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INTERACTION OF DIOXYZIRCONIUM CERAMICS WITH THE SACRIFICIAL MATERIAL OF THE EUROPEAN REACTOR TRAP

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The present paper discusses the complications that can arise in using in the core melt trap of the European nuclear reactor being designed a sacrificial material of 40% FeO_x*–60%* SiO_2 *composition. The investigation of the interaction of zirconium dioxide ceramics with the sacrificial material has permitted the conclusion that at a local baring of the refractory layer its destruction can occur. The addition of neodymium oxide to the melts lowers erosion and excludes regeneration of the ceramics structure.*

Introduction. At present, the reactors that are being designed and built anew at nuclear power stations are equipped with nuclear reactor core melt traps of various designs as an additional safety measure. In the European Community, a design of the European reactor (EPR) in which much consideration is given to its safety aspects has been elaborated; an external two-chamber melt trap lined with materials based on zirconium dioxide (in particular, with zirconium dioxide ceramics) has been designed.

In an accident, the melt flowing out of the reactor consists of an oxide part (uranium oxide, oxides of fission products, and the oxidized part of the zirconium alloy) and a metal one (molten elements of intravessel metal parts, reactor vessel parts, and the unoxidized part of the zirconium alloy).

To prepare the melt for flowing to the second section of the trap (in particular, for the oxidation of the metal zirconium alloy), sacrificial materials are used. In the initial period, after the melt has flown out of the reactor vessel, zirconium is oxidized and the melt of the hull plate and intravessel metal structures remains unoxidized and does not interact with the refractory lining of the melt trap. At the same time, the sacrificial material melts and interacts with the zirconium alloy and uranium and zirconium oxides.

As a sacrificial material, the design of the EPR reactor trap uses a mixture of the $0.4FeO_x$–$0.6SiO_2$ composition (40% of FeO_x–60% of SiO_2) (here and throughout the text, mass % is used).

In [1–3], the interaction of the components of the metal and oxide melt of the reactor core with zirconium dioxide ceramics has been discussed. However, the investigation of the interaction between the ceramics and the oxides entering into the composition of sacrificial materials also seems to be an important problem. These investigations will make it possible to more clearly visualize the processes that can proceed under the interaction of the mixture of the reactor core and sacrificial material melts with zirconium dioxide ceramics and to choose an optimal composition of sacrificial materials not corroding zirconium dioxide.

The process of oxide–zirconium dioxide interaction begins at the contact boundary at the temperatures of eutectic formation (1600 K for FeO–3% of ZrO_2, 1800 K for Fe_3O_4–20% of ZrO_2, and 1950 K for SiO_2–38% of ZrO_2). Moreover, at lower temperatures there occurs an interaction between silicon dioxide and ferric oxide to form eutectics and a chemical compound: eutectics with 38% of SiO_2 (T_{melt} = 1451 K) and with 24% of SiO_2 (T_{melt} = 1450 K) and a chemical compound–fayalite (Fe_2SiO_4, 29% of SiO_2) (T_{melt} = 1480 K) [4]. In the 40% FeO–60% SiO_2 mixture, no more than 57% of fayalite can be formed, and the rest (≈43%) is SiO_2. Silica forms with ZrO_2 a compound, $ZrSiO_4$ (zircon), that melts with a decomposition at 1950 K [4].

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It is also necessary to take into account the chemical reactions of the calcium oxide contained in the cubic solid solution of zirconium dioxide with the ferric–silicate melt.

While under the interaction of the core melt with ZrO_2 the highest corroding effect is produced by ion oxides [2, 3], the presence in the melt of a sacrificial material silicon oxide increases the probability of corrosion of zirconium dioxide ceramics because of the SiO_2 reactions with ZrO_2 as well as with calcium or yttrium oxides — stabilizing additives in zirconium dioxide ceramics.

The aim of this work is to investigate the chemical stability of zirconium dioxide ceramics to the melt of a sacrificial material based on ferric or silicon oxides to be loaded into the EPR reactor trap.

