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FUSION-CAST REFRACTORIES IN THE HIGH-ZIRCONIA REGION OF THE $ZrO_2 - SiO_2 - CaO$ SYSTEM

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The synthesis and properties of fused materials in the $ZrO_2 - SiO_2 - CaO$ system (83.1 – 91.7% ZrO_2 , 0.3 – 9.2% SiO_2 , and 0.6 – 7.8% CaO) are reported. CaO -assisted stabilization of ZrO_2 to yield a cubic modification is reached at a SiO_2 concentration of $\leq 4.3\%$. The arc furnace technology developed can be used to fabricate crucibles, tubes, rings (of diameter 320 mm and height 310 mm), and other shaped components from high-zirconia refractory materials with more than 90% ZrO_2 .

Zirconia-based refractory materials, owing to their high melting point (2420°C) and chemical resistance, are believed to be best suited for service under the conditions of high temperature and exposure to corrosive melts. An inconvenience of the fusion-cast technology of high-zirconia materials (> 65% ZrO_2) is that the necessarily overheated melt, when cast into molds, undergoes rapid crystallization. Another feature to be taken into account when handling ZrO_2 -containing materials is that zirconia undergoes reversible transformation from a monoclinic modification (baddeleyite) to a tetragonal one in the temperature range of 950 – 1200°C. The polymorphic transformations are accompanied by a change in volume, which initiates crack growth and finally failure of the material [1].

The conventional technique to reduce temperature stresses in high-zirconia materials is stress-relief annealing using a high-temperatures furnace [2, 3]. A glass-like phase (if integrated into the refractory's crystalline structure) promotes volume relaxation in the cast material associated with polymorphic transformations. To prevent volume variability, the ZrO_2 structure is stabilized by converting it to a stable high-temperature cubic modification; this is done by introducing structurally close oxides (CaO , MgO , Y_2O_3 , etc.) that are capable of forming stable solid solutions. In practical ceramic technology, CaO is the most-used stabilizer in the $ZrO_2 - CaO$ system [4]. A known fact is that Al_2O_3 and SiO_2 when present in the system inhibit the stabilizing effect of the above additives. To our knowledge, no data on the prepara-

tion of CaO -stabilized fusion-cast ZrO_2 refractories have been reported in the literature.

Here we present results of a study of fused materials in the $ZrO_2 - SiO_2 - CaO$ system containing 83.1 – 91.7% ZrO_2 , 0.3 – 9.2% SiO_2 , and 0.6 – 7.8% CaO (Table 1). Our goal was to determine the limiting concentration of silica at which CaO retains its stabilizing action on zirconium dioxide. To save on the expensive raw material ZrO_2 (the consumption rate was about 100 kg per run), the materials were preliminarily synthesized using a high-frequency unit as described in [5]. Cast ingots of about 6 kg were prepared for use in further experiments.

X-ray phase analysis was carried out using a DRON-1.5 diffractometer (CuK_{α} -radiation). The main crystalline phase of specimen FG-13 (9.2% SiO_2 ; Table 1) is baddeleyite, a

TABLE 1. Chemical Composition of Synthetic Materials

Material (specimen)	Oxide concentration, %					
	ZrO_2	SiO_2	CaO	Fe_2O_3	Al_2O_3	TiO_2
<i>Induction-melted</i>						
FG-13	83.1	9.2	7.2	0.1	0.2	0.2
FG-14	87.6	4.5	7.5	0.1	0.2	0.1
FG-15	91.6	0.2	7.8	0.1	0.2	0.1
<i>Electric arc-melted</i>						
VTs-1	91.2	6.2	0.6	0.1	1.7	0.2
VTs-2	91.7	0.3	7.2	0.2	0.4	0.2

