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# RHEOTECHNOLOGICAL PROPERTIES OF MIXED SUSPENSIONS IN THE $SiO_2 - Al_2O_3$ SYSTEM AND SOME PROPERTIES OF MATERIALS BASED ON THEM. 1. MOLTEN QUARTZ – ALUMINA SYSTEM

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The rheotechnological properties of mixed suspensions in the $SiO_2 - Al_2O_3$ system obtained by the method of mixing of individual suspensions of molten quartz and alumina are described. Some properties of the materials after their heat treatment at 1000 – 1300°C are investigated. The ranges of compositions (30 – 40% $Al_2O_3$, 60 – 70% $SiO_2$) in which the parameters of thermal expansion of the materials are 2 – 3 times lower than those calculated under the condition of additivity are determined. The obtained materials possess an elevated mechanical strength.

Refractory materials of the alumosilicate type are widely found in the form of shaped (fired) [1 – 4] and unshaped refractory concretes (castables) [5]. The aim of the present study consisted of developing a material in the $SiO_2 - Al_2O_3$ system that would combine the advantages of refractories based on molten quartz (high heat resistance, low thermal conductivity) and corundum refractories (elevated chemical stability in casting of high-manganese steels).

**Original materials and suspensions.** The original materials were fused quartz with 99.2% $SiO_2$ and alumina of grade GEF with an acicular-flake structure after calcination at 1300°C. The latter included 99.4% $Al_2O_3$, 0.03% $SiO_2$ and 0.3% $Na_2O$; the content of $\alpha$-$Al_2O_3$ was 92%, the specific surface $S_{sp}$ of the particles of $\alpha$-$Al_2O_3$ was 1 $m^2/g$. Wet milling was performed in a ball mill with uralite balls with the addition of 10% high-dispersity reactive alumina of grade CZ370C (Alcoa, Europe). The latter possessed 99.8% $Al_2O_3$, 0.06% $Na_2O$, $S_{sp} = 2.7$ $m^2/g$, and a bimodal distribution ($d_{mean} = 0.8$ and 0.6 μm). Suspensions of alumina and fused quartz were prepared separately by wet milling in a ball porcelain mill with stage loading of the material and subsequent stabilization by means of hydration mechanical mixing. The mixtures were prepared in requisite proportions from the obtained suspensions. The optimum process and rheological parameters were chosen in accordance with the recommendations given in [5].

The initial suspensions of fuzed quartz and alumina had pH = 6.5 and 9.5 and a density of $\rho = 1.92$ and 2.44 $g/cm^3$, which corresponded to a volume concentration of $C_V = 0.77$ and 0.55 at a moisture content of $W = 12$ and 18%, respectively. The parameter of critical concentration $C_{V_{cr}}$ was 0.88 for the suspension of molten quartz and 0.64 for the alumina suspension. The porosity of the initial castings was 11% for fused quartz and 29% for alumina.

The substantial difference in the characteristics of the original highly concentrated ceramic binding suspensions (HCBS) with respect to the parameters $C_V$ and $C_{V_{cr}}$ is primarily due to the chemical nature of particles of the solid phase. In accordance with the principles of the classification used [6], the HCBS of $SiO_2$ are acid (the value of the ion potential IP is equal to about 100) and the HCBS of $Al_2O_3$ are amphoteric (IP = 52). With allowance for the chosen ranges of IP parameters in the classification of HCBS [6], mixed suspensions with up to 70% $SiO_2$ are acid (IP = 85 – 100), those with 20 – 70% $SiO_2$ are acid-amphoteric (IP = 60 – 85), and those with less than 20% $SiO_2$ are amphoteric. In correspondence with the mentioned ranges of IP calculated under the assumption of additivity, the properties of the mixed suspensions are determined substantially by the proportion of the components.

We determined the grain composition of the suspensions' sedimentation. The integral curves of the grain distribution of the solid phase of the original suspensions are presented in Fig. 1. Comparing the curves, we will see the difference in

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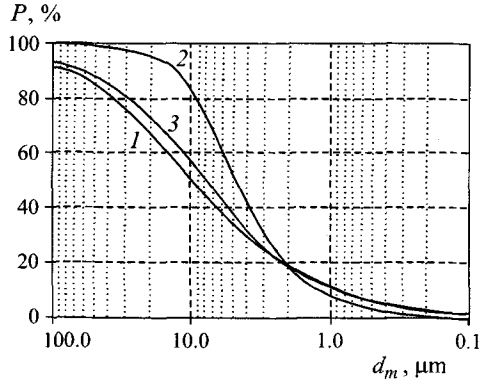


**Fig. 1.** Integral curves of the grain distribution of the solid phase in the original suspensions: *1* ) alumina; *2* ) molten quartz; *3* ) a mixture containing 80% HCBS $SiO_2$ and 20% HCBS $Al_2O_3$.

