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POTENTIAL MEASUREMENTS OF ALUMINUM-
CLAD URANIUM SYSTEMS

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May 4, 1955

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The static and dynamic potentials of selected components involved in aluminum-clad uranium composites were measured in boiling distilled water. The component materials studied were aluminum, aluminum-12 w/o silicon (AlSi) alloy, copper, nickel, uranium-12 w/o nickel alloy, and uranium.

The apparent difference in the ability of two cladding systems, aluminum-AlSi-uranium and aluminum-nickel-uranium, to protect uranium in boiling water was caused by factors^(1,2) other than those associated with galvanic corrosion couples. The experimental data, however, support the fact that uranium corrodes faster when coupled to nickel and aluminum than when coupled to AlSi and aluminum.

INTRODUCTION

Two cladding systems for protection of uranium were investigated: aluminum-AlSi-uranium, and aluminum-nickel-uranium or aluminum-copper-nickel-uranium.

Laboratory exposure tests in boiling distilled water showed apparent differences in the ability of the two cladding systems to protect the underlying uranium. With multiplex coatings there is always the possibility of two or more metals being exposed simultaneously to the water. Such exposure would result in galvanic action. Since galvanic corrosion is an electrochemical process, it was believed that knowledge of the electrochemical properties of the metals and metal couples involved might help explain the differences in the observed corrosion behavior.

Details of methods for measurement of static and dynamic potentials in boiling distilled water were not found in the literature. Techniques in use at Battelle over a period of years were applied to the problem.

(1) References at the end.

EXPERIMENTAL WORK

Apparatus and Methods

A schematic drawing of the apparatus used is shown in Figure 1. The flask had five necks, all having standard taper fittings. The two necks not shown in Figure 1 were fitted with a reflux condenser and a thermometer.

The microammeter had a resistance that was small compared to the resistance of the distilled water. The potentiometer was a Leeds and Northrup, line-operated pH-indicator assembly that could measure up to 1400 mv. Its input impedance was 2000 megohms, and thus it drew virtually no current. Heat was supplied to the distilled water by a 1:1 sulfuric acid bath surrounding the flask. The sulfuric acid bath was heated by a shielded electric hot plate. Earlier attempts to heat by a Glas-Col heating mantle resulted in erratic potential measurements because large static charges built up on the outside of the flask. The sulfuric acid, being an electrolyte, drained most of the static charge.

The metal switching box was grounded. The reference electrode was shielded and grounded. Figure 2 is a detailed drawing of the calomel half-cell electrode system. A Perley bridge⁽³⁾ was used to prevent contamination of the main body of distilled water by potassium chloride from the half cell. The Perley bridge is made by inserting a soft glass rivet into a small hole in a Pyrex glass test tube. On cooling, the soft glass rivet contracts to a greater extent than the Pyrex, leaving a fine capillary crack.

The distilled water had a specific resistivity of about 400,000 ohm-cm at 25 C. The resistivity also was determined after each run, and usually had dropped to about 100,000 ohms.

For static potential measurement, only one metal electrode was tested at a time. The electrode was placed in the assembled apparatus just touching the glass rivet of the reference electrode system. Potential measurements were started when the water boiled and were continued until the potential leveled off.

In practical polarization measurements, the changes in potentials for both anode and cathode are determined by use of individual reference electrodes. The corrosion current is measured at the same time. A satisfactory method has not been developed for making these measurements in situ in the couples formed by a basis metal and a coating. Accordingly, it is necessary to use an experimental setup that only simulates the actual couple.

FIGURE 1. SCHEMATIC DRAWING OF APPARATUS USED TO MEASURE POLARIZATION AND CORROSION CURRENT DENSITIES

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FIGURE 2. DETAILS OF REFERENCE ELECTRODE SYSTEM

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For dynamic potential measurements, the two dissimilar metals were positioned in the flask with each electrode just touching the outside of the glass rivet of its respective reference electrode system. The water was heated to boiling, and with the ammeter switch open, the individual static potentials were measured periodically. When the static potentials became fairly constant, the ammeter switch was closed. The current and individual dynamic (polarized) potentials were then measured from time to time.

