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# STUDY OF THE PHYSICOMECHANICAL PROPERTIES OF MODIFIED RAW MATERIALS OF $Al_2O_3$ – SiC – C COMPOSITES BASED ON HAC AND ACPB

**L. A. Angolenko,[1] G. D. Semchenko,[1] V. V. Povshuk,[2] S. V. Tishchenko,[1] M. A. Kushchenko,[1] and E. E. Starolat[1]**

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Results are given for a study of the dependence of apparent density and ultimate strength in compression on the quantity of silica and form of modifying addition (Al, Si, B and mixtures of them) for materials of the composition $Al_2O_3$ – SiC – C based on high-alumina cement and aluminochromium phosphate binder after low-temperature (400°C) heat treatment. It is established that the most efficient form the point of view of compaction and strengthening of raw material of corundum-graphite refractory is addition of aluminum powder.

**Keywords:** graphite, silicon carbide, silica, modifying addition, high-alumina cement (HAC), aluminochromium phosphate binder (ACPB).

The requirement for developments in the field of implementing effective methods for protecting graphite from oxidation is due to the extensive application of carbon-containing refractory products metallurgy, that embraces a broad spectrum of composite materials in the system $Al_2O_3$ – MgO – $SiO_2$ – $ZrO_2$ – SiC – $Si_3N_4$ – C and objects based on them, among which various unmolded refractories are promising [1 – 3].

Materials based on the composition $Al_2O_3$ – SiC – C [4, 5] make it possible by introduction into their composition of various modifying additions (sintering, antioxidant) and use of binders (mineral, organic, elemental-organic) to improve their physicomechanical properties and expand the field of application.

A study of the effect of grain size composition of refractory mixes of the $Al_2O_3$ – SiC – C system has shown that it is rational to observe the ratio of coarse and fine fractions of electrocorundum of 7:3, and introduction of silicon carbide preferentially in the form of a very fine fraction (~50 μm) in an amount up to 20 wt.%. The modifying additions used are silica (Sa) and reactive alumina (RA), and the binder used is aluminochromium phosphate binder ACPB) and high-alumina cement (HAC) [6]. With the aim of improving the physicomechanical properties of previously developed ramming mixes based on the composite $Al_2O_3$ – SiC – C using HAC and ACPB as a binder [7], and also additions of RA (1 wt.% above 100%) and Sa (0.5 wt.% above 100%) it is proposed to modify them by adding Si, B, Al + Si, Al + B, Si + B, Al + Si + B (Table 1).

Dependences are shown in Figs. 1 and 2 for the apparent density of materials after their low-temperature heat treatment at 400°C for 4 h on the amount of silica added and the form of modifying additions, that were introduced in an amount of 2.5 wt.% (above 100%). As may be seen from Figs. 1 and 2, $\rho_{app}$ of ramming mixes after four hours of isothermal soaking at 400°C is from 2.45 to 2.58 g/cm$^3$, and the maximum value of $\rho_{app}$ is typical for materials without adding Sa. Then $\rho_{app}$ is reduced with an increase in the content of added Sa from 2.5 (change in apparent density $\Delta\rho_{app} \approx 0.5 – 1\%$) to 5 wt.% ($\Delta\rho_{app} \approx 1 – 3\%$).

A study of the effect of the form of modifying addition on $\rho_{app}$ of unmolded refractories of the system $Al_2O_3$ – SiC – C – RA – HAC – ACPB shows that the most effective is addition of aluminum powder (both individually and within the composition of complex modifying additions Al + Si, Al + B, Al + Si + B), that has a plastifying effect promoting more dense packing of the material during compaction.

On the basis of the graphical dependences obtained for $\rho_{app}$ on the amount of Sa trend lines were plotted and an

[1] NTU KhPI Khar'kov, Ukraine.
[2] PO Ukrspetsogneupory, Zaporozh'e, Ukraine.



