar media?

The answer to these questions will allow us to formulate general approaches to the design of highly filled suspensions intended for molding using powder casting and/or 3D printing. This will also contribute to the creation of sound methods for monitoring the quality of suspensions both in the process of developing new products and in the process of their on-line production.

Table 1: Notations

a	particle radius, nm;
K_{Hi}	reduced Henry constant
k_B	Boltzmann constant, J/K;
$Pé$	Péclet number
T	absolute temperature, K;
W	Yukawa potential, 1/m;
ζ	zeta potential, V;
$\dot{\gamma}$	shear rate, s^{-1} ;
λ_D	Debye length, nm;
η	viscosity of continuous medium, Pas
ϕ_i	energy of non-electrostatic interaction of the ion with the surface, J;
ϕ_d	interaction potential of an ion in the plane of closest approach to the particle surface, V.

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