ZIRCONIUM DIOXIDE REFRACTORY EROSION
IN AN IONIZED COMBUSTION PRODUCT FLOW

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Erosion is considered for zirconium refractories in a hot gas flow. Additional ionization of the flow with 1% of atomic potassium in terms of the mass of combustion products increases the wear, and also causes diffusion in the structure. Consequently, local accumulations of carbon occur in the intergranular zones of a coarse-grained specimen.

Refractory materials based on zirconium dioxide are increasingly used in industry because they have exceptionally high strength (compressive strength up to 3.0 GPa, bending strength 90 MPa), hardness (up to 13 GPa) and refractoriness (> 2500°C), as well as chemical stability [1]. Use is made of materials based on ZrO_2 stabilized with the oxides of scandium, cesium, and yttrium, which are promising for working elements in electricity generators, electrolyzers, and oxygen detectors on account of their high electrical conductivity below 1000°C. Zirconium refractories stabilized with CaO are used at higher temperatures as detectors for the state of oxidation in steel and in electricity stations containing MHD generators [2, 3]. However, although there are extensive published data on the properties of zirconium refractories, the information on erosion of them is inadequate.

Erosion involves the loss of part of the surface for physical reasons [4]. It is in part indistinguishable from corrosion, when the loss of material is caused by chemical interaction. In our studies, the damage to the surface of a zirconium refractory may be considered as an example of pure erosion. It can occur only when the gas flow is at a very high temperature, so one may expect not only erosion but also sublimation of the eroding surface, as well as diffusion of the combustion products into the material. The erosion rate is usually estimated from the specific change over time in the specimen mass and from the depth of the surface damage. That damage is favored by solid particles suspended in the gas flow, which move relative to the surface. One then observes abrasive wear. The name gas-abrasive has been given [5] to that type of wear.

A special plant has been built to examine refractory erosion in a high-speed gas flow by members of the laboratory for physicochemical heat-transfer processes at the FTP Power Institute (Lithuania) [6]; data have been obtained on the effects of temperature and gas speed on the erosion during the first hours of tests on refractories.

A description has been given [7] of the mechanism for the damaging action of a high-speed gas flow at high temperatures, where the detachment flow has given rise to erosion clusters over the entire surface. There are two periods of erosion: during the first, there is more rapid movement of material, while in the second the erosion clusters stabilize and the wear rate is reduced. It has been shown [3] that on high-temperature erosion of a refractory in a gas flow, thermal conductivity estimation enables one to determine the changes in porosity and microstructure, and also the ageing processes in corundum, periclase, and zirconium refractories. These changes in the first few hours are related to grain growth, impurity diffusion, and loss of part of the surface.

The hot gas source was a combustion chamber handling the burning of a propane-butane mixture in oxygen. We estimated the effects of readily ionized substances on the properties of the materials by fitting a unit supplying an alcoholic solution of KOH. The erosion equipment consisted of the following parts (Fig. 1): a channel containing the specimens, outside heating ovens, the combustion chamber for burning the fuel mixture in oxygen, power supplies, a system for supplying the ionizable additive, and measuring instruments and regulating devices. The channel (Fig. 1) included a metal jacket with lining *4*, which contained the

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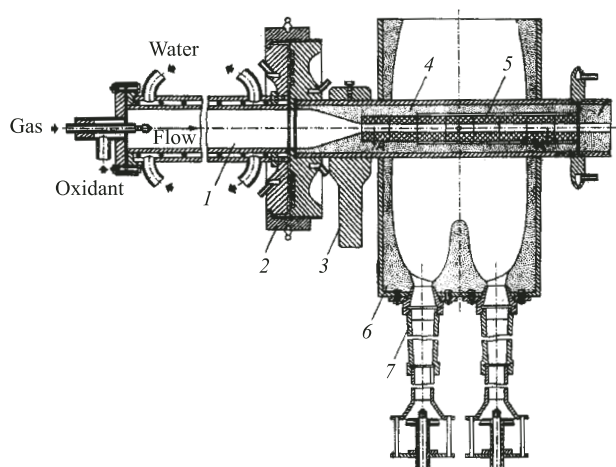
Fig. 1. Apparatus for determining the mass loss of the materials in a combustion product flow: *1*) combustion chamber; *2*) connecting coupler; *3*) support; *4*) channel (lining); *5*) specimen; *6*) outside heating oven; *7*) burners.