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equation was obtained for the dependence of $\rho_{app}$ on the amount of Sa provided in Table 2 (variable $x$ is the amount of Sa addition). Also determined was the reduction in $\Delta\rho_{app}$ (as the ratio of the difference between $\rho_{app}$ of the material before adding Sa and the content Sa added to $\rho_{app}$ of material without added Sa) with an increase in Sa content up to 5 wt.%, whose value depends not only on the weight fraction of silica in the charge of a damming mix, but also on the form an

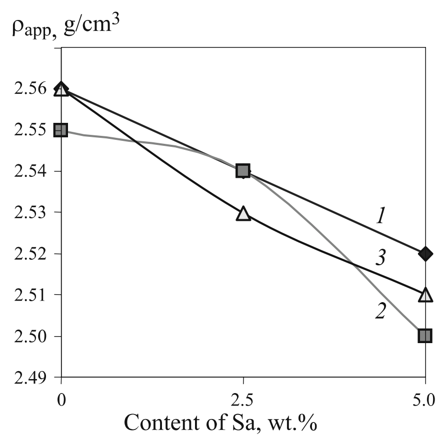


**Fig. 1.** Dependence of apparent density $\rho_{app}$ of materials of $Al_2O_3$ – SiC – C composite based on HAC and ACPB with additions of RC and Sa, containing 2.5 wt.% (above 100%) addition: *1* ) Al; *2* ) Si; *3* ) B.

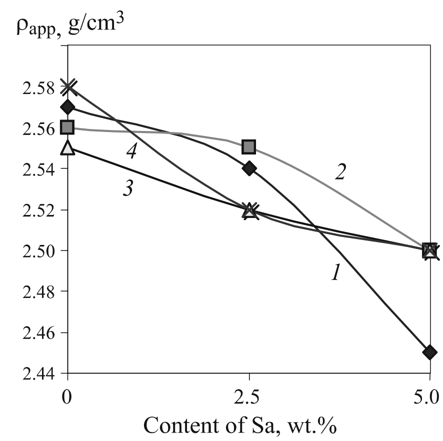


**Fig. 2.** Dependence of apparent density $\rho_{app}$ of materials of $Al_2O_3$ – SiC – C composite based on HAC and ACPB with additions of RC and Sa, containing 2.5 wt.% (above 100%) complex modifying addition: *1* ) Al + Si; *2* ) Al + B; *3* ) Si + B; *4* ) Al + Si + B.

**TABLE 1.** Compositions of Modified Materials of $Al_2O_3$ – SiC – C Composite Based on ACPB, %

| Composition number | $Al_2O_{3sa}$ (70% fraction 400 μm) | $Al_2O_{3m}$ (30% fraction 10 μm) | SiC | C | RA | Sa | HAC | Addition |
|---|---|---|---|---|---|---|---|---|
| 1 | 52.5 | 22.5 | 20 | 5 | 1 | — | 5 | 2.5 (Al) |
| 2 | 52.5 | 22.5 | 20 | 5 | 1 | — | 5 | 2.5 (Si) |
| 3 | 52.5 | 22.5 | 20 | 5 | 1 | — | 5 | 2.5 (B) |
| 4 | 52.5 | 22.5 | 20 | 5 | 1 | — | 5 | 1.25 + 1.25 (Al + Si) |
| 5 | 52.5 | 22.5 | 20 | 5 | 1 | — | 5 | 1.25 + 1.25 (Al + B) |
| 6 | 52.5 | 22.5 | 20 | 5 | 1 | — | 5 | 1.25 + 1.25 (Si + B) |
| 7 | 52.5 | 22.5 | 20 | 5 | 1 | — | 5 | 0.83 + 0.83 + 0.83 (Al + Si + B) |
| 8 | 52.5 | 22.5 | 20 | 5 | 1 | 2.5 | 5 | 2.5 (Al) |
| 9 | 52.5 | 22.5 | 20 | 5 | 1 | 2.5 | 5 | 2.5 (Si) |
| 10 | 52.5 | 22.5 | 20 | 5 | 1 | 2.5 | 5 | 2.5 (B) |
| 11 | 52.5 | 22.5 | 20 | 5 | 1 | 2.5 | 5 | 1.25 + 1.25 (Al + Si) |
| 12 | 52.5 | 22.5 | 20 | 5 | 1 | 2.5 | 5 | 1.25 + 1.25 (Al + B) |
| 13 | 52.5 | 22.5 | 20 | 5 | 1 | 2.5 | 5 | 1.25 + 1.25 (Si + B) |
| 14 | 52.5 | 22.5 | 20 | 5 | 1 | 2.5 | 5 | 0.83 + 0.83 + 0.83 (Al + Si + B) |
| 15 | 52.5 | 22.5 | 20 | 5 | 1 | 5 | 5 | 2.5 (Al) |
| 16 | 52.5 | 22.5 | 20 | 5 | 1 | 5 | 5 | 2.5 (Si) |
| 17 | 52.5 | 22.5 | 20 | 5 | 1 | 5 | 5 | 2.5 (B) |
| 18 | 52.5 | 22.5 | 20 | 5 | 1 | 5 | 5 | 1.25 + 1.25 (Al + Si) |
| 19 | 52.5 | 22.5 | 20 | 5 | 1 | 5 | 5 | 1.25 + 1.25 (Al + B) |
| 20 | 52.5 | 22.5 | 20 | 5 | 1 | 5 | 5 | 1.25 + 1.25 (Si + B) |
| 21 | 52.5 | 22.5 | 20 | 5 | 1 | 5 | 5 | 0.83 + 0.83 + 0.83 (Al + Si + B) |

