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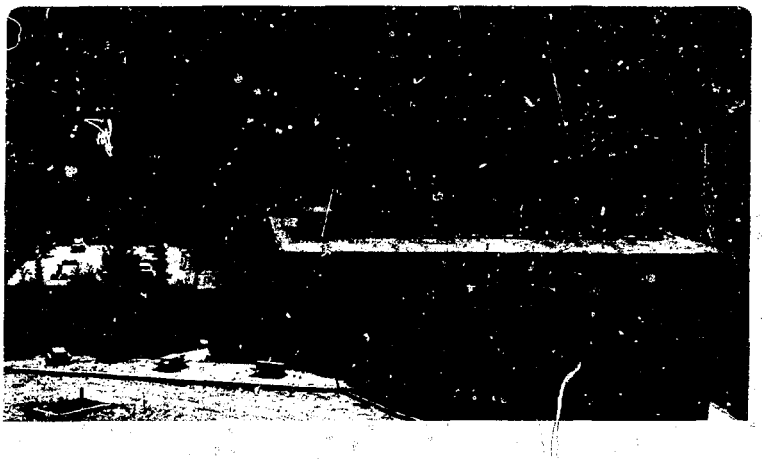

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# REACTION BEHAVIOR OF ZIRCALOY WITH SIMULATED FISSION PRODUCTS*

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The investigation reported in this paper was prompted by the lack of information on the reaction behavior of Zircaloy on long-term exposure to fission product environments in the temperature range 573 - 973 K.

Small Zircaloy-2 (Zircaloy-2 contains by weight 1.5% Sn; 0.15% Fe; 0.08% Cr; 0.05% Ni; rest Zr) strip specimens (ca. 25mm x 3mm x 0.75 mm thick) were exposed to various simulated fission product environments (Cs,I,Br,Cd,In,Sb,Sn,Se as vapor; all others as powders) for times to 5.4 Ms (1500 h) in the temperature range 673 - 973 K. The reaction behavior was characterized by scanning electron microscopy with an EDAX analyzer, optical metallography, and x-ray diffraction.

Cs, $Cs_2O$, CsBr, CsI, RbBr, RbI: Except for $Cs_2O$ the alkali metal compounds did not react with Zircaloy, irrespective of exposure time or temperature. $Cs_2O$ forms a tightly-adhering reaction layer of Cs-Zr-O and $ZrO_2$ compounds on the metal surface which provides an effective barrier to further reaction.

I,Br: Zircaloy showed extensive pitting attack at all temperatures on exposure to the halogens. The reaction products were identified as the respective halides which rapidly hydrolyzed in air.

Se,Te: The specimens (short lengths of tubes, 11.75mm O.D x 0.8 mm wall thickness, exposed to Te) were completely reacted after only 0.9 Ms (250 h) exposure at 973 K (Fig. 1), forming a series of zirconium chalcogenides[1]. At the lower temperatures the reaction was considerably slower.

Ru,Pd,$RuO_2$: At 973, K Ru and Pd penetrated into the Zircaloy matrix, forming the intermetallics, ZrRu and $ZrRu_2$, and $Zr_2Pd$ and $ZrPd^2$, which

precipitate along the grain boundaries. $RuO_2$, on the other hand, formed a compact gray $ZrO_2$ surface layer, which effectively limited the extent of the reaction.

Mo, $MoO_2$: At 973 K, Mo reacted to form $ZrMo_2$ which precipitated along the grain boundaries. Exposure at lower temperatures resulted only in a thin layer (<2 microns) of $ZrMo_2$ on the surface of the specimens. In contrast to $RuO_2$, $MoO_2$ severely embrittled the specimens, the extent of the reaction increasing with exposure time.

Ag, Cd, In, Sb, Sn: Of these elements only Cd in the vapor state (Cd vapor pressure over molten Cd at 973 K) reacted with the Zircaloy specimens forming $Cd_2Zr$ and $Cd_2Zr_3$ [2]. The relatively small extent of the reaction is probably due to the amount of Cd contacting the specimens.

BaO, SrO: These oxides reacted at 973 K to form the zirconates $BaZrO_3$ and $SrZrO_3$ [2] on the surface of the specimens. The surface layers (200 - 230 microns thick) showed large cracks (Fig. 2) and the extent of the reaction was limited by the length of exposure (0.9 Ms). In addition, embrittlement of the specimens, as observed in tensile tests at room temperature[3], suggested oxygen dissolution in the metal.

$La_2O_3$, $Nd_2O_3$, $Y_2O_3$, $CeO_2$: Remarkably, the rare-earth sesquioxides reacted with the Zircaloy specimens at 973 forming a duplex surface oxide layer of the respective zirconates[2] ($RE_2Zr_2O_7$, RE = La, Nd; Y-Zr-O) and $ZrO_2$ Fig. 3a). Thermodynamically the sesquioxides are not favored to react with Zircaloy. However, the formation of a nonstoichiometric double oxide[2] in situ on the surface of the specimens may serve as a

means of transfering oxygen from the sesquioxide to the metal with the formation of $ZrO_2$ and subsequent dissolution of oxygen in the metal.

The reaction with $CeO_2$ at 973 K was expectedly severe; the specimens were completely oxidized within 0.18 Ms (50 h) resulting in a porous structure (Fig. 3b). Further exposure resulted in oxide growth and increased porosity (Fig. 3c). The oxide was identified as consisting of $Ce_2Zr_2O_7$ and $Ce_2Zr_3O_{10}$, and $ZrO_2$.

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3. R. Kohli, "The Mechanical Properties of Zircaloy-2 after Long-Term Exposure to the Alkaline-Earth Oxides", Unpublished SGAE Report, Österreichisches Forschungszentrum Seibersdorf, Austria (1980)

Magnification 5X

Magnification 1000X

XBB 811-381

Fig. 1 Zircaloy Tube Specimen after Reaction with Tellurium at 973 K for 0.9 Ms (250 h)

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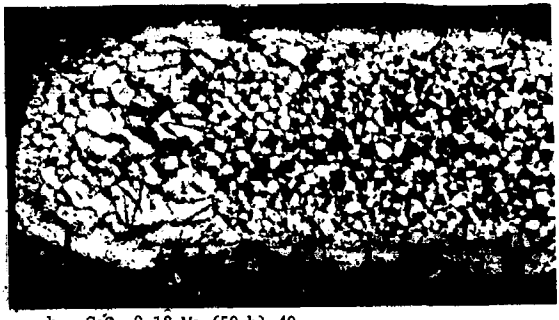
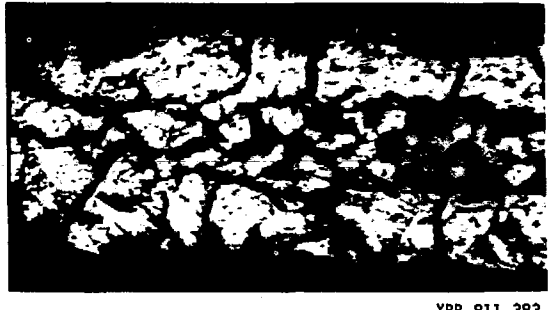
Magnification 80X

Fig. 2 Zircaloy Specimen after Reaction with SrO at 973 K for 0.9 Ms (250 h) showing highly cracked $SrZrO_3$ surface layer

a. $Nd_2O_3$ 0.9 Ms (250 h) 160X



b. $CeO_2$ 0.18 Ms (50 h) 40



c. $CeO_2$ 3.6 Ms (1000 h) 40X

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Fig. 3 Zircaloy Specimens after Reaction with $Nd_2O_3$ and $CeO_2$ at 973 K for Various Times