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ELECTROCHEMICAL AND OTHER STUDIES OF A
URANIUM ALLOY EXHIBITING
STRESS-CORROSION
CRACKING

J. S. Bullock, IV

J. B. Condon

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OAK RIDGE Y-12 PLANT

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**ELECTROCHEMICAL AND OTHER STUDIES OF A URANIUM
ALLOY EXHIBITING STRESS-CORROSION CRACKING**

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Oak Ridge Y-12 Plant

P.O. Box Y, Oak Ridge, Tennessee 37830

operated for the U.S. ATOMIC ENERGY COMMISSION
by UNION CARBIDE CORPORATION—NUCLEAR DIVISION
under Contract W-7405-eng-26

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ABSTRACT

Experiments have been carried out to characterize the electrochemistry and stress-corrosion-cracking properties of a uranium-7.5 weight percent niobium-2.5 weight percent zirconium alloy. Potential variations were detected on the surface of the alloy, and anodic currents were induced in air-equilibrated moisture films on the alloy. Electrochemistry of the stress-corrosion attack was found to be similar to the electrochemistry of the metal having no oxide film. Chloride ions accelerated stress-corrosion cracking apparently because of their ability to penetrate the oxide film on this alloy. Cold-worked alloy was resistant to stress-corrosion cracking, and the stress-corrosion-cracking mechanism was unrelated to a pitting-reaction mechanism.

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SUMMARY

The electrochemistry and stress-corrosion-cracking (SCC) properties of a uranium-7.5 weight percent niobium-2.5 weight percent zirconium alloy (Mulberry) have been studied at the Oak Ridge Y-12 Plant^(a) under a variety of conditions which would give information on its behavior in practical environments. The rest potential of the alloy was studied on a macroscopic scale under varying degrees of surface oxidation in several electrolytes, and on a semi-microscopic scale under a constant degree of oxidation using several electrolytes. The macroscopic rest potential became more noble as oxidation proceeded for all electrolytes used, except halide ion solutions. On the semimicro scale the surface rest potential showed the most inhomogeneity for acidic halide solutions.

The polarization behavior of the alloy was studied in aqueous solution as a function of pH and chloride concentrations, and under a moisture film in equilibrium with atmospheres of varying relative humidity. Flade-like peaks were found in the polarization curves, and polarization currents were generally enhanced by the presence of chloride. Anodic currents under moisture films were found to drop from one cycle to the next.

Measurements of the acoustic emission from stressed alloy specimens were used to determine the relationship of the cracking rate to the environment. Impressed current, pH, halide concentration, and concentration of other ions such as nitrate were found to affect the crack growth rate.

Relationship of the breaking stress, pH, chloride concentration, and potential for Mulberry was studied using stressed wires at high and low stress rates. Similar studies were carried out using unstressed, abraded electrodes. Correlation of these two studies suggested that the SCC properties and bare metal electrochemistry are similarly affected by pH and the chloride concentration.

An experiment was performed which showed that pitting would not be induced in an unstressed sample under conditions which would induce cracking in a stressed sample.

Apparently, the addition of 0.4 weight percent lanthanum to Mulberry increased the resistance of cold-worked material to SCC, but was ineffective in increasing the resistance of Mulberry that was given a subsequent heat treatment.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

INTRODUCTION

GENERAL

Uranium-7.5 weight percent niobium-2.5 weight percent zirconium, usually referred to as Mulberry, is a γ -stabilized uranium alloy that has a high uranium content for favorable nuclear properties, dimensional stability, tarnish resistance, and mechanical properties that can be enhanced by heat treatment.⁽¹⁻³⁾ However, this alloy is subject to stress-corrosion cracking (SCC) and electrochemical corrosion.⁽⁴⁻⁶⁾ This report describes a series of exploratory experiments that were designed to determine the electrochemical characteristics of this alloy and the relationship between its electrochemical behavior and stress-corrosion cracking.

NOMENCLATURE

The phase diagram for the uranium-7.5 weight percent niobium-2.5 weight percent zirconium alloy and the effects of heat treatment on the phase purity and chemical composition of this alloy are described in a report by Dean.⁽²⁾ The possible presence of more than one phase in this alloy on a microscopic scale could possibly result in indigenous couples that could drive an electrochemical corrosion process.

The nomenclature used in the present report to describe the various types of this alloy is:

1. Uranium-7.5 weight percent niobium-2.5 weight percent zirconium alloy that has been water quenched from 800° C and aged in oil for two hours to obtain optimum mechanical properties is referred to as Mulberry.
2. Uranium-7.5 weight percent niobium-2.5 weight percent zirconium alloy that has been annealed at 500° C for two hours, segregating into a two-phase system, and containing a niobium-rich γ phase and an α -uranium phase, is referred to as α, γ Mulberry.

Any modifications to these two types of materials, such as cold working or variations in their chemical composition or heat treatment, are explicitly described. Measurements are also reported for α -phase uranium and for uranium-niobium binary alloys where these measurements contribute to the background information. The formalism and nomenclature used to describe the electrochemical measurements are those described by deButhune.⁽⁷⁾

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STUDIES OF A URANIUM ALLOY EXHIBITING STRESS-CORROSION CRACKING

EFFECT OF OXIDE COATINGS ON REST POTENTIALS

Experimental

Measurements were made of the rest potentials of Mulberry, α,γ_3 Mulberry, and uranium in various electrolytes as a function of the extent of oxidation of the material. These measurements should predict the corrosive driving forces present when more than one of these materials are found in a system.

Measurements were made in 1 N KNO_3 , KOH , K_2SO_4 , KF , KCl , and KBr solutions and in room-temperature-saturated KClO_4 . An Ag-AgCl electrode was used as the standard reference electrode, and values reported here are referenced with respect to the normal hydrogen electrode (NHE).

The four uranium rods and four Mulberry bars used were cleaned by electropolishing in nitric acid before each determination. The α,γ_3 Mulberry bar was abrasively cleaned since treatment in nitric acid was unsatisfactory.^(b) After cleaning, the potential of a sample was measured in one of the solutions. The sample was then baked in air at 90°C for 15 minutes to form an oxide coat and the potential measured again in the same solution. The bake and potential measurement cycle was repeated several times with the same solution to determine any trends in the potential with an increase in oxide coating. This procedure was repeated for each sample.

Results

A summary of the data is presented in Figure 1. Typical scatter in the potential was 0.05 volt. Potentials of the KCl and KBr solutions were affected very little by the amount of oxide coating; whereas, in the other solutions, the potential increased in a fairly reproducible manner. The KF solution was an exception. Its rather unpredictable behavior may be due to flaking or other erratic surface behavior. The increase in potential with a higher degree of oxidation on the electrode surface was to be expected so that the behavior in KOH , KClO_4 , KNO_3 , and K_2SO_4 solutions was readily explainable. Behavior of the chloride and bromide ions was either due to oxide penetration by the ions or an electrode reaction which involved forming a uranyl complex in the presence of the oxide.

The origin of the driving force for an anodic current can be seen in Figure 1. In all solutions, the rest potential of Mulberry is higher than that of pure uranium or of α,γ_3 Mulberry. Therefore, if they were in contact with Mulberry, either the uranium or the α,γ_3 Mulberry would be subject to anodic processes.

(b) Nitric acid is known to have a potentially violent reaction with α,γ_3 Mulberry.