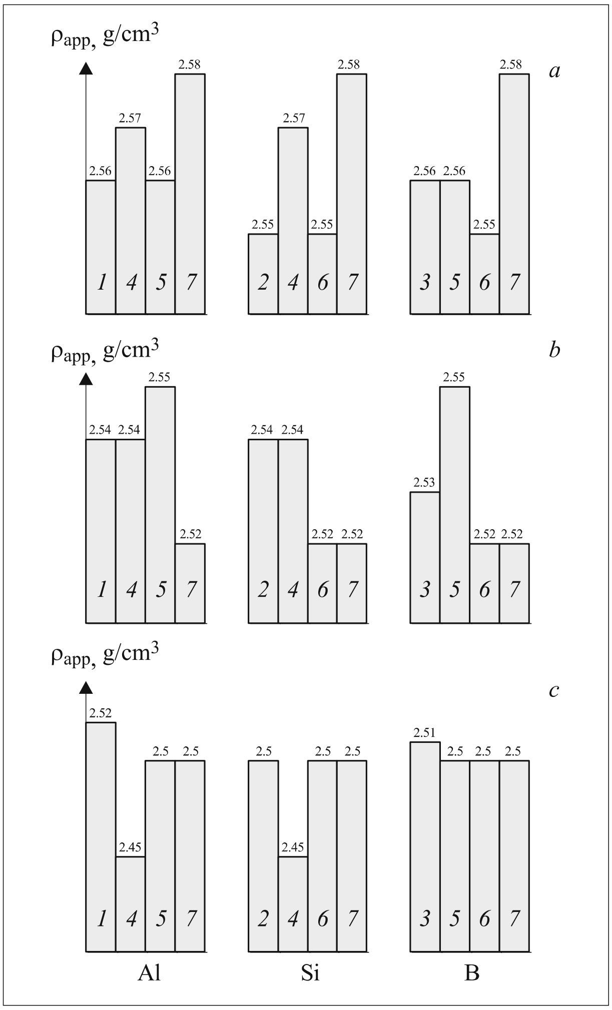


**Fig. 3.** Apparent density $\rho_{app}$ of corundum-graphite materials in relation to the form of modifying addition: *a*) material without added Sa; *b*, *c*) materials with addition of 2.5 (*b*) and 5 wt.% Sa (*c*); *1*) Al; *2*) Si; *3*) B; *4*) Al + Si; *5*) Al + B; *6*) Si + B; *7*) Al + Si + B.

