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PREPARATION AND PROPERTIES OF FUSED ZIRCON

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Melting of zircon with added glass-forming oxides is reported. The structures of the synthesized materials were baddeleyite and a glassy phase, which determined the operating characteristics of the refractory. Corrosion tests of fused zircon samples in Al-alloy melts showed that they were not wetted and minimally corroded. Treatment of fused zircon with HF solution (10%) produced a material with <2% SiO_2. The silica content in the fused zircon decreased by three times with carbothermic melting in an electric arc furnace.

Keywords: zircon, EDP-600M electric arc furnace, fused cast refractories, baddeleyite-silica materials (BSM), carbothermic melting.

INTRODUCTION

Zircon concentrates containing up to 99% $ZrSiO_4$ are a widely employed raw material for the refractory and ceramic industries, including production of zircon refractories. Such refractories are prepared by ceramic technology, are characterized by high physicochemical and corrosion characteristics, and are widely used in metallurgy and glassmaking.

Zircon refractories are not manufactured in the Russian Federation so demand must be satisfied by importation. Manufacturers of zircon refractories are SEPR Group, France (refractories ZPR, ZS 1300, ZS 835); RHI Group, Austria (ZETTRAL 65 G); RS-refractories LLC, China (RS-TsK-65); PAO Krasnoarmeiskii Silica Plant, Ukraine (TsRS-1); etc. Fused granulated zircon ER 120 manufactured by SEPR Group has also been used. Production of zircon materials by melting and crystallization from the melt are practically unknown. Fused zircon materials are difficult to prepare mainly because of its increased viscosity in the molten state due to the high silica content and the lack of smelting units with enough energy to superheat and pour the melt into castings.

The availability of the updated EDP-600M electric arc unit [1] enabled experiments on the melting of refractory oxides, including zircon, to be initiated. Zircon was melted to evaluate the melting regime technology and the ability to produce fused refractories as castings or granules, to estimate the main properties of the fused materials, and to determine their applications. Fused products were prepared by melting Australian zircon (Western Titanium, Ltd.; mass%: ZrO_2, 66.5; SiO_2, 33.0; Al_2O_3, 0.2; TiO_2, 0.17). A coating of Australian zircon was melted onto the wall of the EDP-600M furnace before the melting. The furnace was ignited on a fused solid hearth using graphite plates that were removed from the furnace after the first melt portions appeared. After the whole charge (40 – 45 kg) loaded into the furnace was melted, the melt was poured into a casting fabricated of graphite plates. Granulated material was also produced using dispersion of the melt by air during pouring into a metal container with water.

Ignition of the furnace and melting of the zircon without additives (Z-268, Table 1) characteristically took a long time, up to 3 h, because of the high melt viscosity caused by the high silica content. White cottony threads separated from the melt because silica was reduced to SiO during ignition using graphite plates. The melting stabilized after a mirror surface appeared. A portion of the charge was melted in 40 min. Pouring the melt into forms produced castings of dimensions $145 \times 200 \times 300$ mm that were annealed naturally in the forms under a layer of insulation. Specimens were cut from the working zone of the casting to determine the physicochemical and operating characteristics of the material. Specimens of fused zircon Z-268 had high apparent density and low open porosity (Table 1).

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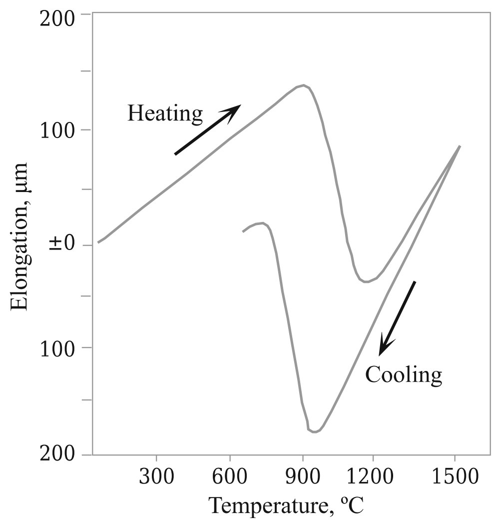

Fig. 1. Dilatometry curve of molten Z-268.