Analysis of the Operation of the EPR Reactor Trap. According to [5, 6], the probable composition of the melt flowing out of the EPR reactor is as follows: 137 tons of UO_2, 30 tons of ZrO_2, 15 tons of Zr, and ~100 tons of steel. The melt temperature reaches 2700 K.

The outgoing melt gets into the first chamber of the trap lined with a ZrO_2-based refractory material (the layer thickness is 210–230 mm, the mass is ~58 tons). The outer surface of the refractory is coated with an ~500-mm-thick layer of the sacrificial material whose total mass is 95 tons (38 tons of FeO_x and 57 tons of SiO_2).

The melt stays in the chamber for about an hour. The temperature of the sacrificial material melt thereby is no less than 2500 K. During this time the entire metal zirconium should oxidize to ZrO_2. For 15 tons of zirconium to get oxidized, about 19 tons of iron oxide will be required. In so doing, ~14 tons of metal iron is formed. The mixture of the melt and the sacrificial material will have the following composition: 137 tons of UO_2, 51 tons of ZrO_2, 19 tons of Fe_3O_4, 57 tons of SiO_2, and 110–120 tons of steel.

It is assumed that under standard conditions the melt interacts only with the sacrificial material. However, nonstandard situations are possible, where a local baring of the refractory layer and an immediate contact of the melt mixture and the sacrificial material with ZrO_2 occur [7].

Earlier it was shown that the 15–60-min action on zirconium dioxide refractories of melts containing 50.5% of UO_2, 25.5% of ZrO_2, 15% of Fe_2O_3, 6.4% of Cr_2O_3, and 2.6% of NiO [8] or 46.6% of UO_2, 17.6% of ZrO_2, and 35.5% of Fe_2O_3 [9] at a temperature of 2100–2300 K and a refractory/melt ratio of 1/1–1/3 leads to erosion and impregnation of the refractory, but the ceramic frame in it is preserved and the refractory can perform preservative functions. The basic corroding agent in the melt is iron oxide forming with ZrO_2 a low-temperature eutectics [4].

The employment in the trap of sacrificial materials based on a mixture of iron and silicon oxides raises the question of their possible interaction with a zirconium dioxide refractory. To this end, we have investigated such an interaction as well as its weakening due to the introduction of neodymium oxide.

Chemical compounds melting without decomposition have a short-range order in the melt near the liquidus boundary [10]. However, a considerable excess of the liquidus temperature leads to the disappearance of the short-range order and the overheated melt represents a chaotic mixture of ions interacting with the ceramics.

Investigated Materials and Experimental Conditions. The objects of the investigation were: granular ceramics based on CaO-stabilized cubic zirconium dioxide of porosity 16–18%. The ceramics body is composed of coarse 2.5–0.2-mm crystal grains forming a crystal frame and fine 60–10-μm grains binding the coarse grains. The ceramics structure is microjointing with interconnecting pores.

We investigated the action on the ceramics of two sacrificial materials: a mixture of 40% of FeO_x and 60% of SiO_2 as well as a mixture of 50% of Nd_2O_3, 20% of FeO_x, and 30% of SiO_2.

Chemically pure silicon oxide and HO-1 neodymium oxide were used. Since neodymium oxide is subject to hydration on a humid air medium, in the initial state it constitutes neodymium hydroxide. However, beginning with 1200 K dehydration of the hydroxide occurs and at the test temperature it appeared in the form of Nd_2O_3. Iron oxides with the general formula FeO_x represented the following mixture: 55% of FeO, 40% of Fe_3O_4, and 5% of Fe.

Tests were carried out for 1 h at $T = 2300$ K in a vacuum furnace in the technical argon atmosphere. With regard for the residual oxygen interaction with the heater tungsten the partial pressure of oxygen (P_{O_2}) at the maximum working temperature was $<1\cdot10^{-7}$ atm. The heating and cooling rate of the specimens was $\sim10^{o}$/min.