TABLE 1. Initial Compositions in % of Specimens

Specimen composition	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	R_2O	$ZrO_2 + HfO_2$
1	0.30	0.78	0.31	0.16	4.45	0.14	0.05	93.81
2	0.90	0.67	0.93	0.10	6.00	0.12	0.17	91.11

TABLE 2. Characteristics of Specimens for Determining Gas-Flow Erosion

Specimen composition	Structure	Phase content, %		Density after firing at 1750°C for 6 h, kg/m³
		cubic	monoclinic	
1	Coarse-grained	74	26	4330
2	Fine-grained	100	–	5450

specimens *5*. The input part of the channel directly adjoining the combustion chamber *1* served to direct and form the flow and had a smooth junction. The three specimens were placed in the channel in such a way that the axes of their central holes completely coincided with the channel symmetry axis. The outside heating and temperature equalization in the channel was based on the oven *6* providing preliminary heating of the channel with inadequately thermally stable specimens (up to 950 – 1150°C).

The purpose of the study was to compare the erosion of a ZrO_2-based refractory in hot unionized combustion products with that in ionized ones (times up to 30 h) and also to evaluate certain changes in the microstructure. We used specimens of ZrO_2-based refractory partially or completely stabilized with calcium oxide.

Calcium oxide stabilizes monoclinic ZrO_2 by the formation of a substitutional solid solution involving the added oxide entering the ZrO_2. In the present case, the stabilizer was CaO, where the ionic radius of Ca^{2+} at 0.106 nm was close to that of Zr^{4+} (0.087 nm) [8]. The stabilized ZrO_2 is a solid solution of the stabilizer oxide and has a cubic (pseudocubic) form, which is stable over a wide temperature range. The complete stabilization of ZrO_2 by electromelting or sintering at 1750°C requires 5 – 6% CaO [9]. We use specimens of composition 1 with partial ZrO_2 stabilization (CaO 4.45%) and specimens of composition 2 with completely stabilized ZrO_2 (CaO 6.0%). Tables 1 and 2 give the chemical compositions and other characteristics of the refractories based on ZrO_2.

The specimens were made as hollow cylinders of internal diameter in the channel 8 mm, outside diameter 30 mm, and length 32 mm. A channel assembled from seven specimens was heated at 400°C/h to 1200°C by gradually increasing the fuel flow. The temperature was raised to 2050°C by burning the propane-butane mixture in oxygen in the combustion

chamber. After the run, the channel containing the specimens was cooled slowly on a set program by reducing the fuel flow, such that on cooling the specimens did not break from thermal shock. The erosion rate m_e is [6] given by

$$m_e = \Delta G/F\tau, \qquad (1)$$

in which ΔG is the amount of eroded material carried off in g as determined by weighing the specimen before and after test (at room temperature), while τ is the duration of the experiment in sec and F is the area of the eroded surface in m^2.

The ZrO_2 refractory erosion tests were performed in a flow of hot combustion products without ionizer or with the addition of 1% of atomic calcium by weight of the combustion products. The neutral components of the gas were ionized by collision with the heavy particles (potassium atoms) with water molecules and by collision of electrons with the neutral components of the plasma. The intensity of the first process is dependent on the gas temperature, while that of the second is dependent on the electron temperature [10].