Figure 1. COMPOSITE OF GALVANIC POTENTIALS OF MULBERRY, α, γ_3 -MULBERRY, AND URANIUM IN 1 N KNO₃, 1 N K₂SO₄, SATURATED KClO₄, 1 N KBr, 1 N KOH, and 1 N KCl SOLUTIONS. (Measurements Shown as a Function of Length of Time at a 90° C Air Oxidation)

REST POTENTIAL CONTOUR MAPS

Rationale

The potential differences between uranium, Mulberry, and α, γ_3 Mulberry are not enough to cause concern unless it can be shown that there exists: (1) segregation of these forms in Mulberry, and (2) that this segregation will cause different potentials to be developed on the Mulberry surface. If these potential differences do occur, it is also desirable to know under what conditions (in this case, what contacting electrolyte) these differences are largest. The simplest method for evaluating these differences was to measure the potential at various points on the surface using a contacting droplet of electrolyte.

Experimental

The experimental setup for making rest-potential measurements on a small scale is shown in Figures 2 and 3. Figure 2 shows the 0.5 by 0.5 by 0.125-inch large-grained Mulberry flat in place in its polystyrene jig. The Mulberry was machined, wrapped in tantalum foil, vacuum annealed at 1,200° C for 48 hours, and slowly cooled to room temperature. The grain faces

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Figure 2. POLYSTYRENE JIG AND LARGE-GRAIN MULBERRY SAMPLE USED FOR DETERMINING LOCAL GALVANIC POTENTIAL WITH ELECTROLYTE DROPLETS.

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Figure 3. ASSOCIATED EQUIPMENT USED TO DETERMINE LOCAL GALVANIC POTENTIALS BY SCANNING WITH AN ELECTROLYTE DROPLET.

appeared by virtue of "thermal etching," a crystalline growth process which takes place during vacuum annealing. The actual crystalline phases and their proportions present in this sample have not been established, but other studies⁽³⁾ with similar treatments have shown that there was likely to have been a mixture of the alpha and gamma phases.

The polystyrene jig was moved in relation to the stationary capillary tip by manual operation of a microscope stage equipped with 0.01-inch resolution scales in both the X and Y directions. The Y axis was set to a definite value and the X axis was driven manually at a rate which was reasonably constant during a scan. The Mulberry specimen and saturated calomel electrode (SCE) used as a reference were connected to an electrometer, the output of which was recorded on a two-pen recorder. The second channel was used as an event marker to establish the beginning, the turn-around point, and the end of a scan. At least three scans at each level were made, and the forward portion of the second scan was used to obtain the potential values. A method was tried whereby the tip was allowed to remain at a point until a constant potential was reached, but this method was not only time consuming but less reproducible than the scanning method. The solutions used, in sequence, in the scans were 0.01 *N* KCl, HCl, KNO₃, and NH₃ (aq). The surface of the Mulberry was rinsed in distilled water between solutions. Approximately 275 points per solution were placed in

an array on graph paper, and the proper isopotential contours drawn. In some cases, potentials at specific points changed from one scan to the next, but these changes are not shown.

Results

Even though the atmosphere and temperature were not controlled and the surface preparation of the metal before each series of scans was not identical, certain observations were made:

1. Density of the contours increased in the order $\text{NH}_3(\text{aq}) < \text{KNO}_3 < \text{KCl} < \text{HCl}$ (Figures 4 through 7). The HCl apparently etched through the surface film, exposing less noble areas or sites and yielding more negative values of the potential.
2. The KCl solution gave the next greater concentration of gradients. Since the solution was neutral, the role of chloride as a complexing or penetrating agent may be suspected.
3. The KNO_3 solution (Figure 5) gave fewer features than the KCl solution (Figure 6). This observation is consistent with the acoustic emission experiments described in **Acoustic Emission Studies** (Page 48) in that NO_3^- had an apparent passivating effect even in the presence of chloride.
4. The aqueous ammonia solution map (Figure 4) was drawn at a resolution of 25 millivolts, whereas the others were drawn at 50-millivolt intervals. Even so, the Mulberry surface contacted by the aqueous ammonia solution appeared relatively featureless. In this case, there would be a minimum disruption of the surface film.

Figure 4. GALVANIC POTENTIAL CONTOUR MAP DETERMINED BY SCANNING THE LARGE-GRAINED MULBERRY SAMPLE WITH A 0.01 N NH_3 SOLUTION DROPLET. (Potential Given as Millivolts Versus Normal Hydrogen Electrode)

These maps may be compared with the microstructure of the Mulberry sample presented in Figure 8.

Figure 5. GALVANIC POTENTIAL CONTOUR MAP DETERMINED BY SCANNING THE LARGE-GRAINED MULBERRY SAMPLE WITH A 0.01 N KNO_3 SOLUTION DROPLET. (Potential Given as Millivolts Versus Normal Hydrogen Electrode)

Figure 6. GALVANIC POTENTIAL CONTOUR MAP DETERMINED BY SCANNING THE LARGE-GRAINED MULBERRY SAMPLE WITH A 0.01 N KCl SOLUTION DROPLET. (Potential Given as Millivolts Versus Normal Hydrogen Electrode)

Figure 7. GALVANIC POTENTIAL CONTOUR MAP DETERMINED BY SCANNING THE LARGE-GRAINED MULBERRY SAMPLE WITH A 0.01 N HCl SOLUTION DROPLET. (Potential Given as Millivolts Versus Normal Hydrogen Electrode)

Whether the film was uniformly removed or penetrated and only certain sites were actually more negative, or whether the film thickness was nonuniform and only certain areas were exposed, is a pertinent question. Rest-potential measurements reported previously (**Effect of Oxide Coatings on Rest Potentials**, Page 11) indicated that chloride has a penetrating ability for the oxide on Mulberry; therefore, it is reasonable to assume that the low-potential spots on the surface of the Mulberry were associated with less noble phases in the metal surface.

For KNO_3 , KCl, and HCl (Figures 5 through 7), the left bottom corners of the maps were consistently heavy with contours and the centers were consistently vacant. There were some cases, moreover, of near congruence of the individual features, although an overall comparison was not encouraging. Possibly, the same surface features are being detected in several different solutions.

The potential differences seen on this sample were of sufficient magnitude to indicate that a serious problem exists concerning whether an anodic current will flow in certain areas of the sample in some environments.

POLARIZATION MEASUREMENTS UNDER MOISTURE FILMS

Experimental

Having established the existence of significant potential differences across a Mulberry surface, it would be well to demonstrate that serious corrosion rates (currents) could occur under conditions which would simulate normal atmospheric exposure. The experimental

Figure 8. ACTUAL AREA OF THE LARGE-GRAINED MULBERRY SAMPLE SCANNED BY THE ELECTROLYTE DROPLET. (20X)

arrangement used to obtain polarization curves under moisture films is explained by Tomashov. (8)

Glass microscope slides, an epoxy glue, and 5-mil Mulberry foil were bonded in a jig under pressure into a glass-glue-metal-glue-glass sandwich (Figure 9). Tabs of the Mulberry were allowed to protrude at opposing ends of the cell to provide ohmic contacts. All edges of the sandwich cell were covered with the glue except one, that one being sanded smooth with fine paper and then metallographically polished to expose the metal edges used as electrodes. Nominally, three inches of the metal were exposed.

Metal foils used were 4.5 to 5.0 mils thick, with surface areas for the electrodes of from 8.71 to $9.68 \times 10^2 \text{ cm}^2$, respectively.

This cell was secured to a polystyrene clamp, as shown in Figure 10, such that moistened strips of filter paper could be placed in contact with the glass close to the exposed electrode surface. The clamp was then secured inside a closed chamber made from a desiccator with a polystyrene cover. A liquid was placed in the bottom of the desiccator to provide humidity control. This same liquid was used to moisten the strips of filter paper. Connections from the metal tabs of the cell to the outside were made through the polystyrene cover, and each side of the cell was provided with its own SCE reference, as seen in Figure 10.