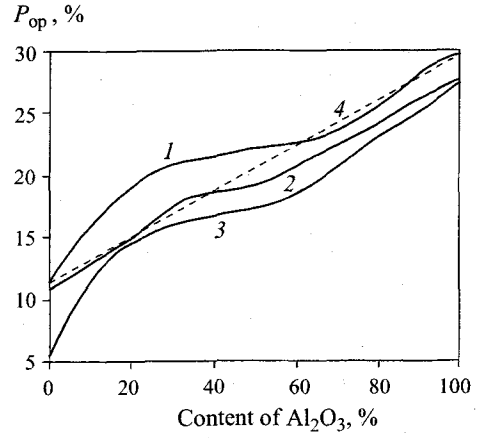


**Fig. 2.** Effect of the composition of mixed suspensions on the open porosity $P_{op}$ of a casting after drying (*1* ), after a heat treatment at 1000 (*2* ) and 1200°C (*3* ), and calculated in accordance with the principle of additivity (*4* ).

the dispersities and polydispersities of the original suspensions. The $SiO_2$ suspension has a higher polydispersity ($K_p$), determined as the $K_{80}/K_{20}$ proportion [5]. For the $SiO_2$ suspension, $K_p = 15$, and for the alumina suspension $K_p = 3.7$. The content of a fraction finer than 2 μm in both suspensions is about the same, but in the HCBS of fused glass the content of particles coarser than 10 μm is substantially higher (by a factor of 1.6), which determines their elevated polydispersity. The difference between curves *1* and *2* (see Fig. 1) is maximum in the range of particles 7 – 30 μm in diameter. The median diameter $d_m$ differs by a factor of 2 (10 and 5 μm for the suspensions of fused quartz and alumina, respectively).

The coefficient of polydispersity, the nature (chemical composition) of the solid phase, and the total degree of dispersity considerably affect the packing density of the solid-phase particles in the process of phase formation. It follows from Fig. 2 (curve *1* ) that the porosity of the castings obtained from the quartz glass suspension after drying is 11% and that of the castings from the alumina suspension is 29%.

**Effect of the content of components on the rheological properties.** The rheological properties of the suspensions were studied with the help of a flow viscometer (the conventional viscosity) and with the help of a "Reotest" rotation viscometer based on the principle $\dot{\varepsilon} = \text{const}$. Analyzing the rheological curves in Fig. 3, we will see that the flow of the original suspensions is fundamentally different. For example, the suspension of fused quartz is characterized by a well-manifested dilatancy, and the alumina suspension has a thixotropic flow. The mixed suspensions have an intermediate thixotropic-dilatant flow. The dilatancy decreases with increase in the content of alumina. The change in the nature of the flow in mixed suspensions with up to 50% $Al_2O_3$ is caused by the formation of mixed acid-amphoteric HCBS.

The increase in the content of $Al_2O_3$ causes a further decrease in $C_V$ and the thixotropy. The variation of the viscosity of mixed suspensions in the $SiO_2 - Al_2O_3$ system is nonuniform and stepped. It is preserved at both low and high values

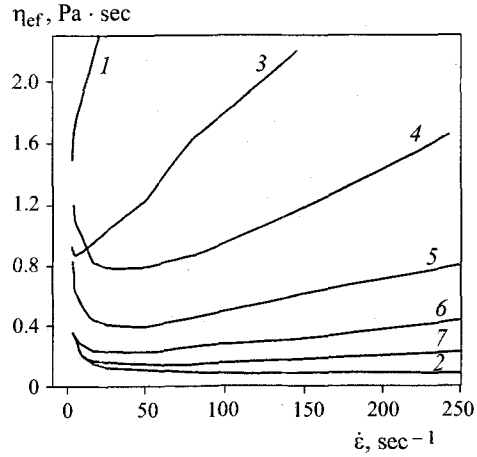


**Fig. 3.** Dependence of the effective viscosity $\eta_{ef}$ on the shear rate $\dot{\varepsilon}$ of the initial suspension of molten quartz with $C_V = 0.77$ (*1* ), of an alumina suspension with $C_V = 0.57$ (*2* ), and of mixed suspensions (*3* – *7* ) with a content of $Al_2O_3$ equal to 8.7 (*3* ), 16.9 (*4* ), 25.5 (*5* ), 34.3 (*6* ), and 46.3% (*7* ).