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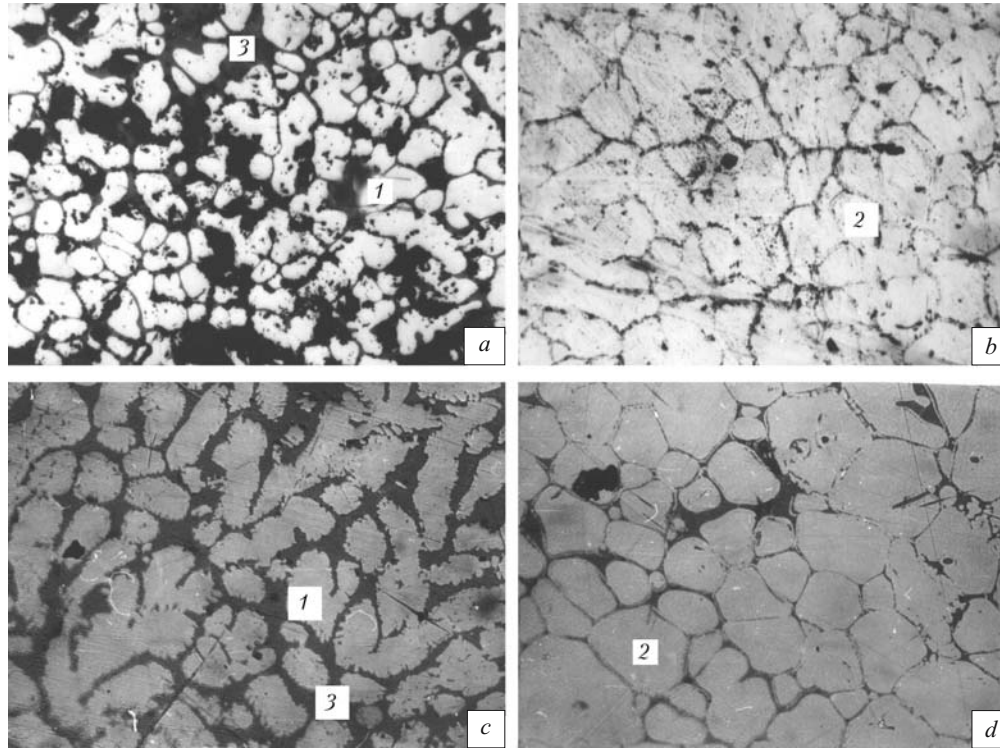


Fig. 1. Photomicrographs of $ZrO_2 - SiO_2 - CaO$ materials: induction-melted specimens FG-13 (*a*), FG-15 (*b*) and arc-melted specimens VTs-1 (*c*) and VTs-2 (*d*): 1) baddeleyite; 2) cubic ZrO_2 ; 3) glass phase. $\times 150$. Viewed in reflected light.

monoclinic ZrO_2 modification ($d = 0.3164, 0.2844, \text{ and } 0.2607 \text{ nm}$). In specimens FG-14 (4.5% SiO_2) and FG-15, the main phase was a ZrO_2 cubic modification ($d = 0.2950, 0.1814, 0.1542, 0.1484, \text{ and } 0.2564 \text{ nm}$).

The FG-13 specimen displayed a partially crystalline structure composed of ZrO_2 crystals $0.02 - 0.3 \text{ mm}$ across embedded in a glass-like phase (Fig. 1*a*). Zirconium dioxide crystallizes in the form of rounded grains or grains of isometric polygonal cross section. With decrease in the mass fraction of silica in the refractory material, the ZrO_2 crystals tended to increase in size, to $0.05 - 1.0 \text{ mm}$ in FG-15 specimen (Fig. 1*b*). Judging from the x-ray analysis data, specimens FG-14 and FG-15 are made up of ZrO_2 cubic crystals.

An induction-melting study has shown that in high-zirconia fused materials of the $ZrO_2 - SiO_2 - CaO$ system the stabilizing effect due to CaO is related to the concentration of silica in the refractory composition. The stabilizing effect due to cubic ZrO_2 was reached in materials at SiO_2 concentration $\leq 4.6\%$. At higher silica concentrations (about 10 wt.%), calcium oxide becomes integrated into a glass-like phase and thus produces no stabilizing effect on ZrO_2 .

The zirconia-based fusion-cast components were prepared using an arc furnace powered from a $450 \text{ kV} \cdot \text{A}$ transformer with the electrode voltage varying in the range $90 - 220 \text{ V}$ was used. Prior to melting high-zirconia materials, the furnace lining was splashed with a scull (protective

slag) of TsrO-B-grade (TU 48-489-87 Specifications, 92.0% $ZrO_2 + 7.0\% SiO_2$). To establish optimum heating regimes, melting operations were preliminarily carried out using a TsrO-B-grade charge material. For an amount of charge of 60 kg and electrode voltage of $110 - 140 \text{ V}$ and current strength of $1.5 - 2.0 \text{ kA}$, the melting time did not exceed 60 min. The molten material was cast in graphite molds with inside dimensions $155 \times 155 \times 250 \text{ mm}$. The ingots of mass about 32 kg were annealed under normal conditions in slow-cooling boxes packed with a heat-insulating material.