For controlled-current polarization experiments, the current was supplied by a 0 to 300-volt power supply whose output was changed to yield the desired current, the current being measured by an electrometer. The current was raised in increments and the potential allowed to stabilize, at which time the potential versus the SCE was read on an electrometer. The voltage sensor was switched to either the cathodically or anodically polarized electrode using a double-pole, double-throw ceramic wafer switch. All connections

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Figure 9. SANDWICH CELL FOR STUDYING THE POLARIZATION BEHAVIOR OF MULBERRY UNDER MOISTURE FILMS. (A Glass-Mulberry-Glass-Mulberry-Glass Sandwich Held Together with Epoxy Glue; the Two Mulberry Strips were Used as Both the Cathode and Anode; 10X)

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Figure 10. SANDWICH CELL SHOWN IN PLACE IN THE CONTROLLED-ATMOSPHERE CHAMBER. (Moist Filter Paper is Used to Provide a Film Contact for the Standard Calomel Electrode)

on the high-impedance side were made with shielded cable up to the desiccator. In some instances, shielding of the desiccator was required. This protection was provided by means of a large, stainless steel mesh cage that completely surrounded the desiccator. This device was especially needed when the polarization curves were taken under conditions of low humidities which resulted in thin moisture films of high resistance. For the controlled potential and for some cases of controlled current, a low-current potentiostat driven by a function generator was used. Using this instrument, the potential of the metal was made to assume a triangular ramp symmetrical about 0.00 volt versus the NHE. The current necessary to obtain the desired potential was recorded simultaneously with the potential.

Results

The manually scanned polarizations gave inconsistent results, probably due to inadequate standardization of the measurement technique. It was then decided to use the potentiostat in preference to the manual method.

A polarization curve (Tafel plot) of the logarithm of the current density versus the potential for a scan using Mulberry foils under 62 percent relative humidity (RH) is shown in Figure 11. The scan was carried out at 0.001 Hz and ± 2.5 volts versus the NHE. The corrosion current ($\sim 3 \times 10^{-7}$ amp/cm²) was somewhat smaller than that seen in the aqueous solution. However, surface-area definition may have been a problem due to a separation of the foil from the glue. The anodic current of the second potential scan was lower than the first, probably because the first scan was taken on a fresh surface, while later scans were performed on metal that had already been heavily oxidized. The zero-current potential (ZCP) coming from the anodic side was about +0.2 volt versus the NHE, while the ZCP coming from the cathodic side was initially about -0.4 volt versus the NHE, becoming more negative with successive scans. Figures 12 and 13 show the pitted surface of the Mulberry after a long series of polarizations.

This experiment showed that at potentials which were previously observed over an aerated Mulberry surface (see the section on **Rest Potential Contour Maps**, Page 13), sufficient currents could be drawn to present a serious corrosion problem. Figures 12 and 13 show that the active area involved in the corrosion was far less than the nominal area, leading to a higher real current density than that indicated.

Figure 11. POLARIZATION CURVE FOR MULBERRY IN THE SANDWICH CELL WITH AN ATMOSPHERIC EXPOSURE AT 62 PERCENT RELATIVE HUMIDITY. (Potential Scanning Rate was 0.001 Hz)

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Figure 12. EDGE OF THE MULBERRY FOIL IN THE SANDWICH CELL AFTER SEVERAL POLARIZATION CYCLES. (Bright Field Illumination; 100X)

G612c

Figure 13. EDGE OF THE MULBERRY FOIL IN THE SANDWICH CELL AFTER SEVERAL POLARIZATION CYCLES. (Bright Field Illumination; 500X)

POLARIZATION STUDIES IN AQUEOUS SOLUTIONS

Experimental

The behavior of this alloy was studied in an aqueous environment since this is the environment contacted by the alloy during preparation and fabrication, and because it is a convenient environment in which to study solute concentration effects.

A potentiostat was constructed which would control either the current passed through the electrolytic cell or the potential between the sample and the standard electrode. This potentiostat could be programmed with an external source such as a function generator or, if desired, a constant current or constant potential could be maintained. In most of this work the potential was made to assume a triangular function by means of an external function generator, the potential and consequent cell current being simultaneously recorded.

The cell used had the working (Mulberry) electrode, the counter electrode, and the standard electrode in separate chambers. These chambers were connected via Teflon-glass stopcocks which prevented gross diffusion by providing a high impedance path from the working electrode chamber to the counter electrode chamber when the stopcock was closed. The working electrode chamber was thermostated and provisions were made for purging the solutions with purified argon to eliminate oxygen. The standard electrode used was a standard calomel electrode (SCE) and the counter electrode was platinum. A Luggin probe (1-mm capillary, to prevent an IR drop from appearing in the potential measured) from the standard cell chamber was arranged coaxially with the current source inlet from the counter electrode chamber for most of the experiments.

All solutions were made from reagent-grade KOH, KCl, HCl, or HNO₃ and near-conductivity-grade water. Periodic checks were made on the conductivity of the water, the highest measurement being 2×10^{-6} mho/cm. Each solution was analyzed, after mixing, for Cl⁻, pH, and carbonate, and spot checks were made on the total elemental content of the solutions by spark source mass spectrometry. After each polarization study, the solutions were checked for Cl⁻, pH, carbonate, and total elements. With the exception of three high-pH solutions which were used for several days, the carbonate content was below 1 ppm. These three high-pH solutions contained 454, 168, and 2.7-ppm carbonate. The worst contaminant other than carbonate was iron, which reached 0.3 μ mole/ml in one batch of distilled water.

The cell was initially flushed with argon to eliminate air before adding the solution. (The argon was purified over uranium chips at 700° C.) Argon bubbling in the solution was continued during the experiment except when the agitation created problems with potentiostat control. In these instances, it is assumed that enough backflow of air occurred through the vents of the cell to allow traces of oxygen to be dissolved in the solution.

Rod, foil, and rectangularly shaped samples of Mulberry and foil samples of uranium were used. The rod samples of Mulberry were first coated with epoxy resin and cured. A cross section was then exposed by abrading the ends of the coated rods. The foil samples were rectangles of approximately 0.5 by 1.0 centimeters. A thin strip extended from the samples across the solution/gas interface for electrical connection to minimize any peculiarities that

might occur at the solution/gas interface. All these samples were etched electrolytically in 50 percent concentrated nitric acid before admission to the cell.

Mulberry samples prepared by different methods were compared (eg, arc-melted Mulberry is chemically less homogeneous than skull-cast Mulberry). Three samples measuring 1/2 by 1/2 by $\sim 1/8$ inch were prepared by each method. Each sample had a long tab to make electrical contact outside the solution. Care was taken to ensure that the oxide was removed from all the sample surfaces.

The rod preparation was not very successful due to the opportunity of crevice corrosion between the epoxy and Mulberry.⁽⁹⁾ For this reason, the results for these samples are suspect. Preparation of the foil samples did not present this complication.

Potential sweep rates from 0.1 to 99 mv/sec were used. The potential was alternately swept positive and negative to a point just under the extremes at which the cell potential became uncontrollable. This point was usually determined by water electrolysis in the counter electrode chamber. This range was best when the counter electrode was partially isolated from the working electrode by closing the stopcock between the two. The polarizing current was carried by a thin water film in the stopcock. This film formed only after the stopcock was turned several times in the electrolyte solution.

Results

The polarization curves (Figures 14 through 49) presented here are those obtained after several successive voltage scans at 25°C. The number of sweeps was determined by the reproducibility of the curves obtained. It sometimes took as many as 40 scans before changes occurring from scan-to-scan would become negligible. Usually, the curve became reproducible between the 10th and 20th scan. This number of scans meant that, at the slower scan rates, several days were required to obtain reproducible curves (eg, at the slow scan rate of 0.3 mv/sec, three or four days were required to obtain results).