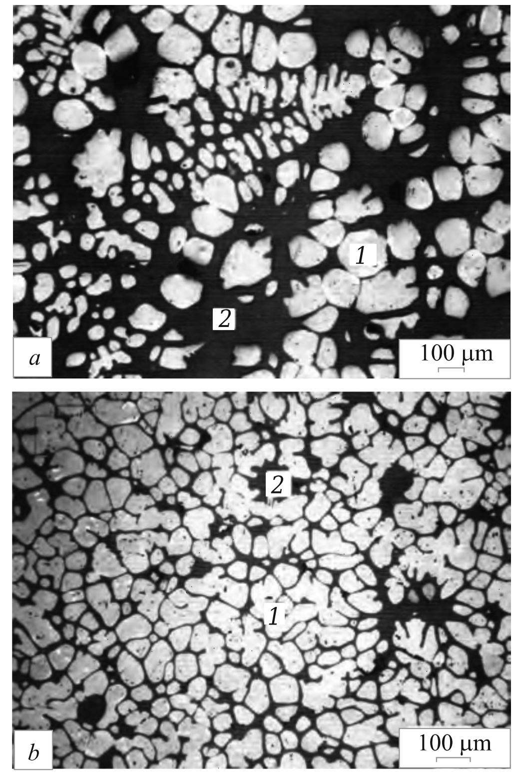

Fig. 2. Microstructure of fused cast BSM: Z-268 (*a*), Z-218P (*b*); baddeleyite (*1*) and glass phase (*2*).

X-ray phase analyses of Z-268 on a DRON-3M diffractometer (Cu K_α-radiation) detected only one crystalline phase, baddeleyite, a monoclinic modification of ZrO_2 with diffraction maxima at 0.3164, 0.2844, 0.221, and 0.1817 nm. Dilatometry curves of Z-268 also confirmed this with a characteristic hysteresis indicating transformation of monoclinic into tetragonal ZrO_2 (Fig. 1). According to petrographic analysis, baddeleyite in the Z-268 structure existed as round crystals of dimensions 50 – 100 μm and skeletal crystals of length up to 0.10 – 0.15 mm that were divided by glass phase, which occupied 50% of the sample volume (Fig. 2*a*). Because baddeleyite was the only crystalline part of the structure and silica together with impurity oxides (Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO) formed the glass phase, the obtained fused refractory was classified as a baddeleyite-silica material (BSM). Thus, all operating characteristics of these materials were determined by the structural components, i.e., baddeleyite and silica glass phase.

Preliminary meltings showed that the zircon melt could be poured into a form only if forcing melting regimes with significant overheating were used. This led to excessive consumption of electrical energy. Therefore, a charge with calcined soda, boric acid, and alumina additives was melted to enhance the processing of the melt and casting by increasing the electrical conductivity and decreasing the melt viscosity. This produced refractories with sodium silicate (Z-269, Z-270) and aluminoborosilicate glass phases (Z-271, Z-273). It was assumed that the aluminoborosilicate glass phase with increased heat resistance would improve annealing of the castings. Test melts showed that castings of refractories with an altered glass-phase composition did not have cracks and chips and were characterized by a dense structure and low

TABLE 1. Compositions and Properties of Fused Cast Zircon Materials

Material	Chemical composition, %						Apparent density, g/cm^3	Open porosity, %	T_{sgs},*2 °C
	ZrO_2	SiO_2	Al_2O_3	Na_2O	B_2O_3	Me_xO_y*1			
Z-268	66.65	32.54	0.20	—	—	0.61	4.05	1.2	1500
Z-269	66.14	32.00	0.15	1.43	—	0.28	3.96	1.0	1500
Z-270	65.50	30.86	0.15	2.75	—	0.74	3.94	1.1	1320
Z-271	65.50	31.20	1.02	0.51	1.37	0.40	3.92	0.9	1480
Z-273	64.00	29.50	1.77	0.84	3.55	0.34	3.79	0.9	1315
Z-218P	85.90	10.90	2.34	—	—	0.86	4.32	1.3	—

*1 Impurities (TiO_2 + Fe_2O_3 + CaO + MgO + etc.).

*2 Temperature of start of glass-phase segregation.