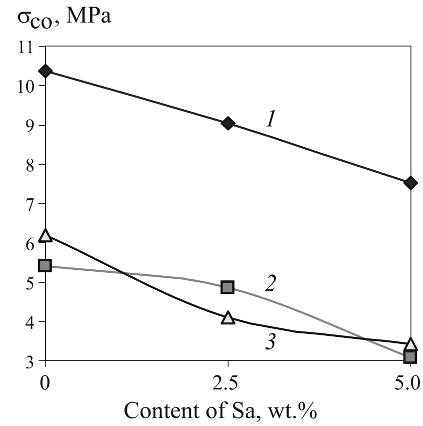


**Fig. 4.** Dependence of $\sigma_{co}$ for materials of $Al_2O_3$ – SiC – C composite based on HAC + ACPB, containing 2.5 wt.% (above 100%) addition on amount of Sa: *1*) addition of Al; *2*) Si; *3*) B.

amount of modifying addition. Values of $\Delta\rho_{app}$ are presented in Table 2. Data indicate that the greatest change in $\rho_{app}$ on introducing Sa in an amount of 2.5 and 5 wt.% is observed in materials containing additions of (Al + Si) and (Al + Si + B), and the least with addition of a complex additive of Al and (Al + B). It is possible to determine from Fig. 3 the degree of efficiency of modifying addition as an increase in $\rho_{app}$ with a specific of silica addition: for corundum-graphite materials, not containing Sa, the most effective addition is (Al + B), and for materials containing 2.5 and 5 wt.% Sa it is addition of (Al + Si + B).

Curves for the dependence of ultimate strength in compression for trough mixes of the composition $Al_2O_3$ – SiC – C on the amount of Sa and the form of modifying addition in an amount of 2.5 wt.% (above 100%) after heat treatment at 400°C are shown in Figs. 4 and 5. Analysis of the dependences obtained indicates that $\sigma_{co}$ for material of

**TABLE 2.** Equations of the Dependence $\rho_{app}(y)$ for Materials of $Al_2O_3$ – SiC – C Composite on Amount of Sa Added

| Modifying addition | Equation | Relative reduction in $\rho_{app}$, %, with addition of Sa in an amount, wt.% | |
|---|---|---|---|
| | | 2.5 | 5 |
| Al | $y = -0.008x + 2.56$ | 0.78 | 1.57 |
| Si | $y = -0.0024x^2 + 0.002x + 2.55$ | 0.39 | 1.97 |
| B | $y = 0.0008x^2 - 0.014x + 2.56$ | 1.17 | 1.98 |
| Al + Si | $y = -0.0048x^2 + 2 \times 10^{-15}x + 2.57$ | 1.17 | 4.67 |
| Al + B | $y = -0.0032x^2 + 0.004x + 2.56$ | 0.39 | 2.34 |
| Si + B | $y = 0.0008x^2 - 0.014x + 2.55$ | 1.18 | 1.96 |
| Al + Si + B | $y = 0.0032x^2 - 0.032x + 2.58$ | 2.33 | 3.10 |

**TABLE 3.** Dependence $\sigma_{co}(y)$ on amount of Sa($x$) in the Form of a Square Parabola Equation

| Modifying addition | Equation | Relative reduction in $\sigma_{co}$, %, with addition of Sa in an amount, wt.% | |
|---|---|---|---|
| | | 2.5 | 5 |
| Al | $y = -0.0168x^2 - 0.49x + 10.38$ | –12.81 | –27.65 |
| Si | $y = -0.0976x^2 + 0.024x + 5.41$ | –10.17 | –42.88 |
| B | $y = 0.1136x^2 - 1.12x + 6.18$ | –33.82 | –44.66 |
| Al + Si | $y = -0.0176x^2 - 0.752x + 7.95$ | –25.03 | –52.83 |
| Al + B | $y = 0.0448x^2 - 1.084x + 8.83$ | –27.52 | –48.70 |
| Si + B | $y = 0.1328x^2 - 1.04x + 5.08$ | –34.84 | –37.01 |
| Al + Si + B | $y = 0.0712x^2 - 0.886x + 6.96$ | –25.43 | –38.07 |

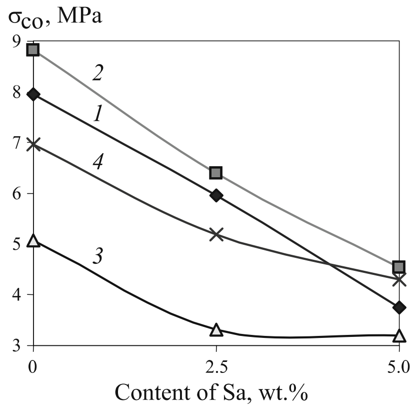


**Fig. 5.** Dependence of $\sigma_{co}$ for materials of $Al_2O_3 - SiC - C$ composite based on HAC+ACPB, containing 2.5 wt.% (above 100%) complex modifying addition on amount of Sa: *1*) Al + Si; *2*) Al + B; *3*) Si + B; *4*) Al + Si + B.