Figure 14. POLARIZATION CURVE FOR URANIUM IN A 1 N KOH SOLUTION. (Slight Oxygen Contamination may be Present since Argon Bubbling was Stopped to Eliminate Agitation; Sweep Rate = 8.36 mv/sec)

Figure 15. POLARIZATION CURVE FOR MULBERRY ROD IN A 1 N KOH SOLUTION. (Oxygen Contamination and Crevice Corrosion may be Present; Sweep Rate = 2.40 mv/sec)

Figure 16. POLARIZATION CURVE FOR URANIUM (FOIL SAMPLE) IN AN ARGON-PURGED 1 N KOH SOLUTION AT 25°C. (Sweep Rate = 0.254 mv/sec)

Figure 17. POLARIZATION CURVE FOR URANIUM IN AN ARGON-PURGED 1 N KOH SOLUTION AT 25°C. (Sweep Rate = 0.103 mv/sec)

For comparison purposes, a few polarization curves for uranium were obtained in the absence of vigorous agitation from either stirring or argon bubbling. The solution had been previously purged with argon; however, to obtain current readings over four decades, it was necessary to avoid agitation. This action presented the possibility of dissolving oxygen in the solution either from the air or from the electrolysis of water.

Uranium has a complex polarization curve, as can be seen in Figure 14. The most reproducible feature of the curve was the Flade potential (10) maximum at +0.25 volt. The Flade potential marks the onset of passive behavior. This value was followed by an increase in current at about +0.80 volt with a maximum at about +1.10 volts. This latter increase was less pronounced and is probably associated with a higher oxide formation (superpassivation). Often this latter peak did not appear at all, but occurred as a shoulder on the current increase associated with either pitting or oxygen evolution. A smaller and broader Flade-type peak often appeared at about -0.50 volt, especially when the voltage was being swept from a very cathodic condition. It did not appear under all conditions and was not reproduced in the anodic-to-cathodic sweep. A similar peak appeared on the cathodic side of an anodic-cathodic sweep at about -0.80 volt. It is assumed that this is an oxide reduction which is diffusion controlled.

The features described for the uranium polarization curves were also present in the Mulberry polarization curves. The Mulberry rod yielded radically different potentials and very high current densities. These differences may be due, however, to a high degree of crevice corrosion, which would have exposed more surface area than normal and would have created a different environment over the part of the sample affected. The results obtained with the Mulberry rod under low agitation conditions are presented in Figure 15. The three anodic peaks appeared at +0.90, +1.27, and +1.55 volts. The cathodic peak, attributed to oxide reduction, appeared at +0.90 volt. The points of zero current are +0.47 volt going from cathodic to anodic and +1.47 volts going from anodic to cathodic. These values are in contrast to the zero points for uranium, of Figure 14, of -0.86 and +0.12 volt, respectively.

It is possible that one of the two peaks about the zero-current potential (ZCP) was due simply to the treatment of the data. It is possible to obtain an anomalous peak on one side of the ZCP in a logarithmic plot of current if two dissimilar reactions (and thus two dissimilar pre-exponential terms) are occurring on the cathodic and anodic sides (ie,

Figure 18. POLARIZATION CURVE FOR MULBERRY IN AN ARGON-PURGED 1N KOH SOLUTION AT 25° C. (Sweep Rate = 0.275 mv/sec)

Figure 19. POLARIZATION CURVE FOR MULBERRY IN AN ARGON-PURGED 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 2.79 mv/sec)

Figure 20. POLARIZATION CURVE FOR MULBERRY IN AN ARGON-PURGED 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 0.313 mv/sec)

nonreversible electrode). Two anomolous peaks, however, are unlikely. Hydrogen analysis of thin samples of Mulberry indicated negligible hydrogen charging when samples were held cathodic for long periods of time. It is therefore assumed that the cathodic peak (-0.90 v for uranium and +0.90 v for Mulberry rods and -0.75 v for other Mulberry samples) is real and is attributable to oxide reduction.

When argon was continuously bubbled through the solution, the curves were changed somewhat. Figures 16 and 17 show the results obtained from a uranium foil; Figures 18 through 24 are polarization curves obtained with Mulberry foil. The curves of Figures 18 and 19 were obtained shortly after the sample was admitted to the cell; Figures 20 through 24 were obtained after several weeks of experimentation. These results are summarized in Table 1. At high sweep rates, the Flade potential peak was missing for Mulberry foil in 1 N KOH; due, possibly, to an incomplete reduction of the protective film during the anodic-cathodic sweep. If this portion of the sweep was slowed down, then the Flade potential reappeared. As would be expected, the Flade potential increased with an increased sweep rate. This trend was repeated in the anodic-to-cathodic portion of the sweep.

For a comparison of sample histories, three samples each of arc-melted and skull-cast material were studied. It would be expected that due to a similarity in the gross chemical composition, the polarization behavior of large samples of Mulberry would be similar regardless of their histories. This assumption was found to be essentially correct in a series

Table 1
SUMMARY OF DATA PRESENTED IN FIGURES 14 THROUGH 24

Sample	Sweep Rate (mv/sec)	Atmospheric Condition	Flade Potential ⁽¹⁾	Super- passivation ⁽¹⁾	First Anodic Peak ⁽¹⁾	Oxide Dissolution ⁽²⁾	Flade ⁽²⁾	Curent Zero Points	
								(1)	(2)
U Foil	8.4	Trace of O ₂	+0.26	+1.10	-0.44	-0.76	+0.22	-0.86	-0.12
U Foil	0.1	Argon Flow	+0.21	+1.0 ⁺	-0.04	-0.64	+0.16	-0.20	-0.06
U Foil	0.25	Argon Flow	+0.21 +0.17 ⁽³⁾	+1.0 ⁺	-0.50	-0.75	+0.17	-0.82	-0.64
Mulberry Rod	2.4	Trace of O ₂	+1.31	+1.55	+0.90	+0.90	(4)	+0.46	+1.40
Mulberry Foil	0.28	Argon Flow	+0.25	+0.87	(4)	-0.70	+0.25	-0.02	-0.02
Mulberry Foil	2.8	Argon Flow	+0.32	~ +1.0	-0.42	-0.70	~ +0.27	-0.67	-0.10
Mulberry Foil	0.3	Argon Flow	+0.17 +0.27 ⁽³⁾	+0.95	(4)	-0.67	~ +0.15	-0.10	-0.10
Mulberry Foil	2.5	Argon Flow	+0.20	+0.92	-0.42	-0.70	+0.17	-0.57	-0.10
Mulberry Foil	10	Argon Flow	+0.25	+0.87	-0.57	-0.75	+0.25	-0.72	-0.10
Mulberry Foil	25	Argon Flow	+0.30	+0.87	-0.60	-0.75	+0.30	-0.72	+0.10
Mulberry Foil	99	Argon Flow	+0.30 ⁽³⁾	(4)	-0.55	-0.75	~ +0.40 +0.15 ⁽⁵⁾	-0.82	+0.20 -0.10 ⁽⁵⁾

(1) For the cathodic-to-anodic portion of sweep.

(2) For the anodic-to-cathodic portion of sweep.

(3) Designates minor peak occurring in same region.

(4) Not discernible.

(5) Peak produced if a slow sweep (10 mv/sec) is used from 0.50 to 0.0 volt on anodic-to cathodic sweep.

Figure 21. POLARIZATION CURVE FOR MULBERRY IN AN ARGON-PURGED 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 2.515 mv/sec)

observed in the polarization curves should be due primarily to experimental error. Comparing all the polarization curves, it is concluded that within experimental error the polarization curves of Mulberry with varying histories, taken in hydroxide solution, are indistinguishable. A gross change in chemical composition would undoubtedly show differences.

