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SHS OF REFRACTORY MATERIALS

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In the SHS production of refractory materials (concretes, coating mixtures) the basic problem is overcoming the scale factor. This is done by imparting a granular structure to the mass being synthesized. Requirements for the granular and chemical composition of the filler are obtained.

The present trend in the development of refractories is to increase the density of unformed refractories, first of all, concretes (ramming masses) and coating mixtures [1-3]. Refractory masses have three main components: a finely milled fraction, filler grains, and a binder. In heating a refractory lining two competing processes take place. One of them is thermal decomposition of the binder and the other is diffusion sintering of the finely milled fraction with grains of the filler. Depending on the particular situation, the operational strength of a refractory can increase or decrease. SHS-produced refractory masses do not have this disadvantage because SHS forms a stable ceramic body of the refractory before operation of the lining.

The specific properties of operation of a refractory consist in the fact that it is subjected not only to high temperatures and active chemical effects, but also to substantial heat and mechanic shocks. Satisfactory thermal stability and crack-resistance are achieved by imparting a granular structure to the refractory. Figure 1 shows variants of this structure. The plastic structure (the "watermelon" structure) is characterized by a high content of the finely milled fraction and small amount of grains, whereas the rigid structure (the "pomegranate" structure) is characterized by a maximum amount of coarse grains and grains of medium and finely milled fractions sufficient to fill the intergrain space of coarse particles. Graininess of the structure induces localization of defects (a crack), which, reaching grains, cannot propagate any longer. In this way the strength is preserved even in the case of large articles and satisfactory crack and heat resistances [4].

For investigation of the scaling effect on SHS masses a model charge was chosen. It consisted of the following components: PA-4 aluminum, finely milled chromite with particle sizes of 0-20 μm, a binder, a chromite filler with grain sizes of 0-5 mm, and a mullite-corundum filler (Al_2O_3 72%) with grain sizes of 0-3, 0-5, 1-5, and 3-10 mm. In the experiments chromite from the Kempirsai deposit in West Kazakhstan was used. It consisted of the characteristic $(Fe, Mg)O(Cr, Al, Fe)_2O_3$ phase and a small amount (4-6%) of $Mg_6Si_4O_{10}(OH)_8$ serpentine. The mineral has the following elemental composition (wt. %): 54.1 - Cr_2O_3, 16.5 - MgO, 8 - Al_2O_3, 7.5 - FeO, 6 - Fe_2O_3, 4.8 - SiO_2, 0.4 - CaO. Well-stirred components were moistened with service water up to a 6-9% moisture content and then rammed in molds of various sizes. After drying, the specimens were placed in a muffle furnance at about 1300 K. The heating induced self-ignition and burning of the specimens under a steady combustion regime. The experimental results are given in Figs. 2-4. Figure 2, which shows the ultimate bending strength versus the thickness of plates made of three-component PA-4 aluminum-chromite-binder (0-20 μm chromite charge), has an unusual scale effect.

In the plot one can see the branch of the ultimate bending strength with increase of the plate thickness to 10 mm. Special studies have shown that at plate thicknesses smaller than 10 mm the synthesis is not complete because some of the aluminum is released into the ambient air in the form of vapor and gaseous AlO suboxide. The completeness of the combustion reaction increases with the plate thickness up to 10 mm. The strength and the sintering level of chromite particles increase proportionally.

The strength of plates thicker than 10 mm decreases due to the dominant role of the growth of the defect number, which is in full agreement with the statistical theory of the scale factor. This example illustrates a case of

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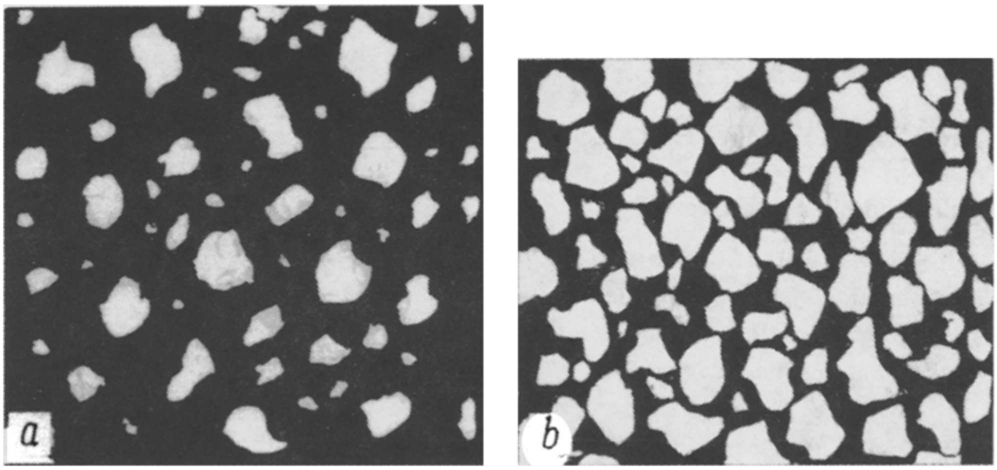
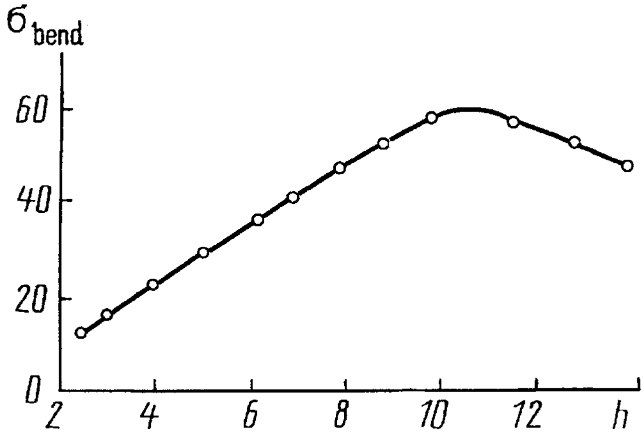


Fig. 1. Types of refractory structures: a) plastic, b) rigid.



