DOI 10.1007/s11148-021-00617-1
Refractories and Industrial Ceramics *Vol. 62, No. 4, November, 2021*

LOW-CEMENT REFRACTORY CONCRETES OF ALUMINUM SILICATE COMPOSITION BASED ON SUBMICRON ALUMINUM OXIDE GRADE NK-Alumina 14

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Translated from *Novye Ogneupory*, No. 7, pp. 33 – 36, July, 2021.

Original article submitted April 14, 2021.

Properties are provided for submicron aluminum oxide developed in SAO PKF NK for low-cement refractory concretes, and also for the LCRC of aluminosilicate composition obtained. It is demonstrated that the properties of concretes prepared on the basis of the alumina developed are no worse than domestic and imported analogs.

Keywords: submicron aluminum oxide, low-cement refractory concrete (LCRC), refractory concrete matrix, aluminum silicate refractories.

INTRODUCTION

Currently almost all unmolded refractories and objects made from them may be prepared within Russian enterprises [1], although the question of using matrix systems of inherent production for low cement-free refractory concretes (LCRC) remains extremely important for the domestic refractory industry as a whole.

Matrix system components for domestic production (high-alumina cement and reactive alumina) and LCRC based upon them are currently produced within Russia only by the Borovich Refractory Combine (www.abkao.ru). The rest of the enterprises producing refractories are obliged to purchase these components from overseas companies: reactive alumina, high-alumina cement, and deflocculants produced by Almatis (www.almatis.com), high-alumina cement and deflocculants produced by Kerneos (www.kerneosinc.com), and reactive alumina produced by Nabaltec (www.nabaltec.de). The aim of the present work is to study the properties of aluminate composition CFRC prepared on the basis of submicron aluminum oxide developed in ZAO PKF NK.

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RESEARCH MATERIALS AND METHODS

Raw materials used during conducting research: mullite-corundum chamotte ShMK (BKO), submicron aluminum oxide NK-Alumina 14 produced by ZAO NPK NK (Al_2O_3 content note less than 99%, d_{50} not more than 2.5 μm, d_{90} not more than 5.5 μm, specific surface S_{sp} not less than 14,000 m^2/g), reactive alumina GRT (BKO), high-alumina cement SRB-710 (Kerneos), and Peramin AL 200 and Peramin AL 300 (Kerneos) deflocculants.

The grain size composition and specific surface of submicron aluminum oxide were determined by means of an Analysette 22 Nano Tecplus laser particle size analyzer. Test specimens were prepared according to GOST R 52541–2006. The CFRC properties were determined by standard methods: ultimate strength in compression according GOST 53065.2–2008, linear shrinkage according to GOST 5402.1–2000, apparent density and open porosity according to GOST 2409–2014.

RESULTS AND DISCUSSION

According to GOST 28874–2004 low-cement concrete should contain less than 2.5% CaO. This specification is due to an unfavorable effect on refractoriness of a high CaO content (typical for traditional concretes) in aluminosilicate refractories. According to the composition diagram for the $CaO–Al_2O_3–SiO_2$ system an increase in CaO content leads to formation of readily melting eutectic [2, 3]. Proceeding from this the CaO content in the test concretes was taken as 2.5% (calculated). This CaO content was provided by addition of 9.5% high-alumina cement.

As is well known, the matrix part of LCRC normally includes the following components: calcined and/or reactive alumina, microsilica, high-silica cement, deflocculants and additives for controlling setting time, and also finely dispersed filler. Therefore, LCRC in contrast to traditional concrete (with CaO more than 5%) contain a deflocculant and very fine component (not less than 2% of submicron particles within concrete) [4]. It is apparent that presence within the CFRC composition of very fine powder (reactive alumina, microsilica) increases particle packing density. This leads to an increase in concrete density, a reduction in porosity, and an increase in the proportion of fine pores (the latter are especially important).

