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TESTS FOR SURFACE CONTAMINANTS ON ZIRCALOY-2

BY

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AND DEVELOPMENT OPERATION

February 1, 1960

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TESTS FOR SURFACE CONTAMINANTS ON ZIRCALOY-2

INTRODUCTION

Nuclear fuel elements clad with Zircaloy-2 by the coextrusion techniques currently employed are subject to objectionable surface contamination of four principal types:

(a) Residual copper remaining in massive islands or thin films on the Zircaloy surface.
(b) A Zr-Cu alloy at the surface; the copper diffused into the Zircaloy base, sometimes to a depth of several mils.
(c) Uranium contamination in the closure, resulting from fusion and intermixing of incompletely removed core material during closure welding.
(d) Retention of fluoride films developed during the pickling operation.

The uranium[1] and the fluoride[2] contamination are known to cause accelerated corrosion of the Zircaloy in high temperature water, and it is strongly suspected that copper contamination may lead to a similar effect. Consequently, there is need for non-destructive means of detecting these contaminants to insure their removal before autoclaving the fuel elements.

SUMMARY

This report describes non-destructive test methods for detecting and locating the position of uranium, copper, and fluoride contaminants on Zircaloy-2 surfaces.

Principles of Electrography

An excellent discussion of the electrographic technique is given by Hermance and Wadlow[3] of Bell Telephone Laboratories. This method, which has been adapted to the present problem, has as its basis the fact that many metals dispel ions into an electrolyte when made the anode of an electrolytic cell. If the electrolyte is retained among the pores of filter paper and held in contact with the anode, the dispelled ions of both the substrate metal and its metallic contaminants are kept from moving far from their point of entry. If the electrolyte contains a precipitating agent, the ions become still more firmly fixed in the paper. Application of a suitable reagent to the paper now develops a characteristic color for specific ions if they are present in concentrations within the sensitivity of the reagent. The concentration of the contaminant in the filter paper may be

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[1] Personal communication from W. L. Wyman.

[2] Shannon, D. W., "Etching and Autoclave Testing Zircaloy-2," HW-58633, January 2, 1959.

[3] Hermance, H. W., and H. V. Wadlow, "Electro Spot Testing and Electrography," Symposium on Rapid Methods for the Identification of Metals, ASTM Publication STP #98, June 28, 1949.

built up to any desired level by prolonging or intensifying the electrolysis so long as the supply of contaminating material lasts on the test object. Thus the paper forms a mirror-image map of the distribution of the contaminant on the surface.

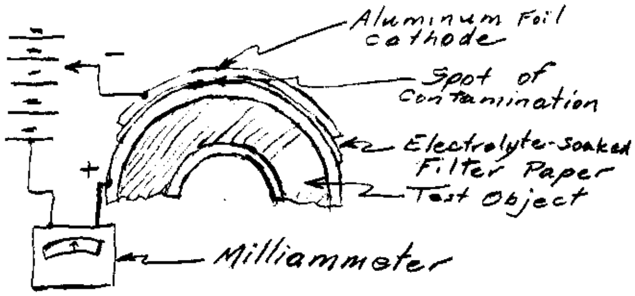

FIG. 1

Schematic of Electrographic Test.

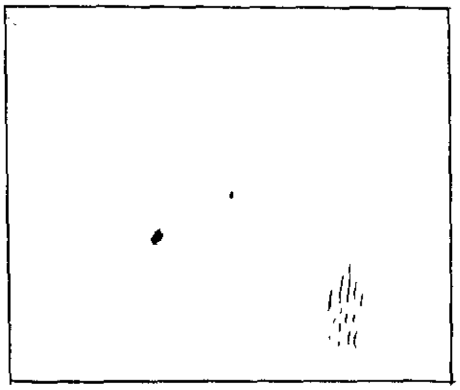

FIG 2

Typical Appearance of Test Paper after Development.

1. Test for Massive Copper Contamination on Zircaloy-2.

   a. Electrolyte: 1/2 M. Na_2CO_3, 3 pts; 1/2 M. $NaNO_3$, 1 pt.
   b. Applied voltage: 3 V, gradually increased to $\sim$12 V as current drops due to oxide film formed on Zircaloy-2. Maintain current density of 2-4 ma/cm^2.
   c. Time of electrolyzing: Until current becomes constant, or only slowly changing. (Ca. 30 sec.).
   d. Detector: 0.5% alcohol solution of α-Benzoin Oxime.
   e. Developer: Fumes from NH_4OH.

