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TITLE

POSSIBLE CAUSES OF ACCELERATED CORROSION

IN THE ~~KER-1~~ LOG

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POSSIBLE CAUSES OF ACCELERATED CORROSION
IN THE KER-1 TUBE LOOP

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R. L. Dillon

Materials Development Operation
Hanford Laboratories

November 29, 1960

~~RESTRICTED DATA~~

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**POSSIBLE CAUSES OF ACCELERATED CORROSION
IN THE KER-1 LOOP**

R. L. Dillon

The KER-1 Zircaloy process tube extracted from the reactor in May, 1960, is currently being examined in Radiometallurgy with particular attention to an area of heavy oxidation and hydriding revealed during a burst test. The area in question is approximately 1 1/4" wide and extends longitudinally an unknown distance from the points where sections have been taken. The oxide layer of interest is about 8 mils thick at the center, thinning at the edges. The "oxide" is quite adherent with only relatively minor systems of longitudinal cracks observed. There is no corresponding thick oxide on the outer surface of the tube.

The hydride region decreases from an estimated 1,000 to 2,000 ppm at the oxide-metal interface to about 30 ppm at the outer surface. Assuming a linear concentration gradient, the average hydrogen content in the affected zone might be about 750 ppm. (Examination of the metal at the midpoint of the tube section suggests 750 ppm is probably excessive.) The region of high hydride concentration extends circumferentially past the heavily "oxidized" region, presumably because both tube temperature and hydride concentration gradients are favorable to hydrogen diffusion.

Tube History

The tube has operated at about 500°F outlet for most of its irradiation history.* The hydrided section is located somewhat downstream of the midpoint and probably saw local water temperatures less than 450°F. One rupture occurred in the vicinity of the hydrided zone but the good appearance of the fuel rod does not encourage belief it should be associated with the tube condition.

*D. R. Dickinson has written "KER-1 Operating Summary" to which the reader is referred for details.

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Relation of Oxide Layer and Hydrogen Content

The layer of oxide appears sufficient in extent to account for local hydrogen content. Thus:

$$\begin{aligned} 8 \text{ mils oxide} &= 8 \times 560 \text{ mg/dm}^2 = 4.480 \text{ gms/dm}^2 \text{ O}_2 \text{ reacted,} \\ &= \frac{4.480}{8} = .560 \text{ grams H}_2 \text{ produced} \end{aligned}$$

$$1 \text{ dm}^2 \text{ of } 0.18" \text{ Zr stock weighs } 640 \text{ g} = 293 \text{ gms}$$

$$750 \text{ ppm} \times 293 \text{ gms} = .220 \text{ gms hydrogen (estimated content of metal)}$$

$$\frac{0.220}{0.560} = 39\% \text{ theoretical hydrogen pickup}$$

It appears that the hydrogen present in the tube in the region of heavy oxidation is readily explained in terms of corrosion product hydrogen.

Estimate of Tube Surface Temperature from Heat Transfer Considerations

In calculating the surface temperature of the Zircaloy tube at the oxide-metal interface, the following assumptions are made:

- a) Bulk water temperature 450°F
- b) Oxide thickness 8 mils
- c) Thermal conductivity of the oxide 1 BTU/ft²·hr·°F/ft
- d) Avg heat flux through tube from graphite ~ 5% of total
~ 25,000 BTU/hr·ft²
- e) Max heat flux (due to restricted contact between graphite & tube, local flux perturbations, etc.) = 150,000 BTU/hr·ft²
- f) Heat transfer coefficient across water film 10⁵ BTU/ft²·°F
- g) The oxide layer may be considered infinite in extent

$$\Delta T_{\text{avg}}^{\text{OF}} = \frac{\text{heat flux} \times \text{film thickness (ft)}}{\text{coef. of thermal conductivity}} = \frac{25,000 \times .008}{1 \times 12} = 18^{\circ}\text{F}_{\text{avg}}$$

$$\Delta T_{\text{max}}^{\text{OF}} = \frac{150,000 \times .008}{12 \times 1} = 100^{\circ}\text{F}_{\text{max}}$$

If the stagnant water film is considered:

$$\frac{150,000}{105} = 15^{\circ}\text{F}$$

$$\Delta T_{\text{max}}^{\text{OF}} = 115^{\circ}\text{F}$$

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Maximum Zr surface temperature probably will not exceed 600°F.