of the shear rate gradient. The viscosity decreases markedly when the alumina content increases to 30% and is almost invariable in the range of 40 – 90% content of alumina. At $\dot{\varepsilon} = 2\ sec^{-1}$, the viscosity at the extreme points differs by a factor of 6 (curve *1* in Fig. 4), whereas at $\dot{\varepsilon} = 80\ sec^{-1}$ it differs by a factor of 16 (curve *2* ). This is caused by the strong dilatancy of the HCBS of quartz glass. The obtained data agree well with those presented earlier in [5]. The parameter of conventional viscosity is maximum in the initial HCBS of $SiO_2$. The dependence described by curve *3* in Fig. 4 behaves similarly to curve *2*.

**Interdependence of the properties of suspensions and castings based on them.** The volume concentration of mixed suspensions $C_V$ is a function of the content of the components and determines their rheological properties to-

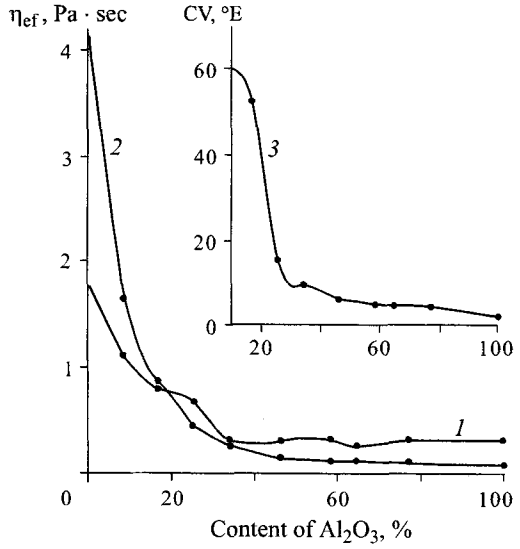


**Fig. 4.** Dependences of the effective viscosity $\eta_{ef}$ that corresponds to a shear rate of $\dot{\varepsilon} = 2$ sec$^{-1}$ (*1*) and 80 sec$^{-1}$ (*2*) and the conventional viscosity CV (*3*) on the proportion of components in mixed suspensions.

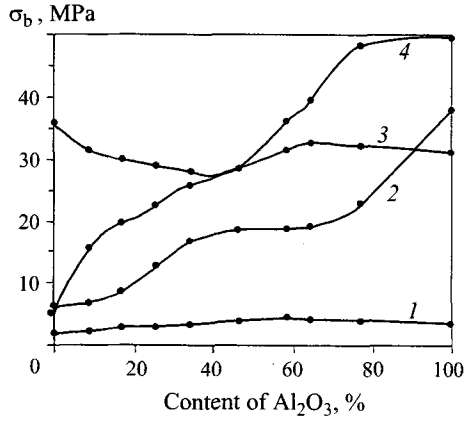


**Fig. 5.** Effect of the composition of mixed suspensions on the ultimate bending strength $\sigma_b$ of specimens after drying (*1*) and heat treatment at 1000 (*2*), 1100 (*3*), and 1200°C (*4*).

gether with the nature and the dispersity of the particles of the solid phase, as well as the porosity and the strength of the semiproducts based on the suspensions.

Comparing the rheological characteristics of suspensions and castings based on them, we established a clear dependence between the conventional viscosity of the mixtures, their $C_V$, and the porosity of castings from the corresponding suspensions (see Fig. 2). The increase in the porosity is connected with the elevated content of $Al_2O_3$ and the decrease in the parameter $K_p$ of the solid phase of the suspensions.