The jacket should be wiped with Kleenex soaked in Xylene or similar solvent to remove fingerprints, etc., followed by a dry wipe, before beginning the electrolysis. The apparatus is arranged as shown in Figure 1. The cathode, a thin aluminum sheet, is held firmly against the work with a strip of filter paper, moistened with the electrolyte, sandwiched between the aluminum and the Zircaloy-2 jacket. Neither zirconium nor aluminum interfere with the action of the reagent.

With the milliammeter switched to the 100 ma range, three volts are applied across the electrographic cell. A high (ca. 100 ma) current flows momentarily, rapidly dropping to nearly zero. The voltage is increased as necessary to maintain about 2-4 ma/cm^2 current density until at about 18 V the current is dropping very slowly (about 30 sec. elapsed time).

The filter paper is then removed, and on the side that had been in contact with the jacket surface suspected of copper contamination, a few drops of the α-Benzoin Oxime copper test solution is spread. A convenient way of applying the test solution is to place a few drops on a clean watch-glass and lay the filter paper face down in the puddle, moving it about to insure complete coverage of the surface. Where copper ions have been driven into the filter paper, a green spot now becomes apparent, the intensity of the color being dependent chiefly upon the concentration of the copper on the Zircaloy surface, the current density during the electrolytic action, and the duration of current flow. The intensity of the green copper indication is heightened by exposing the moist filter paper to ammonia fumes. In this way, copper concentrations too low to develop a color when treated with the detector solution alone become clearly visible.

If the filter paper and the surface being tested are marked with index lines before separating them to develop the color, the positions of the contaminated areas may be precisely located by comparison with the developed test paper.

2. Test for Copper Diffused into Zircaloy-2.

The conditions and equipment are the same as above except that a dilute solution of HNO_3-HF is used for the electrolyte. This solution is made by adding five drops of 48% HF to 2 ml of conc. HNO_3 and diluting the mixture with distilled water to 100 ml volume.

3. Test for Uranium or Iron Alloyed with Zircaloy-2 (principally in weld beads).

   a. Electrolyte: 1/2 M. $NaNO_3$, 1 pt; 1/2 M. Na_2CO_3, 1 pt.
   b. Applied voltage: 3 V, gradually increased or decreased as necessary to maintain 2-4 ma/cm^2 current density. (Whether the current increases or decreases is largely determined by the relative size of the contaminated area and the concentration of uranium therein.)
   c. Time of electrolyzing: 10-30 sec. depending on uranium concentration. Lower concentrations require longer electrolysis time.
   d. Detector: 1% alcohol solution of 8-Hydroxy Quinoline ("Oxine").
   e. Developer: NH_3 fumes.

The area to be tested is examined for cleanliness. If it is sooty or coated with oxide, spattered droplets from the weld, etc., it should be briefly etched in HNO_3-HF to remove superficial contamination, following which it is thoroughly rinsed and dried. The filter paper is soaked, and kept quite moist with the electrolyte during electrolysis to insure the fluid's penetrating into any crevices or indentations in the weld bead surface. This effect is further promoted by using a thin aluminum foil cathode sandwiched between a resilient rubber pad and the moist filter paper, against which the surface to be tested is held during electrolysis, with firm pressure. About .01% Duponol (sodium lauryl sulfate) or other wetting agent added to the electrolyte improves the chances of detecting jacket leaks.

Uranium ions are readily dispelled from the uranium-Zircaloy-2 alloy, so that about 10 seconds current flow is normally adequate to deposit a detectable amount in the filter paper. Patches of very low uranium concentration may require longer time; thus, where uranium contamination is suspected, if negative results are obtained on short electrolyzing, a repeat run should be made with up to 30 seconds electrolyzing period.

After completion of the electrolysis, the filter paper is removed and treated with the "Oxine" test reagent in the same manner described under the test procedure for copper contamination, followed by exposure to ammonia fumes. A positive indication for uranium consists of a bright brown-orange coloration where the uranium ions were deposited on the filter paper; for iron, the developed color is black, and when treated with ammonia fumes it forms an oily-looking iridescent scum on the surface.