Chloride ions were added to see what modifications would occur in the polarization curves. The most apparent modification (Figure 37) was the increase on the negative side of the current peak occurring as the Mulberry became cathodic. The first anodic peak may also be modified. These changes are attributed to either a complexing interaction of

of polarization experiments (Figures 25 through 36) using the three arc-melt and three skull-cast samples.

Polarization curves for all six specimens are presented for the 1.1 mv/sec sweep rate. For the other sweep rates, some of the polarization curves are not included since they are similar to the ones presented. The most reproducible feature was again the Flade potential peak at +0.23 volt. The differences in 1 N KOH between Samples 1, 2, and 3 of the arc-melt or skull-cast material were just as great as the differences between the various types of samples. Since each of three samples (representing two treatments) were made as identically as possible, the deviations

Figure 22. POLARIZATION CURVE FOR MULBERRY IN AN ARGON-PURGED 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 10.0 mv/sec)

Figure 23. POLARIZATION CURVE FOR MULBERRY IN AN ARGON-PURGED 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 25.0 mv/sec)

Figure 24. POLARIZATION CURVE FOR MULBERRY IN AN ARGON-PURGED 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 99.2 mv/sec; the Dashed Line Represents the Results Obtained when the Potential Range between 0.5 to 0.0 volt—Anodic-to-Cathodic—was Swept at 10 mv/sec; the Rest of the Full Scan is at 99.2 mv/sec)

chloride with the oxide film or chloride penetration of the film to allow a higher current density.

POLARIZATION STUDIES IN AQUEOUS CHLORIDE SOLUTIONS

Manual Potential Sweep Method

Due to the importance of chloride solutions with respect to stress-corrosion cracking, this separate section is devoted to polarization in the presence of chloride.

Voltage-current curves in both anodic and cathodic regions were obtained from samples in chloride solutions of various hydrogen ion concentrations. The electrodes used were flat bars with about four square centimeters exposed to solution. The standard electrode was held at about two centimeters from the Mulberry electrode. Potassium and nitrate ions were used as the counter ions for chloride and hydrogen ions where necessary, and the ionic strength was approximately 1.0 in all solutions. These data were obtained by fixing the

Figure 25. POLARIZATION CURVE FOR ARC-MELTED MUL-BERRY SPECIMEN 1 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 1.11 mv/sec; with Argon)

Figure 26. POLARIZATION CURVE FOR ARC-MELTED MUL-BERRY SPECIMEN 2 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 1.11 mv/sec; with Argon)

Figure 27. POLARIZATION CURVE FOR ARC-MELTED MULBERRY SPECIMEN 3 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 1.11 mv/sec; with Argon)

Figure 28. POLARIZATION CURVE FOR SKULL-CAST MULBERRY SPECIMEN 1 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 1.11 mv/sec; with Argon)

Figure 29. POLARIZATION CURVE FOR SKULL-CAST MULBERRY SPECIMEN 2 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 1.11 mv/sec; with Argon)

Figure 30. POLARIZATION CURVE FOR SKULL-CAST MULBERRY SPECIMEN 3 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 1.11 mv/sec; with Argon)

Figure 31. POLARIZATION CURVE FOR ARC-MELTED MULBERRY SPECIMEN 1 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 5.43 mv/sec; with Argon)

Figure 32. POLARIZATION CURVE FOR SKULL-CAST MULBERRY SPECIMEN 1 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 5.43 mv/sec; with Argon)

Figure 33. POLARIZATION CURVE FOR ARC-MELTED MULBERRY SPECIMEN 1 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 10.85 mv/sec; with Argon)

Figure 34. POLARIZATION CURVE FOR SKULL-CAST MULBERRY SPECIMEN 1 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 10.85 mv/sec; with Argon)

Figure 35. POLARIZATION CURVE FOR ARC-MELTED MULBERRY SPECIMEN 1 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 54.3 mv/sec; with Argon)

Figure 36. POLARIZATION CURVE FOR SKULL-CAST MULBERRY SPECIMEN 1 IN A 1 N KOH SOLUTION AT 25° C. (Sweep Rate = 54.3 mv/sec; with Argon)

Figure 37. POLARIZATION CURVE FOR MULBERRY IN A 1 N KOH-0.01 N HCl SOLUTION AT 25° C. (Sweep Rate = 1.11 mv/sec; with Argon and Stirring)

Figure 38. MULBERRY IN A 1 N $[H^+]$ SOLUTION.

Figure 39. MULBERRY IN A 0.1 N $[H^+]$ SOLUTION.

Figure 40. MULBERRY IN A 0.01 N $[H^+]$ SOLUTION.

potential and allowing the current to settle (Figures 38 through 41). There appear to be some trends in the curves on the anodic side, indicating a chloride dependence in the anodic reaction.

Figure 41. MILBERRY IN A 0.001 N [H⁺] SOLUTION.

Figure 42. ESTIMATED REST POTENTIALS AS FUNCTIONS OF THE CHLORIDE AND HYDROGEN ION CONCENTRATIONS.

Figure 43. MULBERRY IN A 0.01 N HCl SOLUTION. (Sample 2; Sweep Rate = 0.13 mv/sec)

Figure 44. POLARIZATION BEHAVIOR OF MULBERRY IN A 0.01 N HCl SOLUTION. (Sample 3; Sweep Rate = 0.13 mv/sec; Highly Pitted Condition)

Figure 45. POLARIZATION BEHAVIOR OF MULBERRY, FRESH FROM MECHANICAL CLEANING, IN A 0.01 N HCl-1.0 N KCl SOLUTION. (Sweep Rate = 0.34 mv/sec)

Figure 46. POLARIZATION BEHAVIOR OF MULBERRY IN A 0.01 N HCl-1.0 N KCl SOLUTION. (Sweep Rate = 0.33 mv/sec)

Figure 47. POLARIZATION BEHAVIOR OF MULBERRY IN A 0.01 N KCl-0.01 N KOH SOLUTION. (Sample 1; Sweep Rate = 0.20 mv/sec)

Figure 48. POLARIZATION BEHAVIOR OF MULBERRY IN A 0.01 N KCl-0.01 N KOH SOLUTION. (Sample 2; Sweep Rate = 0.20 mv/sec)

Figure 49. POLARIZATION BEHAVIOR OF MULBERRY IN A 0.01 N KCl-0.01 N KOH SOLUTION. (Sample 3; Sweep Rate = 0.30 mv/sec)

Data from semilogarithmic plots of current versus potential were used to obtain the value of the potential at what was assumed to be the exchange or corrosion current. The values obtained are plotted in Figure 42 as a function of the hydrogen and chloride ion concentration. The extrapolation to exchange current was rather large and the values for the voltage are therefore very uncertain.

It was found that a plot of $\log \{[\text{Cl}^-]^2/[\text{H}^+]\}$ (where $[\text{Cl}^-]$ represents chloride ion concentration and $[\text{H}^+]$ hydrogen ion concentration) versus the rest potential of a Mulberry electrode, yields a linear relationship. Actually, an acceptable range of values for the $[\text{Cl}^-] : [\text{H}^+]$ and $[\text{Cl}^-] : e^-$ ratios would require that a complexing reaction occur for uranium oxide in the range UO_2 to $\text{UO}_2.3$, such that uranium would go to a +6 or a less likely +5 oxidation state in the form $\text{UO}_2\text{Cl}_4(\text{OH})_2^x$.