Tests were carried out on 65 × 50 × 30-mm ceramic specimens with a mass of ~450 g. Oxide mixtures were briquetted in the form of parallelepipeds on an organic binder without subsequent thermal treatment. The briquettes were placed on the surface of the ceramic specimens. The specimens were set upon a tungsten rest. The interaction of refractories with oxides showed up as an erosion of the contact surface of the specimen and its impregnation with the

TABLE 1. Parameters Characterizing the Experiments and Their Results

Experimental conditions and results	Oxides	
	$0.4FeO_x$–$0.6SiO_2$	$0.2FeO_x$–$0.3SiO_2$–$0.5Nd(OH)_3$
Temperature and duration of experiment	2300 K, 1 h	2300 K, 1 h
Mass of oxides (M_{ox}), g	163	153
Mass of a ceramic specimen (M_{cer}), g	465	460
Mass ratio between oxide and specimen, $K = M_{ox}/M_{cer}$	1:2.85	1:3
Mass loss of melt due to its flowing out of the specimen, g	150	105
Mass loss of ZrO_2 in the hole due to erosion, (M_{ZrO_2}), g	50	No erosion
Mass ratio between oxide and eroded ZrO_2, $L = M_{ox}/M_{ZrO_2}$	1:0.32	0
Phase composition of ceramics specimens after experiments	Decomposition of cubic solid solution of ZrO_2, main phase — monoclinic ZrO_2, in interlayers $Ca_2ZrSi_4O_{12}$, SiO_2, $FeSiO_3$, Ca_2SiO_4	Main phase — cubic solid solution of ZrO_2 with Nd_2O_3, in interlayers $Ca_2Nd_4(SiO_4)_4$, $ZrSiO_4$, $FeSiO_3$, $CaSiO_3$

melt. The impregnation caused a change in the structure of the ceramics. In the case of a small amount of the melt, it was held in the body of the porous ceramics due to the capillary forces, and when a certain limit was exceeded, it flowed out of it.

The mass of the oxide briquette (M_{ox}) and of the ceramic specimen (M_{cer}) was measured before experiments, and after experiments the mass of the ceramic specimen with the melt was determined.

We introduced the parameter K, which is the ratio of the initial mass of oxides studied (M_{ox}) to the mass of the ceramic specimen (M_{cer}) ($K = M_{ox}/M_{cer}$).

Erosion of ceramics was characterized by mass loss of ZrO_2 in the hole (M_{ZrO_2}).

We also introduced the parameter L, which is the ratio of the oxide mass to the mass of reacted ZrO_2 in the hollow ($L = M_{ox}/M_{ZrO_2}$).

After testing, the specimens were investigated by the methods of optical and electron microscopy and by X-ray phase (XPA) and X-ray spectral (XSA) analyses.

Experimental Results on the Estimation of the Melt Interaction with Zirconium Dioxide Ceramics. The experimental results are given in Table 1.

Under interaction the eutectic melts formed penetrate into porous ceramics and leave the contact surface. The dissolution of the ceramics on the contact surface at a fixed temperature goes on until all the briquette material is expended in the melt formation.

A further increase in the temperature leads to the formation of a chemical compound or to a melt enrichment with a refractory component. The surface erosion practically ceases when the whole of the melt penetrates into the ceramics and its content on the surface sharply decreases.

After tests with the EPR sacrificial material ($0.4FeO_x$–$0.6SiO_2$ composition), a specimen erosion is observed. Analysis of the structure and composition has shown that as a result of the interaction with the melt, the initial structure of the ceramics has undergone complete destruction throughout the bulk and ZrO_2 has been recrystallized due to the decomposition of the cubic solid solution. The material is represented by monoclinic ZrO_2 in the form of rounded particles 5–70 μm in diameter surrounded by interlayers of iron and calcium silicates. The interlayer material is mainly in the R-amorphous state. Throughout the cross section of the specimen a small amount of the crystal phase of $Ca_2ZrSi_4O_{12}$ was registered. In the upper part of the specimen, crystalline Fe_2SiO_4, Ca_2SiO_4, Ca_3SiO_5, and SiO_2 were present in small amounts. The content of the initial ZrO_2-based cubic solid solution throughout the cross section constituted 2.5–3%.