It follows from Fig. 2 that the variation of the porosity of the castings is not additive (curve *4*) but has a stepped nature preserved under all regimes of heat treatment. Comparing the actual values of $P_{op}$ with the additive ones, we will see that

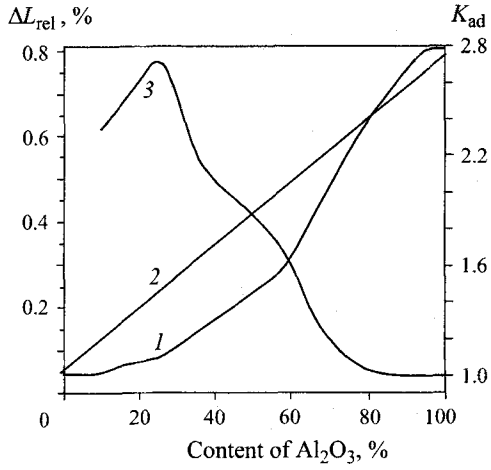


**Fig. 6.** Effect of the composition of mixed suspensions on the relative linear elongation $\Delta L_{rel}$ [*1*) experimental; *2*) calculated] and the coefficient of additivity $K_{ad}$ (*3*).

the actual porosity in the system with less than 50% $Al_2O_3$ exceeds the calculated one and in the system with more than 50% $Al_2O_3$ is below the calculated one. A maximum deviation of the porosity by 3 – 4% occurs at 20% $Al_2O_3$. In the region with 10 – 40% $Al_2O_3$, the deviation of the porosity parameter is higher than in the region with 60 – 90% $Al_2O_3$. This is due to the heterocoagulation of particles of the solid phase and the formation of aggregates that hamper the approach of the particles upon the removal of layers between them. A similar effect of heterocoagulation has been observed earlier in [7]. In the given case, the porosity changes markedly upon the introduction of 25 – 30% of the second component, and there exists a range of equilibrium compositions in the middle part of the plot. A relatively even region (30 – 70% $Al_2O_3$) indicates that a kind of equilibrium state appears in the system, where the variation of the content of the components does not change the porosity.

**Effect of heat treatment on the properties of materials.** Having in mind that the studied materials should be used at a high temperature, we studied the effect of heat treatment on some of their properties. We investigated the effect of the roasting temperature up to 1200°C on the properties of the heat-treated material. It follows from Figs. 2 and 5 that the proportion of components of the studied materials affects their porosity and strength after roasting at various temperatures. With increase in the firing temperature to 1200°C the open porosity of the materials decreases by 5% on the average, and in the region with an elevated content of $Al_2O_3$ it decreases by 1 – 2%, which indicates that fused quartz sinters more actively. Even a low amount of $Al_2O_3$ increases the ultimate bending strength substantially, despite the elevation of the porosity of the material (see Fig. 5). For example, $\sigma_b$ of the material with 34% $Al_2O_3$ is 3.5 MPa after drying, and 16 and 26 MPa after firing at 1000 and 1100°C, respectively. This is accompanied by active mullite formation from the fine disperse $SiO_2$ component and reactive alumina. The

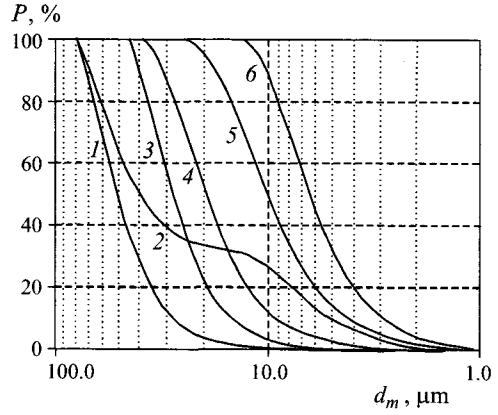


**Fig. 7.** Grain distribution of alumina suspensions in the initial state (*1*, *2*) and after milling for 8 (*3*), 50 (*4*), 85 (*5*), and 100 h (*6*).

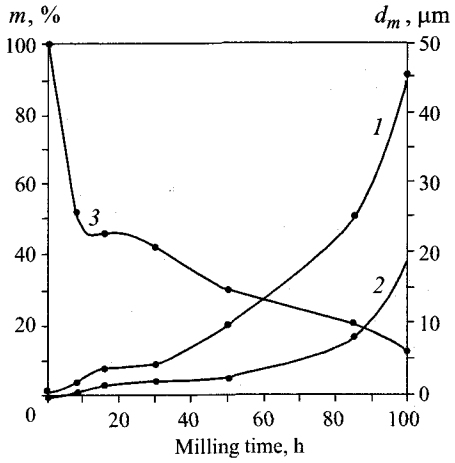


**Fig. 8.** Variation of the content $m$ of particles 10 (*1*) and 5 μm (*2*) in diameter and $d_m$ (*3*) during milling of a suspension.

growth in strength continues with the growth in the content of $Al_2O_3$, despite the elevated porosity of the material.