$Al_2O_3 - SiC - C$ composite based on HAC + ACPB with addition of Sa after heat treatment at 400°C is from 3 to 10.5 MPa, and the maximum value of strength $\sigma_{co}$ is typical for materials without added Sa; then $\sigma_{co}$ decreases significantly with an increase in Sa content from 2.5 to 5 wt.% due to weakening of the material as a result of polymorphic transformation of $SiO_2$.

A study of the effect of modifying addition on $\sigma_{co}$ for ramming mixes based on the composite $Al_2O_3 - SiC - C -$ ACPB shows that the most effective is addition of aluminum powder (both individually and within the composition of a complex modifying addition Al + Si + B), that promotes strengthening of the material due to occurrence oxidation and formation of $Al_2O_3$ reaction product in the interpore space, exhibiting high hardness and strength. On the basis of the dependences obtained for $\sigma_{co}$ on the amount of Sa trend lines were plotted and equations were obtained for the dependence of strength $\sigma_{co}$ on the amount of Sa provided in Table 3 (variable *x* is the amount of Sa added).

The relative reduction was also determined for the ultimate strength in compression $\Delta\sigma_{co}$ for (as the ratio of $\sigma_{co}$ for material without Sa addition to $\sigma_{co}$ for material containing Sa) with an increase in Sa content up to 5 wt.%, whose value depends both on the weight fraction of $SiO_2$ in the charge, and also on the form of modifying addition. Values of $\Delta\sigma_{co}$ are presented in Table 3. Data show that the greatest change in $\sigma_{co}$ with introduction of Sa in an amount of 2.5 and 5 wt.% is observed in materials containing addition of B, and the least with addition of Si and a complex addition Al + Si + B.

The degree of the effect of modifying addition on $\sigma_{co}$ is shown in Fig. 6 for a specific amount of Sa and it has been established that for all corundum-graphite materials based on HAC + ACPB without addition and with addition of Sa strengtheners are additions of Al and (Al + B).; the least effective after heat treatment of materials at 400°C is addition of Si.