It is found [11] that the ionized gas differs in properties from ordinary gases in that its pressure is lower and its thermal capacity is higher, so there are various forms of interaction between particles in such gases. In an unionized gas, there are van der Waals forces between the particles, while in the ionized case there are Coulomb forces, which are inversely proportional to the square of the distance between particles. The Coulomb forces are of long range by comparison with the van der Waals one, so the force interaction between the particles occurs at larger distances in an ionized gas. We observed partial organization of the gas, which may be considered as a mixture of three ideal gases: neutral atoms, ions, and electrons. It is assumed that there is thermodynamic equilibrium between the atoms, ions, and electrons [11]. The alcoholic KOH solution was injected directly into the combustion chamber, in which the flow speed is lower than in the channel, while the flow temperature is the highest. This is provided by good mixing of the added potassium with the flow, which increases the
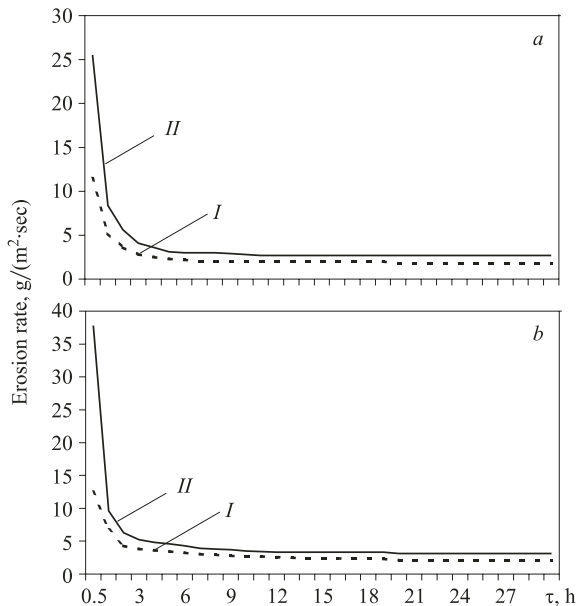
Fig. 2. Erosion rates of CaO-stabilized ZrO$_2$ specimens with compositions 1 (*a*) and 2 (*b*) on testing for up to 30 h: *I*) no ionizer; *II*) with ionizer.

Fig. 3. Zonal microstructure of fine-grained specimen based on ZrO$_2$ (composition 2) after exposure to hot ionized gas for 30 h.

TABLE 3. Atomic Composition of Fine-Grained Structure in a Composition 2 Specimen, Mass %

Zone	C	O	Ca	Zr
Surface (Spectrum 1)	7.66	27.79	3.41	61.44
Deep (Spectrum 2)	8.21	21.51	3.76	66.52

Fig. 4. Microstructure of a coarse-grained ZrO$_2$ specimen (composition 1) after exposure to hot ionized gas for 30 h.

time it spends in the burning zone, and consequently the degree of ionization. We use hydrolysis alcohol and KOH with content of the main substance not less than 85%.

These erosion tests on CaO-stabilized ZrO$_2$ were performed at 2050°C with a gas flow speed in the channel of 500 m/sec (Fig. 2). Tests lasting up to 30 h were performed in a flow of propane-butane-oxygen combustion products without ionizer or with it. We found that the erosion rates for specimens of the two compositions in a flow with ionizer were 10 – 15% larger than in specimens tested without ionizer. There were only minor differences in the character of the erosion rate curves from differences in grain size and structure and degree of stabilization of the ZrO$_2$. The measurements of compositions 1 and 2 showed that the thickness of the wall was reduced after 5 h of test by 0.6 – 0.8 mm. The denser specimens of composition 2 were subject to less erosion.