Heat resistance is a very important property for the kind of material studied. Its can be estimated approximately in terms of the elongation $\Delta L_{rel}$ of specimens fired preliminarily at 1000°C. Figure 6 presents the dependence of $\Delta L_{rel}$ of the studied mixtures on their composition, from which we can see that the experimental data (curve *1*) do not coincide with the calculated ones (curve *2*). The coefficient of additivity (curve *3*) has been calculated as the proportion of $\Delta L_{rel}$ established experimentally to the calculated theoretical value of $\Delta L_{rel}$. In the region with less than 40% $Al_2O_3$, the actual elongation is two times lower than the theoretical one, and at $Al_2O_3 > 70\%$ the values approach each other. At $Al_2O_3 > 90\%$, $\Delta L_{rel}$ is equal to the elongation of pure aluminum. It seems that the component dominating in the structure of the material forms a spatial skeleton which determines the linear expansion of the material. It can be assumed that the material with less than 30% $Al_2O_3$, which has $\Delta L_{rel}$ 2.5 times lower than the theoretical value, should possess a higher heat resistance, because its elongation does not exceed 0.1% and is close to $\Delta L_{rel}$ of fused quartz.

**Effect of dispersity of the alumina suspension on the properties of materials.** The introduction of alumina of different dispersity into the suspension of fused quartz changes the grain composition of mixed suspensions. This causes a change in the rheological properties of the suspensions, the polydispersity of the particles of the solid phase, the porosity of the castings, and some physicomechanical properties of the materials. We prepared the alumina suspension by suspending the initial powder of grade GEF to a maximum concentration at which the suspension preserved fluidity. Then it was milled in a porcelain mill by uralite milling bodies. In the initial state, the suspension was characterized by $W = 36\%$, $\rho = 2.17$ g/cm$^3$, pH = 8, CV = 6°E, and $C_V = 0.4$ and had a coarse multi-fractional grain composition, i.e., $K_p = 2.3$ and $d_m = 50$ μm (curve *1* in Fig. 7). Figure 7 presents the curves of the grain distribution of the suspensions

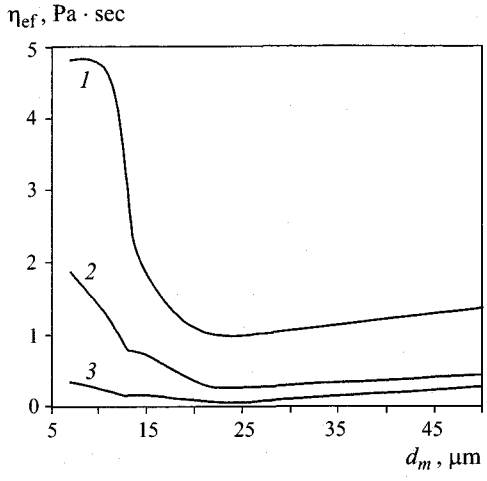


**Fig. 9.** Effect of the parameter $d_m$ on $\eta_{ef}$ $Al_2O_3$ suspensions of grade GEF in the process of milling at $\dot{\varepsilon}$ equal to 2 (*1*), 10 (*2*), and 50 sec$^{-1}$ (*3*).

in different milling stages. It can be seen that in the course of the milling the polydispersity of the solid phase of the suspension virtually does not change, the proportion of the colloidal component does not increase, and the value of $K_p$ lies within 2.3 – 2.6. It can be assumed that alumina is introduced in the form of a single fraction, the dispersity of which corresponds approximately to the parameter $d_m$. Figure 8 shows the variation of $d_m$ and the content of particles 10 and 5 μm in diameter during the milling. It can be seen that the milling intensity increases after 30 h of milling. This is accompanied by an increase in the viscosity of the suspension at low values of the gradient of the shear rate (curve *1* in Fig. 9). The high intensity of the milling seems to be explainable by the optimum value of the viscosity of the suspension.