Automatic Potential Sweep Method

Polarization curves with chloride were also obtained with the automatic sweep method. These curves looked quite different from the ones obtained without chloride. In addition to the solutions already mentioned and typified in Figure 37, three different solutions were used: 0.01 N HCl, 0.01 N HCl-1.0 N KCl, and 0.01 N KCl-0.01 N KOH. Analysis of the solutions was made at various points in the experiment to determine any significant changes.

The polarization curves presented in Figures 43 through 49 reveal that, in an acid solution, cycling the potential high enough for pitting created a highly negative ZCP on the anodic-to-cathodic sweep. Also, from highly positive polarizing potentials the open-circuit potential was initially highly negative and increased with time with an exponential approach to a value around 0.0 volt versus NHE. The rest potential of the 1 N chloride solution had a tendency to develop spontaneous negative transients, indicating pitting in the absence of an external current. A lower anodic-to-cathodic ZCP was also obtained in the basic solution with increased anodic treatment except when a black powder (presumably oxide) formed on the surface. Table 2 illustrates the trend of the anodic-to-cathodic ZCP with the surface condition.

Table 2
TREND OF THE ANODIC-TO-CATHODIC ZERO-CURRENT POTENTIAL
WITH THE SURFACE CONDITION

Solution	Maximum Anodic Potential (volts)	Zero Current Potential (anodic→cathodic)	Condition
0.01 N HCl	+0.16	+0.15	Moderately pitted.
	+0.20	-0.10	Highly pitted.
1 N KCl - 0.01 N HCl	+2.75	-0.25	Highly pitted.
	+1.17	+0.02	
0.01 N KCl - 0.01 N KOH	+0.45	+0.25	Moderate amount of black oxide present. Copious amount of black oxide present.
	+0.67	+0.05	
	+1.25	+0.05	
	+1.25	+0.11	

Pitting of the sample caused a sharp rise in the current density. In the case of the 0.01 N HCl solution, this sharp rise was observed as soon as the sample became anodic; whereas, in the case of the 0.01 N HCl-1.0 N KCl and 0.01 N KCl-0.01 N KOH solutions, a sharp break occurred in the polarization curves. This breakpoint was not very reproducible, especially in the basic solution. In the basic solution this break occurred above the passivation potential, and the current measurement above this break was very noisy. This noise may indicate alternate pitting and passivation, or possibly the formation and spalling of the black powdered oxide which was visible on the sample.

The role of the halide ions in Mulberry cracking may be only as a charge transporter in solution and in the oxide film. Results of conductivity measurements on bulk uranium oxide exposed to tetramethylammonium chloride solution (with tetramethylammonium sulfate solution as a control) does not support this idea since the conductivity did not increase on exposure to chloride ions; however, extrapolations from observations on bulk oxide to oxide films on Mulberry are probably questionable.

If chloride is not solely a charge transporter, another possibility is that the formation of nonreactive chlorine-oxygen ions to prevent passivation may be occurring. Fast voltage sweeps in Figure 50 indicate the presence of some oxidizable species near the surface with a current peak at +0.5 volt. The reduction peak is 0.55 volt below the oxidation peak, indicating a high degree of kinetic inhibition.

Figure 50. FAST VOLTAGE SWEEP (0.795 v/sec) FOR MULBERRY IN A 0.01 N HCl SOLUTION.

SPINNING ELECTRODE STUDIES

Experimental

It is not realistic to consider the electrochemistry of an advancing crack tip in a metal specimen experiencing SCC as being identical to that of the samples used in the previous section. The surfaces in the advancing crack tip should be more nearly approximated by the bare metal surface than by a surface that has an oxide film. Difficulty in measuring the polarization behavior of the bare metal due to the very rapid rate of oxidation of the surface in an aqueous medium was overcome by using a cylindrical sample that was spun in an abrasive slurry at a speed high enough to abrade the surface faster than an oxide film could form. The criterion used for the attainment of an adequate abrading rate was a negligible change in the galvanic potential with any greater abrasion rate. The measurements were generally taken by controlling the current. A further criterion for the proper abrasion rate was the reproducibility of the polarization curve, regardless of whether the current was being swept from the anodic side or the cathodic side.

The cell arrangement used is represented in Figure 51. A grinding motor was used to rotate a cylindrical sample in an abrasive slurry. A stainless steel shaft was used as the sample holder and also as the armature for the stainless steel brushes for electrical contact. Teflon was used for spacers (for the water interface) and as insulation from the grinding motor. In this arrangement, care was taken to ensure that the brushes to the sample did not heat up to produce a thermocouple effect. At the higher rotating speeds, the brushes were often held off the armature except for a measurement. Coarse, high-purity sand was found to be an ideal abrasive.

Figure 51. EXPERIMENTAL ARRANGEMENT FOR THE SPINNING ELECTRODE EXPERIMENT.

The counter electrode used was a platinum mesh in the bottom of the container, and a SCE was used as the reference. Due to the open container, all the solutions were assumed to be air saturated. The working electrodes were skull-cast Mulberry in the form of 1/2-inch-diameter by 1/4-inch-long cylinders which were rotated at approximately 15,000 rpm. Solutions were made from near-conductivity-grade water and reagent-grade HCl, KCl, and KOH.

Results

The polarization curves obtained from the cathodic-to-anodic sweep are shown in Figures 52 and 53. The polarization curves on the anodic-to-cathodic sweep in the most basic solutions were shifted slightly toward a more positive potential, indicating that the abrasive action was not sufficient to overcome the rapid oxide formation.

A tabulation of the rest potentials obtained from these polarization curves as well as some obtained as open-circuit potentials indicates that there is a complex relationship between pH

Figure 52. POLARIZATION CURVES OF MULBERRY USED AS A SPINNING ELECTRODE. (In Various KOH-KCl Solutions)

Figure 53. POLARIZATION CURVES OF MULBERRY USED AS A SPINNING ELECTRODE. (In Various KOH-KCl and KCl-HCl Solutions)

and the chloride ion concentration. Table 3 illustrates that the potential decreased with increased chloride concentration and was lowest in the region of neutral pH.

ACOUSTIC EMISSION STUDIES

Experimental

With some knowledge of the electrochemical behavior of unstressed Mulberry, an investigation was initiated to study the effect of stressing the specimen and to observe what effect the electrochemical environment has on the crack propagation rate. A convenient method of following the crack propagation rate is to measure the acoustic emission from the strained specimen. A relative functional relationship can be determined between the potential of the sample and the rate at which it is cracking.

The acoustic emission apparatus consisted of a lead zirconate-titanate transducer, a differential amplifier, and an oscilloscope with a special acoustic emission plug in. The transducer was split in half, and one-half was inverted so that electrical background noise would be subtracted out by the differential amplifier. The output is seen as a single spike for each pressure release, the amplitude of the spike being proportional to the amplitude of the emission. Since it is difficult to get the same efficiency of pickup on a transducer of the pressure releases in all samples, the proportionality constant between the cracking rate and

the acoustic emission detection varied from sample to sample.

The Mulberry strain samples (bend specimens) were prepared in strips measuring 0.0625 ± 0.001 inch by 0.375 ± 0.004 inch by 4.375 ± 0.005 inches. The deviation from flatness along the length of the strip was within 0.032 inch. For acoustic emission measurements, these strips were strained in a polystyrene mount to one percent strain on the outer curved surface, which would correspond to a deviation from flatness of ~ 0.5 inch. The special polystyrene device consisted simply of four pegs between two rectangular sides, two in the middle and one at each end, across which the sample was bent. The transducer was attached to the Mulberry strip which was the working electrode. The Mulberry sample was completely masked with a nonconductive lacquer except for 1 cm^2 in the middle of the outer surface; ie, the highly stressed region. A platinum counter electrode and a silver-silver chloride or SCE were used in the other chambers of the cell. A variable external power source supplied the current through the cell. This source was usually a potentiostat, although in some cases it consisted of only a constant current source.