Properties were studied for concretes based on the submicron aluminum oxide NK-Alumina 14 and its analog, i.e., reactive alumina GRT developed in ZAO PKF NK. Alumina NK-Alumina 14 contained 29.8% submicron particles (d_{50} = 1.89 μm, d_{90} = 4.95 μm, S_{sp} = 14,753 cm^2/g). The matrix was represented by finely milled mullite-corundum chamotte ShMK (<0.090 mm), submicron aluminum oxide, or reactive alumina, high-alumina cement, and deflocculants of the polycarboxylate group (Peramin AL 200 and Peramin AL 300). The matrix composition has a considerable effect on LCRC rheological properties, and also on technological efficiency (setting time), strength (including high-temperature), volume constancy, and wear resistance at the service temperature. The calculated compositions of aluminosilicate composition CFRC are shown in Table 1. The filler used was fractionated mullite-corundum chamotte ShMK (with the greatest bulk density of mixture for the fractions used). The amount of setting water within compositions *1* and *2* was 4.5% with an equal amount of deflocculants. Water and deflocculants were added above 100% of dry components.

Comparative evaluation was performed for the properties of concretes based on the submicron aluminum oxide developed and its analog. It should be noted that the phase composition of the solid concrete hydration products depends to a considerable extent on temperature and exposure. Depending on hydration product composition the properties of freshly prepared concrete may differ [5]. Specimens of vibrocast concrete were prepared in the form of a cubes with a side of 70 mm. A mold with specimens was held for 24 h at (20 ± 2)°C and with a relative moisture content of 95% (GOST R 52541–2006), the specimens were extracted from a mold and held for 72 h under the same conditions (in a normal hardening chamber). Concrete properties were determined after drying for 24 h at 110°C, after heat treatment at 800, 1300, and 1450°C with exposure at each temperature for 5 h.

TABLE 1. LCRC Compositions Based on Developed Sub-Micron Aluminum Oxide NK-Alumina and Reactive Alumina GRT

Component	Component content, wt.%, in composition	
	1	*2*
Mullite-corundum chamotte ShMK (<6 mm)	71	71
Milled mullite-corundum chamotte ShMK (<0.09 mm)	7	7
Submicron aluminum oxide NK-Alumina 14	13.5	—
Reactive alumina GRT	—	13.5
High-alumina cement SRB-710	8.5	8.5
Deflocculant (above 100%):		
Peramin AL 200	0.07	0.07
Peramin AL 300	0.07	0.07
Water (above 100%)	4.5	4.5

As these studies have shown, as a result of breakdown of crystal hydrates during heat treatment [5, 6] the ultimate strength in compression σ_{co} for specimens of compositions *1* and *2* decreased from 102.3 to 104.9 MPa after drying at 110°C to 70.1 and 67.9 MPa respectively after heat treatment at 800°C (see Fig. 1*a*). An increase in heat treatment temperature to 1300°C did not lead to an increase in σ_{co}. With an increase in temperature to 1450°C σ_{co} increases as a result of sintering and for compositions 1 and 2 it was respectively 83.9 and 84.5 MPa.

Apparent density (ρ_{app}) of specimens as a result of dehydration after heat treatment at 800°C decreases the same as σ_{co} (see Fig. 1*b*). Open porosity Π_{open} for specimens after heat treatment at 1450°C was 17.4 and 17.3% respectively for compositions *1* and *2* (see Fig. 1*c*). it should be noted that Π_{open} for the concretes developed is no higher than for example for extensively used high-alumina objects MLS-62 and MKS-72 (according to GOST 24704–2015); open porosity of the latter reaches 24%. However, the LCRC developed as a result of high density are subject spalling and therefore in order to facilitate water removal it is necessary to add organic fiber to these concretes (<1%) [4].

It is apparent that LCRC with a higher proportion of pores with size less than 1 μm than traditional concretes resists chemical and erosion by melts better [2]. A significant proportion of the LCRC of the compositions presented and similar to them may be used in nonferrous metallurgy for lining melting units for aluminum production (furnace bath, doors, door frames, banks, thresholds, burner devices, arches) [2, 7]. According to [2] molten aluminum penetrates into pores 1 – 2 μm in diameter. Presence with the LCRC of submicron aluminum oxide prevents this process. In addition, within the concrete composition in contact with molten aluminum in order life and antiwetting additive is employed (for example $BaSO_4$) [7].

It is well known that the maximum temperature for concrete utilization is considered to be that at which during 5 h without a load linear shrinkage does not exceed 1% [8]. Linear shrinkage Δl at 1450°C is shown as a result of sintering comprising 0.3% for compositions *1* and *2*. After heat treatment at 800°C there is no linear shrinkage. Therefore the maximum concrete utilization temperature for concrete prepared on the basis of submicron aluminum oxide developed is not lower 1450°C.