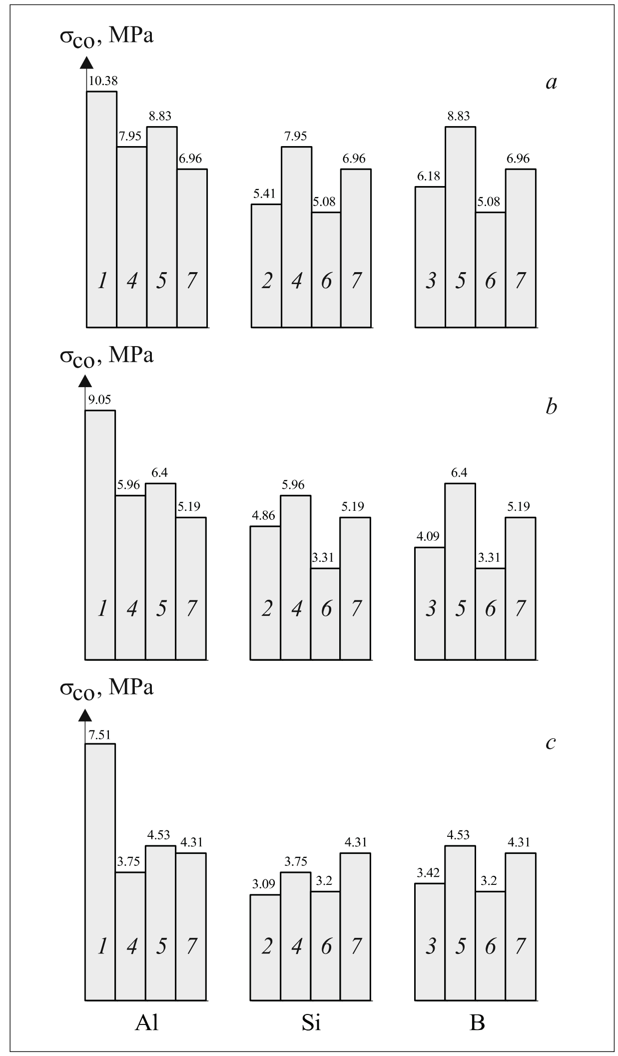


**Fig. 6.** Ultimate strength in compression $\sigma_{co}$ of corundum-graphite in relation to the form of modifying addition: *a*) materials without addition Sa; *b*, *c*) materials with addition of 2.5 (*b*) and 5 wt.% Sa (*c*); *1*) Al; *2*) Si; *3*) B; *4*) Al + Si; *5*) Al + B; *6*) Si + B; *7*) Al + Si + B.

Thus, in order to achieve high physicomechanical properties for materials of $Al_2O_3 - SiC - C$ composites based on complex binder HAC + ACPB in the low-temperature field it is most rational to use aluminum powder and a complex modifying addition (Al + B) with a weight ratio of aluminum powder and amorphous boron of 1:1.

## CONCLUSION

The effect of adding aluminum powder, crystalline silicon and amorphous boron on the apparent density and ultimate strength in compression of materials of $Al_2O_3 - SiC - C$ composites based on a complex binder HAC + ACPB after heat treatment at 400°C for 4 h has been studied. It has been shown that an addition promoting compaction of a mix is aluminum powder (both individually and within the composition of complex modifying additions Al + Si, Al + B, Al + Si + B) due to its plastifying effect making it possible to achieve an apparent density for the material of 2.55 – 2.58 g/cm$^3$.

For corundum-graphite materials based on HAC + ACPB without addition and with addition of Sa strengtheners at lower temperatures are addition of Al and Al + B; the least effective after heat treating materials at 400°C is addition of Si. On introducing aluminum powder material is obtained with an ultimate strength in compression up to 10 MPa.

## REFERENCES


1. J. Dabinski, J. Baranski, and I. Majchrowicz, "Influence of thermal treatment conditions on the mechanical and resistant properties of various $Al_2O_3$ – SiC – C low- and ultralow cement castables," XIII Konferenz über feuerfeste Baustoffe, Prague, March 29 (2000).
2. W. E. Lee and Cheng-Feng Chang, "Microstructures and slag resistance of $Al_2O_3$ – $SiO_2$ – SiC – C refractories," UNITECR'97, p. 1593 – 1602.
3. D. N. Borzov, "Development of low-cement refractory concretes based on the system $Al_2O_3$ – SiC – C," *Ogneupory Tekhn. Keram*., No. 4, 30 – 34 (2002).
4. L. A. Angolenko, G. D. Semchenko, S. V. Tishchenko, et al., "Study of physicomechanical properties of taphole mixes of $Al_2O_3$ – SiC – C composition based on aluminochromium phosphate binder," *Visnik Natsional'nogo Tekhnichnogo Universitetu, Kharkhiv. Politekh. Inst.,* No. 33, 103 – 107 (2008).
5. L. A. Angolenko, G. D. Semchenko, and S. V. Tishchenko, "Study of the influence of storage on the physicomechanical properties of corundum-graphite-silicon carbide materials," Proc. XVII Ukrainian Conf. on Inorganic Chemistry, Publ. Center of Lviv National University, Lviv (2008).
6. L. A. Angolenko, G. D. Semchenko, V. V. Povshuk, et al., "Physicomechanical properties of modified materials of $Al_2O_3$ – SiC – C composite based on HAC and ACPB binders, their structure and phase composition as predetermining factors of refractory slag resistance," *Ogneupory Tekhn. Keram*., No. 4, 5, 3 – 8 (2009).
7. L. A. Angolenko, G. D. Semchenko, S. V. Tishchenko, et al., "Optimization of the influence of a $Al_2O_3$ – SiC – C mix by the method of a repeated factored experiment," *Visnik Natsional'nogo Tekhnichnogo Universitetu, Kharkhiv. Politekh. Inst.,* No. 39, 34 – 39 (2008).