A fast-response two-channel recorder was used to record peaks corresponding to the cracking and either the current through the cell or the potential of the Mulberry. With the apparatus set up in this manner, the rate of cracking could be correlated with the specimen current or potential.

Results

The acoustic emission experiments were carried out in a variety of solutions: 1 N KCl, 1 N KNO_3 -0.01 N KCl, 0.01 N KOH-0.01 N KCl, 0.001 N KOH-0.01 N KCl, 0.001 N KOH, 1 N KOH, 1 N KNO_3 , 0.1 N KF, 0.1 N KBr, 0.001 N HCl, and 0.1 N KI. Anodic cracking occurred in all solutions which contained halide ions, and cathodic cracking occurred in the fluoride solution. The 1 N KNO_3 -0.01 N KCl solution showed evidence of a passivating effect.

Figure 54 represents a typical recorder trace of the acoustic emission under anodic conditions in halide solution. Emission was suppressed as the sample approached cathodic conditions. Very often the sample was still anodic when the emission was completely

Table 3
REST POTENTIALS OF SPUN-ABRADED
MULBERRY SAMPLE

pH(1)	pCl(1)	Rest Potential (with respect to std H_2)
0	0	- 0.687(2)
0	0	- 0.96(3)
2	0	- 1.24(3)
2	4	- 1.04(3)
4	2	- 1.17(2)
4	2	- 1.1(2)
5.7(4)	3	- 1.20(3)
6(4)	0	- 1.34(3)
10	0	- 1.42(2)
10	0	- 1.26(3)
10	2	- 1.25(2)
10	2	- 1.22(3)
10	4	- 1.21(3)
12	0	- 1.28(3)
12	4	- 1.02(3)
14	0	- 1.13(2)
14	0	- 1.08(3)
14	1	- 0.435(2)
14	1	- 0.45(2)

(1) Calculated from the mixing—air saturated.

(2) As determined from zero current point on cathodic-to-anodic sweep.

(3) Open circuit potential.

(4) As measured.

Figure 54. AN EXAMPLE OF A RECORDER TRACE OF ACOUSTIC EMISSION SPIKES FROM STRESSED MULBERRY IN A 0.001 N HCl SOLUTION WITH ITS POTENTIAL APPROXIMATELY -230 MILLIVOLTS WITH RESPECT TO THE HYDROGEN ELECTRODE. (Each Spike is a Pressure Release Due to Crack Propagation)

suppressed. It was also observed that after the sample was held slightly cathodic, the cracking occurred in the anodic region only after an induction period. Figure 55 presents the cracking dependence of Mulberry in 1 N KCl, 0.001 N HCl, and 0.01 N KOH-0.01 N KCl. The 1 N KCl solution had a very sharp cutoff point where cracking could be suppressed. This same behavior can be seen with the 0.1 N KI solution in Figure 56. It is evident from this figure and observations of the current in other solutions that the cracking rate does not have a simple dependence on the anodic current.

In the case of 0.1 N KBr, the anodic current was below 1×10^{-7} amp/cm² at the time of cracking initiation, as seen in Figure 57. Cracking in this case apparently exposed a new surface with a much lower potential which caused an anodic current to flow. This behavior, observed in Figure 57, was followed by what appeared to be passivating action; ie, a rise in potential with a decrease in anodic current. In this case, each crack produced a current surge followed by passivation.

No evidence of cracking appeared with stressed Mulberry at any potential in either 1 N KOH or 1 N KNO₃. In the halide solutions, the results showed a monotonic relationship between potential and cracking rate with the exception of the 0.1 N KF solution. In the KF solution, both anodic and cathodic conditions produced emission, and a minimum emission was observed between the two extremes. This behavior is illustrated in Figure 58. The behavior of Mulberry in the 1 N KNO₃-0.01 N KCl mixed solution is illustrated in Figure 59. Cracking appeared to occur in rapid clusters, and a functional relationship between emission and electrode conditions was difficult to obtain. This behavior may be due to a depletion of the chloride ion concentration in the microcrack, allowing temporary passivation by nitrate ions. This action would be followed by slow diffusion of chloride ions (as opposed to rapid migration in solutions with only chloride) to again initiate SCC.

Under the influence of a constant current, Mulberry exhibits some rather peculiar characteristics. In 0.01 N KCl-0.01 N KOH at 1×10^{-6} amp/cm² (anodic), the potential increased momentarily and then dropped to +0.04 volt versus the NHE. The potential was not constant, however, but had transients of ± 0.02 volt. In the stressed conditions, these transients were followed by cracking as observed by the acoustic emission and by a large

negative potential transient. With rapid crack propagation, the negative potential transients dropped the potential to as low as - 0.50 volt versus the NHE.

When the specimen had catastrophically failed, the potential would again increase and settle out at + 0.04 volt versus the NHE, with the same transients as observed before complete breakage. Figure 60 shows the fractography of one such sample after it had been left in solution with an anodic current of 1×10^{-6} amp for about eight hours after breakage. The face of the cracked surface was about 0.5 cm^2 ; therefore, if the original flat surface of the specimen were ignored, the current density could have been as high as $2 \times 10^{-6} \text{ amp/cm}^2$. This micrograph shows that the sample broke by the normal intergranular cracking; then, an oxide coat built up and cracked, giving a "mud cracking" appearance. This cracking of the oxide film on the sharp grain boundaries may be the origin of the initial potential transients.

A spherical corrosion product was observed on the crack surface of some bend specimens, as can be seen in Figure 61. This product was obtained when potential sweeps were used and

Figure 55. CRACK PROPAGATION RATES OF STRESSED MULBERRY AS A FUNCTION OF THE MULBERRY ELECTRODE POTENTIAL.

Figure 56. CRACKING IN A 0.1 N KI SOLUTION THAT DEMONSTRATES THE CRITICAL POINT AT WHICH CRACKING BEGINS AND CEASES.

Figure 57. ACOUSTIC EMISSION OUTPUT IN RELATION TO THE POTENTIAL AND ANODIC CURRENT FOR A STRESSED MULBERRY SAMPLE IN 0.1 N KBr. (Point of Initiation was Approached Slowly from the Cathodic Current Conditions; Decay of Current after Each Burst Illustrates Effect of Passivation)

Figure 58. CRACKING RATE AS A FUNCTION OF THE POTENTIAL ON STRESSED MULBERRY IN A 0.1 N KF SOLUTION. (Inserts Show Recorder Output of the Acoustic Emission Apparatus)

Figure 59. CRACKING IN 1 N KNO_3 and 0.01 N KCl DEMONSTRATING PASSIVATING EFFECT OF THE NITRATE ION.

the sweep was continued well past the potential at which the sample broke. In this particular case, the sample broke at - 0.21 volt versus the NHE and the potential was swept to + 0.04 volt versus the NHE.

It was incidentally determined in this study that a ≥ 1 N CN^- solution would not cause cracking in Mulberry bend specimens under anodic currents that would quickly crack Mulberry if applied in chloride solution (10^{-3} amp/cm²).

Effect of Cold Working

During this study, cold-worked Mulberry was found to be resistant to stress-corrosion cracking in the transverse direction. Samples containing unrecrystallized, cold-worked areas were tested for SCC in chloride solutions. Some samples were found to be extremely resistant to cracking even under highly anodic conditions in 1 N KCl -0.01 N HCl . It was found that if the sample did fail, the (intergranular) stress-corrosion crack avoided crossing the cold-worked areas. Figure 62 shows what effect cold working has on stopping the progress of a crack. Even secondary cracks avoided crossing the cold-worked areas, as shown in Figures 63 and 64, indicating that a crack does not easily propagate in the parallel direction. This fact implies that mechanical effects are not prominently at work here, but rather that the grain boundaries of the cold-worked areas lack the proper chemical composition to allow the anodic action needed in stress-corrosion cracking. The stress-corrosion cracking may be due to high concentrations of either niobium or zirconium on the grain boundaries, which should have an effect on the anodic reaction.