Estimate of Temperature from Normal Zircaloy-2 Corrosion Behavior

Referring to corrosion curves published in Lustman and Kerze, it becomes apparent that 8 mils of corrosion of normal Zircaloy-2 would require metal surface temperatures in excess of 800°F. It is quite unlikely that the calculations of internal tube surface temperatures from heat transfer considerations are low by 200°F. One must conclude the high local corrosion rates are associated with some local peculiarity in the metal surface.

Incidentally, the appearance of the external surface of the tube in the affected area and the pattern of hydride distribution across the tube wall make a strong argument against high local metal temperatures. The hydrogen distribution, high at the internal surface, low at the outer surface, indicate the tube was cooler at the inner than the outer surface. There is abundant evidence that oxidation rates are pressure-independent in the range 1500 psi - 1 mm, which approximates the water vapor pressure inside and outside the tube. Since the oxide on the hot outside surface of the tube was normal, a fraction of a mil, it is difficult to argue the internal surface of the tube was abnormally hot.

Acceleration of Corrosion Rates

The examination of the heavily oxidized area of the tube indicates the high corrosion rates were associated with local surface contamination or metal quality rather than abnormal metal temperature. Possible surface contaminants are copper, incompletely removed after the tube extrusion; and residual fluoride ion from the tube etching process. These two kinds of contamination have been observed to accelerate corrosion during exposure to 680°F water and 750°F steam. Corrosion and Coatings Operation has not

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studied the effects of copper or acid staining at lower temperatures, so it is not entirely certain that observed rates are satisfactorily accounted for. Nor should the possibility of contamination by some less-common agent be excluded at this point.

HAP0 experience with etching and autoclaving of PRTR process tubes has shown very few local areas of poor metal quality unrelated to surface contamination. In fact, only one such incident is thought to have occurred in the 85+ PRTR tubes inspected. However, at the time the KER tubes were fabricated, the tube extrusion art was rather primitive. All sorts of fabrication artifacts were then more probable than with current levels of experience.

Tube Examination

The KER-1 tube examination described here points to surface contamination or metal quality as the source of the accelerated corrosion and metal hydriding noted locally in the tube. It is intended in the following to suggest analytical methods (and other procedures) which might assist in the post mortem. The very competent tube examination program conducted by Mr. Defferding and Mr. Teats is understood by the writer to include all or most of the recommended analyses. The purpose of listing the analyses here is to indicate, briefly, how the cause of accelerated corrosion will be looked for.

A. Complete tube inspection to delineate the extent of the accelerated corrosion.

1. Crush test of sections of tube taken at six- to twelve-inch intervals to indicate the presence of embrittled metal.

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2. Evaluation of a heavy etch to delineate areas of unusually severe oxidation. (This may require vapor blasting to remove the normal oxide layer, in which case this procedure becomes impractical.)
- B. Identification of "oxide-like" layer over hydrided portion of tube.
X-ray analysis of material ground from sample has verified ZrO_2 .
- C. Analysis for surface contamination
 1. Spectrographic analysis of oxide ground from the area of heavy oxidation.
 2. Activation analysis of oxide grindings.
 3. Spectrographic analysis of metal beneath the heavy oxide.
 4. Autoclave-testing of cold portions of tube to establish general levels of contamination.
- D. Metal quality in affected zone
 1. Careful metallographic examination of metal structure with emphasis on presence of proper level of second-phase material and its local distribution.
 2. Possible autoclave test of small section of metal from affected zone after removal of existing oxide and etching.
 3. Autoclave testing as in C.4 for general level of tube corrosion resistance.

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