The variation of the rheological characteristics of the suspension as a function of the dispersity, which is controlled by the duration of the milling, is presented in Fig. 10. It can

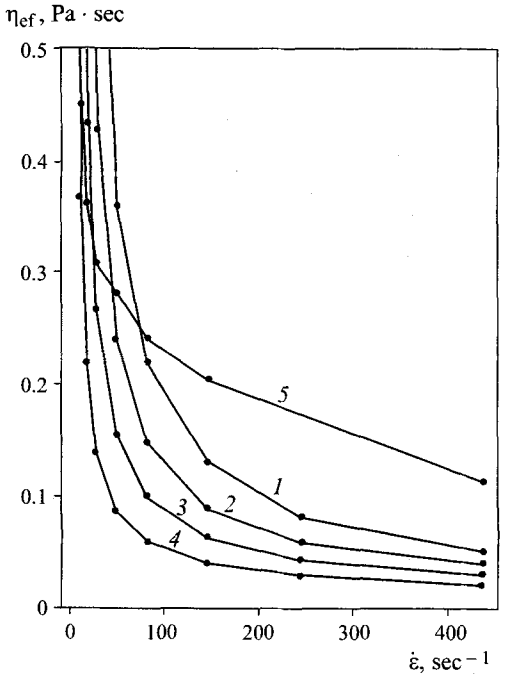


**Fig. 10.** Dependence of $\eta_{ef}$ on $\dot{\varepsilon}$ of an alumina suspension at $d_m$ equal to 50 (*1*), 27 (*2*), 15 (*3*), 11 (*4*), and 7 μm (*5*).

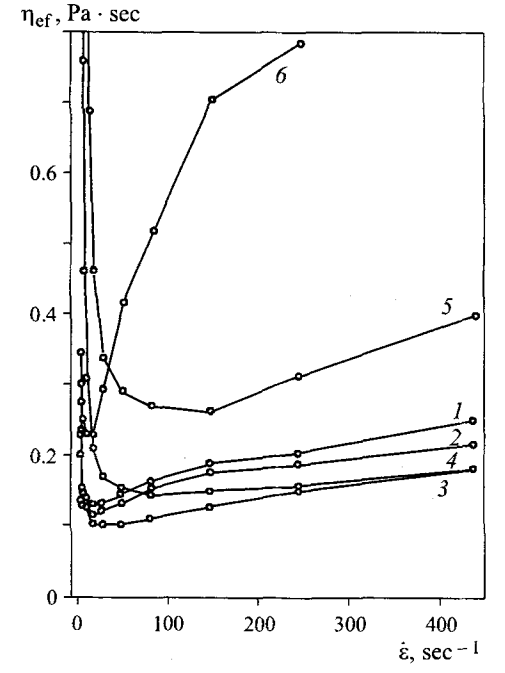


**Fig. 11.** Dependence of $\eta_{ef}$ on $\dot{\varepsilon}$ of a quartz glass suspension with an additive of 20% alumina of grade GEF and $d_m$ equal to 50 (*1*), 27 (*2*), 15 (*3*), 11 (*4*), and 7 μm (*5*), or alumina produced by the Alcoa Corporation (*6*).

be seen that the suspensions have a well-manifested thixotropic flow. After the first 8 h of milling ($d_m$ is equal to 50 and 27 μm) the viscosity decreases markedly and then grows considerably from 1 Pa · sec after 20 h to 5 Pa · sec after