We used an SEM-LEO electron microscope to examine the microstructure after 30 h of exposure to ionized gas together with an EVO50 (UK), and an energy-dispersive spectrometer EDS. We examined the details of the coarse-grained and fine-grained structures and the atomic mass fractions of the individual elements. Figure 3 shows a cleavage of a specimen with composition 2 with the zone formed in it at the surface to a depth of 1 – 2 mm. Table 3 gives the atomic composition of the structure in the individual zones. It is evident from Table 3 that the zirconium content in the surface zone of the composition 2 specimen was somewhat less than that at depth. The results were very different when the ionized gas acted on specimens of coarse-grained composition 1 (Fig. 4). The microstructure of the surface zone in a composition 1 specimen is an almost
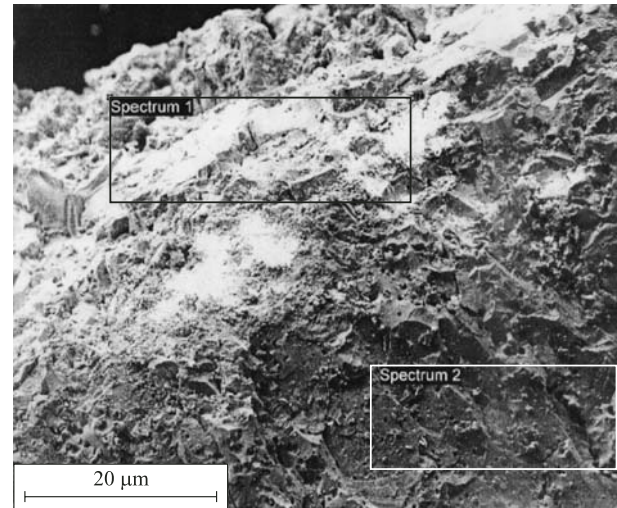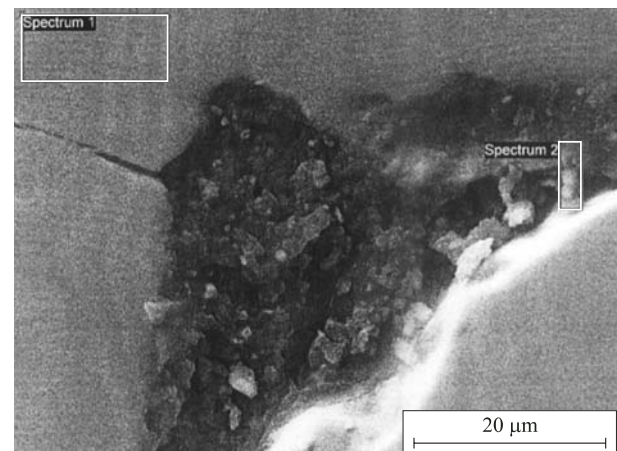
homogeneous layer of zirconium and calcium oxides, while the space between grains is filled by fine-crystal material. Table 4 gives the atomic compositions of the surface and intergranular zones of a composition 1 specimen, which shows that they differ radically. In the intergrain zone of the composition 1 specimen, there is a very considerable accumulation of carbon, which in individual cleavages formed dark spots, while the zirconium content in that zone was very low. That zone also contains calcium atoms and other elements not found in the surface zone.

TABLE 4. Atomic Composition of Coarse-Grained Structure in a Composition 1 Specimen, Mass %

Zone	C	O	Na	Al	Si	K	Ca	Zr
Surface (Spectrum 1)	8.36	20.90	–	–	–	–	3.71	67.03
Intergranular (Spectrum 2)	70.15	13.00	0.58	0.91	1.46	0.53	3.94	9.43

When specimens containing dark spots were fired at 1300°C for 10 h, there was up to 4.85% mass loss, evidently from the oxidation of the carbon. The mass losses of other specimens on firing did not exceed 0.3%.

CONCLUSIONS

It is found that a hot gas flow from the combustion of a propane-butane mixture in oxygen produces an erosion rate for CaO-stabilized ZrO_2 refractory that decreases over time (30 h). There are three stages: loss of $10 - 12$ g/(m²·sec) over 1 h, loss of $3 - 4$ g/(m²·sec) up to 3 h, and almost undetectable loss on heating in the hot gas flow for 3 to 30 h. In an ionized flow, the erosion rate is $10 - 15\%$ higher than that in an unionized one. There was only a small effect on the 30 h erosion process from the chemical composition of the specimens with ZrO_2 contents from 91 to 94%, or from the microstructure and the density, as well as from the phase contents.

The microstructure changes produced by ionized flow show that there was substantial diffusion, particularly of carbon. In certain intergranular layers, the local production at the grain boundaries attain 70%. Also, a considerable fraction of the ZrO_2 was replaced by other oxygen-combining elements (Al, Si, Ca). Potassium atoms from the gas also penetrate the structure. The properties of a ZrO_2-based refractory are relevant to the prolonged action of hot gases, which determines not only the erosion but also the diffusion of carbon and other elements in the structure.

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