The molded VTs-1-grade material prepared from TsrO-B-grade fused zirconia had a compact structure, showed a pronounced shrink hole, and had transverse cracks.

The VTs-2-grade material was prepared using a mixture composed of TsrO-1-grade zirconia (State Standard GOST 21907-76, 99.1% $ZrO_2 +$ commercial-grade calcium carbonate). The molded material had a compact structure, with no visible cracks or streaks. The VTs-1 and VTs-2 fused materials varied in color from bright gray to greenish, depending on the specified oxidation melting regime. For comparison, it was reported in [6] that during the arc reduction melting of a mixture based on baddeleyite and chalk, a deviation from the zirconium dioxide stoichiometry was observed, and the ingots acquired a color dark-gray to black. These materials were reannealed to restore the ZrO_2 stoichiometry.

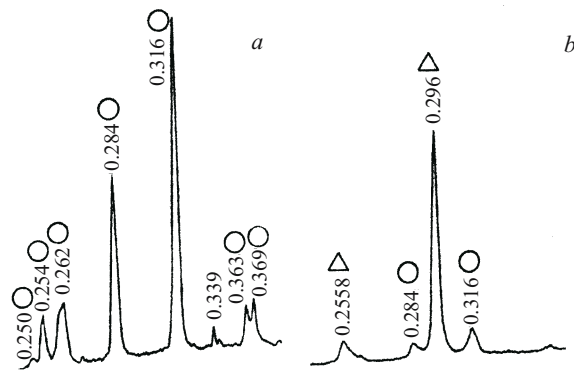


Fig. 2. X-ray diffraction patterns of fused refractories in the ZrO₂ – SiO₂ – CaO system: *a*) VTs-1; *b*) VTs-2; ○) monoclinic ZrO₂; △) cubic ZrO₂.

X-ray phase analysis data showed baddeleyite to be the only crystalline phase in the VTs-1 specimen ($d = 0.316, 0.284, 0.262, 0.254$ nm, etc.) (Fig. 2*a*). In the VTs-2 specimen, the ZrO₂ cubic modification is predominant ($d = 0.296$ and 0.2558 nm), with trace amounts of baddeleyite ($d = 0.316$ and 0.2558 nm) (Fig. 2*b*). The peak $d = 0.339$ nm (Fig. 2*a*) may be assigned to an aluminosilicate compound of the type $3Al_2O_3 \cdot 2SiO_2$ present in a minor amount.

Based on petrographic analysis data, the VTs-1 material had a not fully crystalline (partially crystalline) structure made up of skeletal crystals of baddeleyite $0.01 - 0.3$ mm across embedded in a glass-like phase (Fig. 1*c*). Baddeleyite grains, mostly of rounded or oval shape, might occasionally form separate chain-like aggregates. The glass phase displayed a fine crystalline structure and accounted for about 10 vol.%. The VTs-1 material was composed of a pure ZrO₂ phase and an aluminosilicate glass phase containing 8.8 – 9.4% CaO and 1.9 – 2.9% ZrO₂ (Table 2). The minor raw components TiO₂ and Fe₂O₃ (present in trace amounts) were completely contained within the glassy phase. The increased concentration of Al₂O₃ in both refractory material (see Table 1) and glassy phase comes in part from the fouling

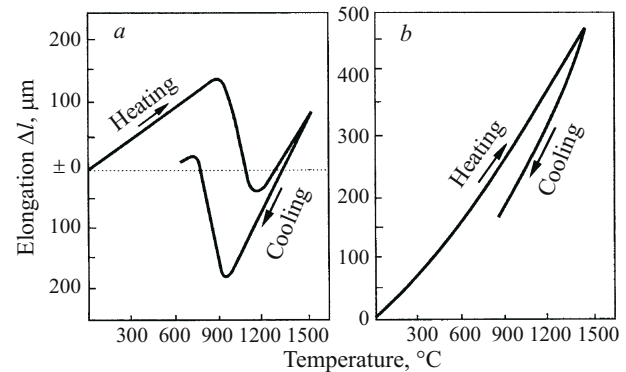


Fig. 3. Dilatometric curves of the fused materials VTs-1 (*a*) and VTs-2 (*b*).

of the melt with corundum impurities from the bottom lining of the arc furnace (at $2400 - 2600^\circ\text{C}$).