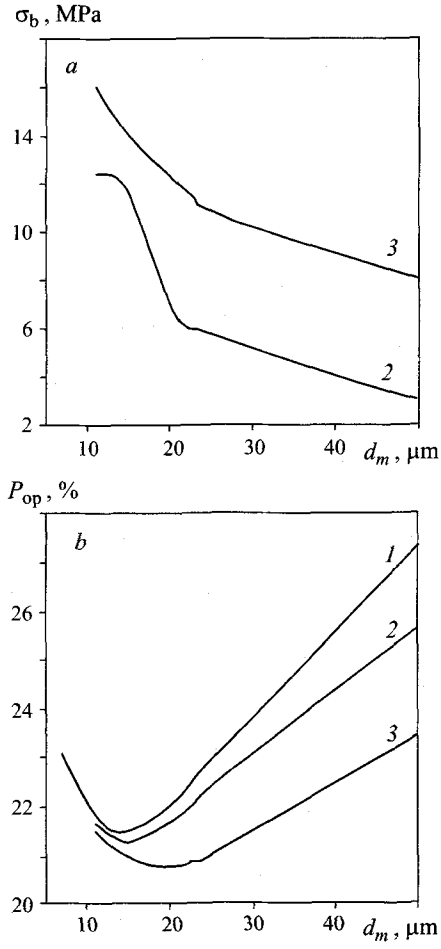


**Fig. 12.** Variation of $\sigma_b$ (*a*) and $P_{op}$ (*b*) of castings containing 20% alumina of grade GEF with different dispersities after a heat treatment at 100 (*1*), 1000 (*2*), 1100°C (*3*).

100 h of milling at low values of the gradient of the shear rate and $\dot{\varepsilon} = 2$ sec$^{-1}$. This is caused by the growth in the specific surface of the solid phase from 600 to 3500 cm$^2$/g and, as a consequence, the strong thixotropic hardening.

The effect of the dispersity of alumina was studied at a constant content of it in the mixture (20%), which corresponds to optimum properties of the mixed systems.

It follows from Fig. 11 that the increase in the milling time of alumina is accompanied by a decrease in its polydispersity and does not affect the nature of flow of mixed suspensions with 20% $Al_2O_3$. These suspensions have a weakly dilatant flow. The decrease in their viscosity is due to the thinning caused by the introduction of a large amount of water with the alumina suspension. In this case, the total moisture content of the mixture increases to up to 18%. At an alumina dispersity characterized by $d_m \ll 11$ μm, the mixed suspensions possess a high thixotropy due to the elevated content of the finely dispersed component.

After a heat treatment at 1000°C, the best properties with respect to $P_{op}$ and $\sigma_b$ are exhibited by materials cast from the mixture with an alumina additive and $d_m = 15$ μm (Fig. 12),

**TABLE 1.** Properties of Materials Bearing 20% $Al_2O_3$ after a Heat Treatment at 1000°C

| Kind of additive | $K_p$ | $P_{op}$, % | $\rho_{ap}$, g/cm$^3$ | $\sigma_b$, MPa |
|---|---|---|---|---|
| Alumina with added reactive alumina | 4.5 | 15.0 | 2.03 | 8.0 |
| Original alumina produced by Alcoa | 10.0 | 14.8 | 2.04 | 7.7 |
| Alumina: | | | | |
| with $d_m$ = 50 μm | 2.3 | 25.7 | 1.75 | 3.0 |
| with $d_m$ = 15 μm | 2.0 | 21.3 | 1.87 | 11.6 |

namely, $P_{op}$ = 21.2% and $\sigma_b$ = 11.6 MPa. This is explainable by the closeness of the grain compositions of the suspensions of quartz glass ($d_m$ = 10 μm) and alumina ($d_m$ = 14 μm). An increase and a decrease in the $d_m$ of the alumina suspension causes deviation of the grain composition of the suspension from the optimum one, which prevents fabrication of a material with a high density. Table 1 presents the properties of materials with an additive of 20% $Al_2O_3$ introduced in different forms after a heat treatment at 1000°C.

The use of monodisperse alumina did not allow us to obtain results exceeding those for polydisperse alumina. It seems that castings with a high density can be obtained in the case of closeness of the grain compositions of the quartz glass suspension and the additive and also of the values of $K_p$. This is confirmed by the cases of the use of reactive alumina imported from Alcoa, which is represented by a mixture of two fractions of 6 and 0.8 μm. Preparation of a polydisperse alumina suspension by the method of stepped loading turned out to be inappropriate. Milling alumina with $K_p$ = 7.7 in the initial state (curve *2* in Fig. 7), we established that only the coarse fraction crushed to $K_p \sim 2.5$ and then the milling occurred as has been described above.

## CONCLUSIONS

In performing the present work, we obtained a new advanced material with properties improved relative to the known analogs. We established that the rheological properties of molding mixtures in the $SiO_2 - Al_2O_3$ system can be controlled successfully and the mechanical properties of the materials can be improved. In the studied system, the materials bearing 30 – 40% $Al_2O_3$ and 60 – 70% $SiO_2$ exhibit a thermal expansion 2 – 2.5 times higher than the theoretical value and an elevated mechanical strength.

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