An alternate method, and one which appears to be a little more sensitive, though unfortunately more laborious, is to polish the suspected surface bright with fine abrasive cloth, wiping dust away with clean cloth or Kleenex tissue. The suspected area is then immersed in the electrolyte, the test object being made the anode. The aluminum foil cathode is immersed in the electrolyte in such a manner as to surround the anode, with a layer of filter paper interposed between them to prevent shorting. Electrolysis is continued at 4-10 ma/cm^2 for about 25 seconds. The test object is then removed, washed, dried and examined. Under the test conditions, pure Zircaloy becomes bluish-black coated, while a uranium-contaminated spot, even one very low in uranium, develops a reddish rusty coloration, more pronounced with increased concentration. It is not necessary to apply the uranium-detector solution to the metal to obtain this positive indication, but only to compare the colors of the areas. Repeat runs require only repolishing of the surface to remove the film, followed by a repetition of the electrolysis procedure.

Since, under the test conditions, most contaminating ions are dispelled more readily than those of the Zircaloy substrate, prolonged or repeated electrolysis tends to form pits at the site of uranium-contamination. Thus the development of pits by electrolysis is another indication of surface contamination, though the identity of the contaminant is not specifically revealed by the appearance of the pits.

4. Test for Fluoride Deposited as Film on Zircaloy-2 Surface, Adsorbed on Surface, or Concealed in Crevices Opening to Surface.

This condition may be general or localized. It occurs almost exclusively on regions of the fuel element where incomplete or inadequate preparative procedures were followed, such as insufficient rinsing following the HNO_3-HF pickle. The presence of fluoride ion on the Zircaloy-2 surface at the time of autoclaving, or presumably, during in-reactor irradiation, is reported[2] to cause accelerated corrosion of the jacket. Hence it is desirable to establish that the fuel elements are free of fluoride before autoclaving them. If they are free from crevices which might hold the HNO_3-HF pickle solution, an optimized process would provide for suitable pickling procedures and sufficiently thorough rinsing practice to insure that the

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[2] Op. cit.

fluoride ions are completely removed before autoclaving. Hence, testing for fluorides may serve three useful purposes:

a. Aiding in the selection of optimum procedures for pickling and rinsing Zircaloy-2 clad uranium.
b. Identifying fluoride-contaminated material for reprocessing, before it is ruined in the autoclave.
c. Monitoring the output to determine when laxities arise in pickling and rinsing procedures.

The test procedure is as follows: Collect about 5 ml of washings from the suspected sample. These may be drippings from the element as it drains after final rinse following HNO_3-HF pickle, or, the suspected area may be washed with $\sim$5 ml of 7.2 M HCl (Conc. acid diluted with equal volume of water) or preferably, soaked in the acid for several minutes. If drippings are used they should be acidified with an equal volume of conc. HCl. The strongly acid sample is placed in a 10 ml beaker, and into a similar beaker an equal volume of fluoride-free 7.2 M HCl is poured, to serve as a control. These beakers are set side by side on a white surface such as clean paper. Five drops of the fluoride-test solution, prepared as described below, are added to each of the beakers, with thorough stirring, after which they are allowed to stand a few minutes. If fluoride is present in the test sample, the pink color changes through orange to yellow, while the control sample remains pink. The rate of color change is dependent principally upon the fluoride ion concentration, although it is affected also by the temperature and by the concentration of the zirconium-alizarin lake (supplied by the test solution). In development tests, a .5 mg lump of NaF dissolved in 100 ml of water caused the color change to take place in about one minute at room temperature.

Preparation of Fluoride Test Solution

This procedure is based on the instructions given by Stone[4] but has been necessarily modified to make use of available materials. The zirconium dichloride ($ZrCl_2$) called for in this reference was found to be inaccessible; in fact, further study indicates its properties to be incompatible with the desired use.[5] Some fresh $ZrCl_4$ was procured and used in its stead.

A saturated solution of $ZrCl_4$ in ethyl alcohol is diluted with an equal volume of conc. (37%) HCl. This forms a white precipitate, which is thoroughly stirred to form a mushy slurry. Distilled water is added, with stirring, until the precipitate just dissolves; then a saturated solution of Alizarin S is added to give a deep wine-red liquid. A few drops of this liquid added to water-clear concentrated or high molality HCl imparts a lasting pale pink coloration. However, the presence of relatively low concentrations of fluoride cause the pink color to fade and convert to yellow as described earlier.

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Fuels Fabrication Development Operation

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[4] Stone, "Detection of Fluoride Ion by Use of Zirconium-Alizarin Lake," J. Ch. Education 8:347 (1931).

[5] Blumenthal, W. B., "The Chemical Behavior of Zirconium," Van Nostrand, 1958, pp 121-22