Experiments on the investigation of the interaction between the 50% Nd_2O_3–20% FeO_x–30% SiO_2 composition and the zirconium dioxide ceramics have shown the absence of specimen erosion. In the refractory body, changes in the structure took place mainly in the fine-dispersion fraction of ZrO_2. The dominant phase throughout the cross section is cubic zirconium dioxide. In the pores between grains, interlayers of the Fe–Si–Ca-based glassy phase as well as new formations of prismatic form enriched with Nd–Si–Ca and Nd–Fe–Si and linear sizes of 2–7 μm are observed. The CaO going out of the initial solid solution was compensated by the dissolution of Nd_2O_3 in the ZrO_2 lattice. Small amounts of $Ca_2Nd_4(SiO_4)_4$, $ZrSiO_4$, Fe_2SiO_4, and $CaSiO_3$ are registered.

The loss of the melt mass due to its flowing out of the specimen in the second case is 1.5 times smaller than in the first case.

Results and Discussion. In the literature there is no information on the ZrO_2 interaction with fayalite. We have not registered any treble compound in the specimen investigated by us. It may be suggested that the fayalite contacting ZrO_2 dissociated and FeO and SiO_2 interacted with zirconium dioxide. Indeed, our experiments revealed iron and calcium silicates (Fe_2SiO_4, Ca_2SiO_4, Ca_3SiO_5).

Upon cooling of the melt, zirconium dioxide is represented by particles of monoclinic modification due to both its secondary recrystallization from the melt and the CaO going out of stabilized ZrO_2.

The large amount of the glassy phase observed in the specimen is characteristic of compounds of silica, which is a glass-forming oxide.

The introduction of neodymium oxide into the composition of the sacrificial material is due to its higher, compared to zirconium dioxide ceramics, activity of interacting with the oxides and their mixtures under consideration. This activity is associated with the highly developed surface of powder upon $Nd(OH)_3$ dehydration. Neodymium oxide forms with ZrO_2 a wide region of solid solutions. Cubic solid solutions exist in the presence of additives of 20–40 mole % of Nd_2O_3. Thus, the exit of the ZrO_2–CaO solid solution of calcium oxide is compensated by the entry of neodymium oxide into the lattice. The ceramics structure thereby remains unchanged.

The results of the interaction of the mixture of iron and silicon oxides with zirconium dioxide ceramics were obtained at $K = 2.85$, i.e., the amount of ceramics was 2.85 times larger than that of the mixture of oxides. In the case of the interaction of the mixture of the core melt and the sacrificial material with zirconium dioxide ceramics, in the first compartment of the EPR trap the mass ratio between the refractory and oxides K will be about 0.8. Moreover, at a local melt of the sacrificial material layer the unprotected refractory will be subjected to a more intense action of the melt. The rate of the ceramics impregnation with the melt is 1.2–1.5 mm/sec. It may be expected that in 1 h the refractory material will interact with the sacrificial material throughout the layer thickness. The negative result, as to the lining stability, obtained already at $K = 2.85$ points to the danger of using a sacrificial material of the $0.4FeO_x$–$0.6SiO_2$ composition in the melt trap. Such a situation (with respect to the chemical stability of the ceramics) can be eliminated by either changing the ratio between the iron and silicon oxides and going to only the fayalite composition or adding neodymium oxide.

Conclusions. The investigation performed shows that in the case of unsanctioned interaction of the sacrificial material with the refractory material (e.g., at a local baring of the refractory layer) the structure degenerates and the ceramics in destroyed. In so doing, a spread of radioactive products from the containment to the environment can occur.

Preserving the general concept of the EPR project, it is necessary to give consideration to the development of a sacrificial material compatible with zirconium dioxide ceramics.

The addition of neodymium oxide to the sacrificial material considerably decreases the intensity of erosion and degeneration of the ceramics structure.

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