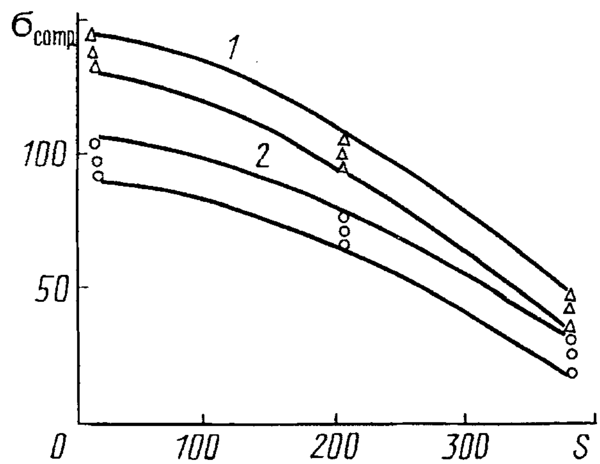


Fig. 2. Plot of the ultimate bending strength versus the plate thickness h (T. A. Ketegenov and A. N. Karabalin's data). σ_{bend}, MPa; h, mm.

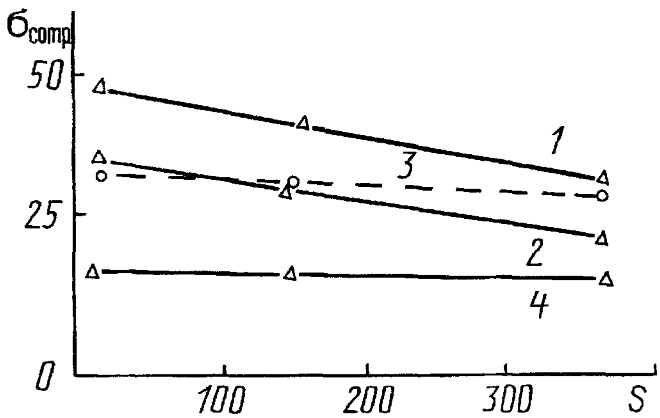
Fig. 3. Plot of the ultimate compressive strength versus the area of a cubic specimen face: 1) 0-20 μm finely milled chromite as a filler; 2) 0-5 mm chromite grains as a filler. σ_{comp}, MPa, S, cm^2.

complex behavior of the scale factor. Thus, a decrease in the strength with increase in the specimen size is not necessary.

In Fig. 3 the ultimate compressive strength of cubic specimens as a function of the face area is shown for two filler fractions of 0-20 μm and 0-5 mm. It can be seen that the presence of grains of the chromite filler does not reduce the scale effect. Analysis of the post-synthesis refractory structure did not show a distinct granular structure. As a result of SHS the grain boundaries appeared to be "smeared" and coalesced with the cementing fraction. Therefore, the filler grains must be inert and should not react with aluminum. Mullite-corundum (72% Al_2O_3) of 0-3, 0-5, 1-5, and 3-10 mm fractions was chosen as a filler.

The experimental results are given in Fig. 4, which shows that the scale effect decreases with increase in the grain size. With a 3-10 or 1-5 mm filler it is practically zero.

In Fig. 5 the resistance of the synthesized refractories (1273 K, running water cooling) [5] is plotted versus the grain number and the composition of filler from the same model charge as was shown in Fig. 4. It can be seen from Fig. 5 that the thermal resistance increases with the grain size and has a maximum at 1-5 mm, followed by a decrease.



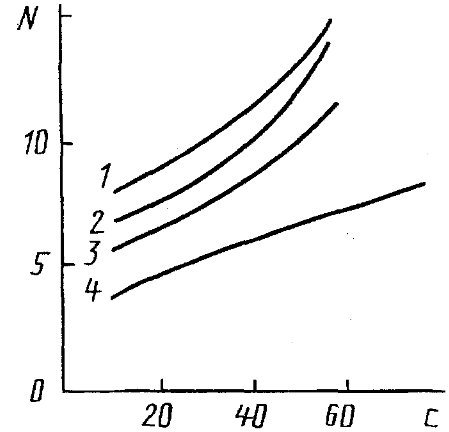


Fig. 4. Strength of cubic SHS refractory specimens with various granular compositions of mullite-corundum filler versus the area of a specimen face. Grain fractions: 1) 0-3 mm; 2) 0-5; 3) 1-5; 4) 3-10 mm.

Fig. 5. Dependence of the thermal resistance (1273 K, water) (*N* is the number of heat cycles) of SHS refractories on the number c and size of grains of mullite-corundum filler. Grain fractions: 1) 1-5 mm; 2) 3-10; 3) 0-5; 4) 0-3 mm. *c*, wt. %.

Thus, to eliminate the scale effect in SHS refractories, it is necessary to create a rigid structure with an optimum grain size of the filler of ~5 mm. Moreover, this will allow using concrete guns in lining. The filler must be chemically inert to prevent "smearing" of the grains in the combustion process.

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