Results

The static potential measurements for aluminum, aluminum silicide, copper, nickel, uranium, and uranium-12 w/o nickel alloy are given in Table 1. These measurements are those taken after the electrodes had been exposed to boiling water for 2 hr or more. The potentials had stabilized fairly well. However, those for copper and uranium were drifting slightly after 2 hr.

The results of dynamic polarization measurements on three couples are given in Table 2. The open-circuit potentials recorded in Table 2 for a pair of electrodes may be different than those calculated from the values in Table 1. The difference is due to these electrode pairs having been on open circuit for only 20 to 40 min, whereas the values in Table 1 were obtained after a 2-hr or longer exposure.

TABLE 1. STATIC POTENTIAL VALUES FOR INDIVIDUAL METALS INVOLVED IN CLADDING URANIUM

Measurements in Boiling Distilled Water

Cladding System 1	Potential(a)	Cladding System 2	Potential(a)
Aluminum	-0.90	Aluminum	-0.90
AlSi	-0.92	Copper	-0.26 (b)
Uranium	-1.33 (b)	Nickel	-0.545
		UNi (c)	-0.588
		Uranium	-1.33 (b)

(a) Saturated calomel scale.

(b) At the conclusion of the tests, the potentials of these metals were still drifting slowly and can only be considered roughly quantitative.

(c) Eutectic alloy, 12 w/o nickel.

TABLE 2. CORROSION CURRENT DENSITY MEASUREMENTS FOR THREE METAL COUPLES
ENCOUNTERED IN CLADDINGS FOR URANIUM

Couple	Cell Open-Circuit Potential Just Before Closing Circuit, v	Initial Current, μa	Average Current, μa	Average Anode Current Density, μa per cm^2	Closed-Circuit Potential Difference, v
Uranium-AlSi	0.294	25	23.8	3.01	0.045
Uranium-Aluminum	0.208	15	17	2.15	0.040
Uranium-UNi	0.547	46	54.5	6.9	0.075

DISCUSSION

The individual static potential values in Table 1, confirm that uranium is the most active (most easily corroded) metal in the series, and that copper is the most noble (least corroded). If an aluminum cladding were penetrated, copper would accelerate the corrosion of the aluminum. This aluminum-copper couple effect has been observed in other studies.

Static electrode potentials can only indicate the probability of a given reaction occurring. No reliable prediction can be made as to the rate of corrosion. The larger the potential difference between two metals, the greater is the probability for a given galvanic reaction to occur. The driving force (potential difference) in the system aluminum-AlSi-uranium is about 0.4 v. In the case of the system aluminum-nickel-uranium, the driving force is about 0.7 v. With copper in the latter system, aluminum-copper-nickel-uranium, the driving force would be about 1.0 v.

Even though the potential driving force for one reaction is larger than another, it does not follow that the reaction with the larger emf will be more rapid. Current, generated by the galvanic reaction, can cause one or both electrodes to develop a potential different from that when no current is flowing. The effect is to create a back emf or polarization. Polarization could control the speed of a corrosion reaction.

In systems where the electrolyte has a high resistance, the current may be so small that no significant polarization occurs. In this case the rate of galvanic corrosion is controlled by the resistance of the corrodant.

With these systems polarization did not appear too important, because the flow of current was resistance controlled. In Table 2, all three couples

showed a current that was proportional to the open-circuit-potential difference. The fact that there was a closed-circuit-potential difference shows that complete polarization did not occur.

Therefore, under the conditions of measurement, uranium in the uranium-uranium nickel couple would corrode faster than uranium in either uranium-aluminum or the uranium-AlSi couples.

Using the knowledge gained in the above preliminary experiments, it is now possible to modify the techniques so that the actual conditions will be more nearly approached. This in turn will make possible more accurate measurements and provide a better basis for a proposed corrosion mechanism.

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