During refractory concrete operation apart from chemical wear, erosion by melt, mechanical breakdown, and melt-

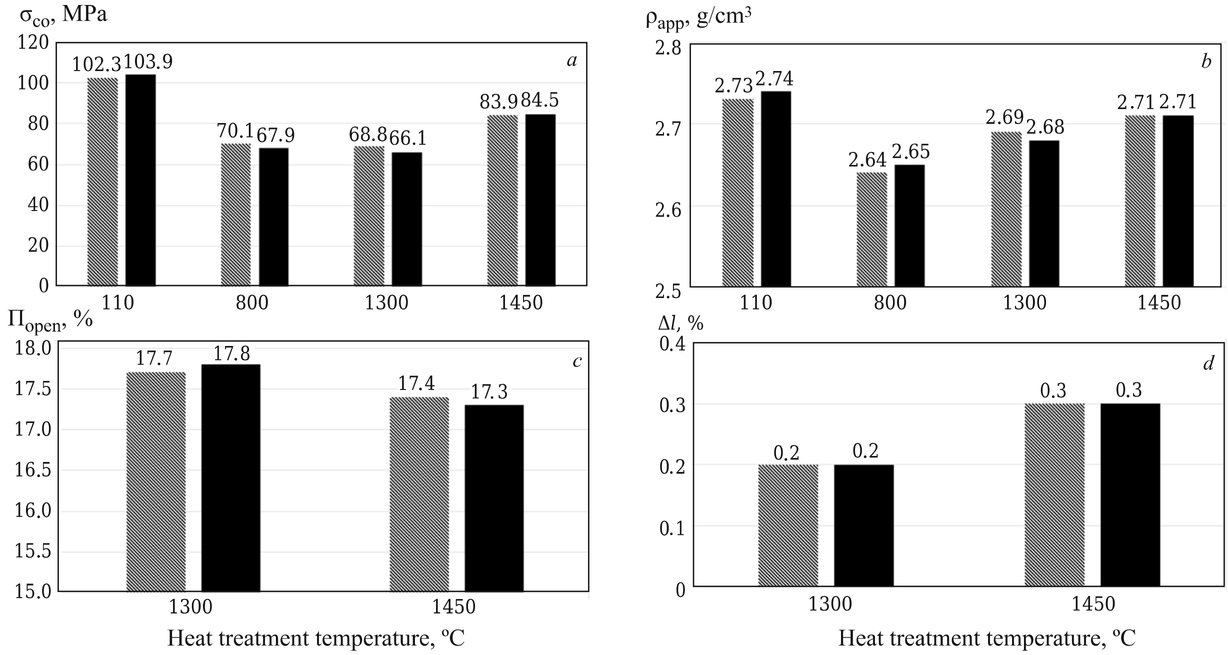

Fig. 1. Effect of heat treatment temperature on LCRC σ_{co} (*a*), ρ_{app} (*b*), Π_{open} (*c*) and Δl (*d*): ■) composition *1*; ■) composition *2*.

ing, there is possibly thermal spalling as a result of the cyclic action of temperature. In this case it is necessary to ad fibers made of stainless steel to a concrete composition in an amount of 2 – 4 wt.% (with a concrete operating temperature not above 1200°C) [4, 9].

Aluminosilicate unmolded refractories based on the submicron aluminum oxide developed may also be used in ferrous metallurgy, for example within the reinforcing layer of a tundish lining, in the lining of hearth of heating and processing furnaces, and also in other branches of industry [10, 11].

CONCLUSION

Results of studying the properties of LCRC of aluminosilicate composition based on submicron aluminum oxide grade NK-Alumina 14 have demonstrated that the material developed provides good physicochemical properties. These refractory concretes may be recommended for ferrous and nonferrous metallurgy heating units and for other branches of industry.

Work was conducted with financial support of the Russian federation Ministry of science and Higher Education within the scope of an agreement on the theme "Creation of import substitution production of matrix system components and heat engineering composite material of a new generation based upon them" in accordance with the RF Government statement 9 April 2010 No. 218 "Measures of state supporting development for creating higher teaching establishments and organization implementing complex products for creating high tech production". Agreement No. 075-11-2020-038 of 14 December 2020.

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