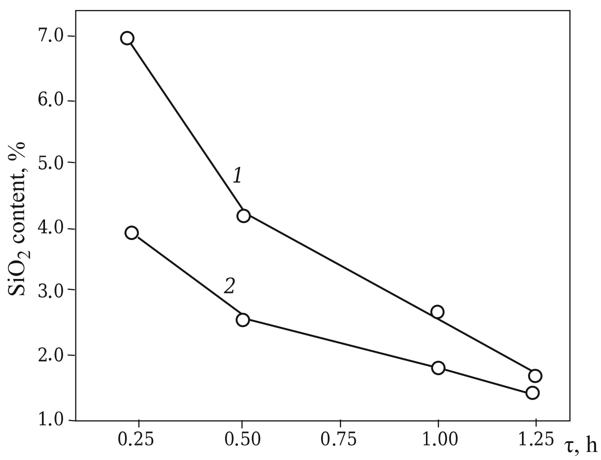

Fig. 3. SiO_2 content in Z-270 as a function of treatment time τ by HF solution (10%) at 20 (*1*) and 50°C (*2*).

TABLE 2. Corrosion Resistance of Fused Cast Zircon Materials

Test conditions			Corrosion rate, mm/d
melt	temperature, °C	time, h	
Refractory Z-268			
Glass E	1450	12	0.9
Glass C52-1	1450	24	0.8
Alloy AK12M2	800	12	0.1
Refractory C-269			
Alloy D16	750	12	0.1

open porosity after annealing under natural conditions (Table 1). X-ray phase analysis of the BSM with an altered glass phase confirmed that their structures were biphasic and analogous to Z-268 with the monoclinic ZrO_2 modification and a glass phase. According to petrographic analysis, all synthesized specimens had the characteristic structure of Z-268 with a tendency to increase the amount of glass phase as the oxide content ($Na_2O + B_2O_3$) increased.

Preliminary tests of the operating properties of the obtained materials showed that they depended on the characteristics of the glass phase. Thus, T_{sgs} during heating decreased from 1500°C (specimen Z-269 with 1.43% Na_2O) to 1320°C (specimen Z-270 with 2.75% Na_2O). The main operating characteristics of the refractories were corrosion resistance, heat resistance, and minimal contamination by destruction products of the refractories in contact with the melt. Table 2 presents corrosion test results under static conditions for melts without basic borosilicate glass E (composition, mass%: SiO_2, 54.0; B_2O_3, 9.0; Al_2O_3, 15.0; CaO, 17.0; MgO, 5.0); of electrovacuum glass C52 – 1 (composition, mass%: SiO_2, 68.09; B_2O_3, 18.9; Al_2O_3, 3.55; Na_2O, 4.5; K_2O, 4.5); Al cast alloy AK12M2 (composition, mass%: Al, 85; Si, 12; Cu, 2); and Al deformed alloy D16 (composition, mass%: Al, 93; Cu, 4.5; Mg, 1.5; Mn, 0.5).

The analysis of the properties of the obtained materials found that they corroded extensively on contact with aggressive mineral melts (glass C52-1 and E), which prevented their use in borosilicate glass manufacturing. However, the high T_{sgs} values of refractories Z-268 and Z-269 indicated that their glass phases were refractory and could probably be used to manufacture high-quality glasses. Tests of molten Z-269 samples in Al alloy melts showed that they had zero wettability and minimal corrosion. Obviously, these BSM (Z-268 and Z-269) could be used in liners of smelter and refiner systems for Al manufacturing.

Possible uses of the molten zircon products to produce raw materials with high contents of ZrO_2 were also studied in addition to the production of fused refractories [2]. The main problem was to study the removal of silica from the fused products as much as possible relative to its content (31 – 32%) in the starting zircon. The first removal method was hydrometallurgical processing of molten zircon products to remove silica from them. Thus, the SiO_2 content was 1.5% in the fused product from treating ground Z-270 with HF solutions (10%) at 50°C for 1.25 h (Fig. 3). It was also shown that leaching of ground granulated material gave high degrees of silica removal.

The second method for removal of silica from zircon was carbothermic melting with a carbon reductant. Thus, melting of zircon concentrate with a carbon reductant produced Z-218P with 10.9% SiO_2, i.e., the SiO_2 content was reduced by almost three times. Material Z-218P consisted of large crystals of baddeleyite as skeletal crystals and oval and round grains up to 0.1-mm in size with average size 0.05 – 0.06 mm (Fig. 2*b*). Although these materials could be used to manufacture fused-cast baddeleyite refractories, wide use of ZrO_2 (sintered refractories, ceramics, abrasives, glassmaking, ferroalloys) would require reducing the Si content to 1 – 2%. This could be achieved by a complex of pyrometallurgical processes (carbothermic melting) and additional leaching of the fused products by fluoride solutions. Considering the pilot nature of carbothermic fusions, the last adjustment of the technology should focus on increasing the efficiency of the reductant, compacting the charge, etc.

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