The VTs-2 material had likewise a partially crystalline structure composed of zirconia and a small amount of glassy phase (Fig. 1*d*). Crystals $0.15 - 0.35$ mm across viewed in thin section plane had a polygonal isometric shape. A specific feature of the material was that grains of the main crystalline phase were rimmed with a strip $0.002 - 0.003$ mm wide. The structure of most specimens may be characterized as a uniformly granular one.

The glassy phase occurs at the faces of zirconia grains as thin films of width $0.006 - 0.01$ mm. The glassy phase shows a nonuniform distribution within a particular specimen; in places, fine zirconia crystals (about 0.001 mm across) of elongated oval shape are found in small amounts, which imparts a clearly ceramic character to the glassy phase. X-ray microprobe data show (see Table 2) that the VTs-2 specimen features two types of glassy phase: an aluminosilicate phase, high in CaO (33.6 – 34.7%) (compositions 1 – 3), and a calcium silicate phase, high in zirconia (13.3 – 13.5%) (compositions 4 – 6).

The crystalline phase of VTs-2 material [containing 7.0 – 7.8% CaO and some 0.4% of impurity oxides Al₂O₃, TiO₂, and Fe₂O₃ (see Table 2)] is a solid solution in the ZrO₂ – CaO system [4].

TABLE 2. Chemical Composition of High-Zirconia Refractories (based on x-ray microprobe analysis data)

Component	Specimen VTs-1			Specimen VTs-2								
	glass phase, composition			glass phase, composition						crystal, composition		
	1	2	3	1	2	3	4	5	6	1	2	3
SiO ₂	62.7	62.7	62.3	38.5	39.4	37.9	26.5	26.1	26.8	–	–	–
Al ₂ O ₃	22.0	23.2	23.9	22.8	22.5	22.9	1.9	2.3	2.1	0.3	0.2	0.2
CaO	8.8	9.4	9.2	34.4	33.6	34.7	56.2	56.1	55.4	7.8	7.6	7.0
TiO ₂	1.9	1.8	1.8	1.8	1.8	1.6	1.7	2.1	2.2	0.4	0.4	–
Fe ₂ O ₃	1.7	1.0	0.9	1.2	1.1	1.1	0.2	0.1	0.2	–	0.2	0.1
ZrO ₂	2.9	1.9	1.9	1.3	1.6	1.8	13.5	13.3	13.3	91.5	91.6	92.7

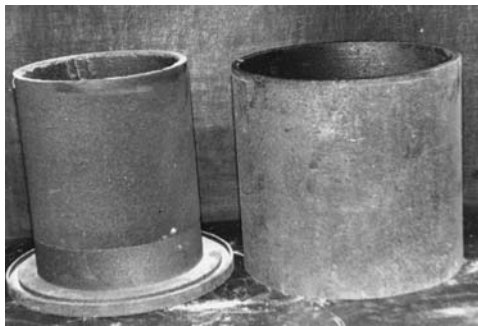


Fig. 4. A graphite mold for making ring components by the casting technique.



Fig. 5. Fusion-cast ring components prepared from a high-zirconia refractory material.

The high degree of stabilization of zirconia with CaO in the VTs-2 specimen has been confirmed by dilatometric test data (Fig. 3); one will note the absence of a hysteretic loop characteristic of baddeleyite-based materials.

Furthermore, cast components shaped as rings of outside diameter 320 mm, wall thickness 30 mm, and height 300 – 310 mm were tested.² Such rings make up part of the

² The help of P. P. Mamochkin is gratefully acknowledged.

lining in induction furnaces that are used to fabricate quartz glass tubes at temperatures as high as 2000°C [7].

To prepare rings, the molten mixture was cast in graphite molds (Fig. 4) that were placed in boxes filled with a heat-insulating pack. The annealing time for components of mass about 40 kg under uncontrolled cooling conditions was two days. The cast rings (Fig. 5) showed no visible cracks and displayed sufficient mechanical strength.

Our study has shown that, in high-zirconia fused materials of the $ZrO_2 - SiO_2 - CaO$ system, the CaO-assisted stabilization of zirconia to yield a cubic modification is reached at a SiO_2 concentration of $\leq 4.3\%$. Arc furnace technology can be used to fabricate crucibles, tubes, rings, and other shaped components from high-zirconia refractory materials with $> 90\%$ ZrO_2 .

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