STRESSED WIRE STUDIES

Stress Application Apparatus

Having studied Mulberry SCC at one stress level under a variety of electrochemical conditions, the next logical step was to make stress level a variable, in addition to pH, chloride concentration, and potential.

(a) At 3,000X

SM-16076

(b) At 1,000X

SM-16077

(c) At 300X

SM-16078

(d) At 100X

SM-16079

Figure 60. FRACTOGRAPHY OF A MULBERRY BEND SPECIMEN WHICH HAD BEEN LEFT IN A 0.01 N KCl-0.01 N KOH SOLUTION FOR EIGHT HOURS AFTER FRACTURE WITH AN ANODIC CURRENT OF $1\mu\text{AMP}$ BEING PASSED. ("Mud Cracking" Seen Here may Explain the 20-millivolt Transients Observed in the Unstressed Condition)

(a) At 3,000X

SM-16080

(b) At 1,000X

SM-16081

(c) At 300X

SM-16082

(d) At 100X

SM-16083

Figure 61. FRACTOGRAPHY OF A MULBERRY BEND SPECIMEN WHICH HAD BEEN EXPOSED TO HIGH ANODIC CURRENTS AFTER FRACTURE TO YIELD SPHERICAL CORROSION PRODUCTS.

G771-3a

Figure 62. MICROGRAPH OF A MULBERRY BEND SPECIMEN WHICH HAD SOME UN-RECRYSTALLIZED, COLD-WORKED AREAS PRESENT SHOWING THE EFFECT ON CRACK PROPAGATION. (This Micrograph is an Edge View and Indicates that Cracks do not Readily Propagate Across the Elongated Grains of the Cold-Worked Area; the Leading Edges of the Crack are also Blunted, Indicating that an Anodic Dissolution Process was the Propagating Mechanism; Etched in 5% Oxalic Acid; Bright Field Illumination; 250X)

G771-1b

Figure 63. CROSS-SECTIONAL VIEW OF THE SAMPLE SEEN IN FIGURE 62, SHOWING A SECONDARY CRACK AND ITS AVOIDANCE OF COLD-WORKED AREAS. (Blunting is also Observable Here; Etched in 5% Oxalic Acid; Bright Field Illumination; 250X)

S-70-0476-4

Figure 64. CROSS-SECTIONAL VIEW OF THE SAMPLE SEEN IN FIGURE 62, SHOWING THE PROPAGATION OF A SECONDARY CRACK WHICH AVOIDS THE COLD-WORKED AREAS. (250X)

An instrument for applying stress to wire samples is shown in Figures 65 through 68. The mechanism was essentially a large-scale balance with an aluminum weight cage, stainless steel beam and pivots, a stainless steel back-tare box on the sample side, and a framework made of four-inch carbon steel channel and Type 304L stainless steel angle. The pivot edges were cut to a 1/32-inch radius. The whole apparatus was placed on a specially braced stainless steel table.

The wire clamps (Figures 67 and 68) were made from Type 304L stainless steel and were insulated from the framework by fiber-phenolic composite blocks. The bottom insulator holder (Figure 66) was made laterally adjustable to allow for positioning of the lower wire clamp directly below the upper clamp.

Two sets of standard brass weights (maximum weight - 2 kgs) were used together with lead weights made to the approximate dimensions of 1 7/8 by 1 7/8 by 3 7/8 inches. Each weight was individually weighed on a three-kilogram top-loading balance to the nearest gram, with the weight being stamped on one end. The average weight was about 2,620 grams.

The table and framework were electrically grounded together, and the table was grounded to a steel building girder.

Wire Preparation

Twelve-inch wires were made from arc-melted alloy swaged to 40 mils and heat treated to yield "Mulberry". They were then electropolished using the apparatus shown in Figure 69.

The wires were positioned between, and 3/4 inch from, each of two gold wires that served as counter electrodes. About 11 inches of the wire were electropolished. This length of wire exposed an area of 8.8 cm² when using a 40-mil wire. The wires were polished using a saturated solution of K₂CrO₄ in concentrated H₃PO₄. The anodic polishing was accomplished by slowly increasing the applied voltage to the desired value. If the voltage was suddenly raised, the possibility of sudden breakdown of the oxide coat at a small area was increased. When this occurred, active dissolution of the metal over this area proceeded at a rapid rate, causing local thinning of the wire.

Normally, the electropolishing was done by slowly increasing the voltage to about 15 to 20 volts. The steady-state current at that voltage was less than 0.10 ampere, which corresponded to a current density less than 0.011 amp/cm². Each wire was then thoroughly rinsed in distilled water and ethyl alcohol and/or acetone. The electropolished Mulberry wire had a dull, straw-colored appearance.

High-Stress-Rate Experiments

Mulberry Wires - In this section, a method is described for following the potential versus stress on Mulberry wires using a flowing electrolyte. Figure 68 shows the electrolyte reservoir with a SCE, a capillary delivery tube, a Teflon suction tube, and the wire under tension. The electrolyte solution was drawn over the surface of the wire.

134993

Figure 65. STRESSED-WIRE APPARATUS WITH THE ELECTROLYTIC CELL IN PLACE. (The Apparatus Consists of a Balance Arrangement to Apply Stress and a Glass Electrolytic Cell with Standard Calomel and Platinum Counter Electrodes)

134991

Figure 66. STRESSED-WIRE APPARATUS WITH THE FLOWING ELECTROLYTE ARRANGEMENT. (A Small Teflon Suction Tube was Used to Draw Electrolyte across the Stressed Wire and the Potential was Measured with a Standard Calomel Electrode in the Electrolyte Reservoir)

134996

Figure 67. CLOSEUP OF THE ELECTROLYTIC CELL USED IN THE STRESSED-WIRE APPARATUS.

134995
Figure 68. CLOSEUP OF THE FLOWING ELECTROLYTE ARRANGEMENT FOR THE STRESSED-WIRE APPARATUS.

The potential difference between the wire and the SCE was monitored by an electrometer, and the output of the electrometer was fed to a two-pen, strip-chart recorder.

134994

Figure 69. ELECTROPOLISHING APPARATUS USED TO PREPARE WIRE SAMPLES.

A generalized recorder trace for high-stress-rate studies is shown in Figure 70. This figure shows all the features to be expected in these experiments, and gives a nomenclature to be used in interpreting Table 4, a summary of the behavior of the wires studied by the method just described. The nomenclature used in Figure 70 has the following meaning: E_1 is the potential of the wire before applying stress (at least two kilograms were always applied to the wire initially to straighten it, equal to 3.5 ksi for a 40-mil wire). The self-healing transients shown are similar to those reported by Funk⁽¹¹⁾ for other metals, except that a longer time is associated with their growth and decay. Apparently, strain caused rupture of the surface film, which gave a negative transient. This action was shortly followed by self healing, as indicated by the decay of the potential to a stable value. The stress which begins a spontaneous, irreversible change of the potential in the negative direction, terminating in the breaking of the wire, is S_B . The potential from which this irreversible change begins is designated by E_2 . The potential at which the coefficient $\Delta E/\Delta t \rightarrow \infty$ (the point of breaking) is E_3 , and the maximum negative potential reached as the wire breaks is E_{max} .

Figure 70. GENERALIZED STRIP-CHART RECORDER TRACE FOR STRESSED WIRES. (Direction of the Arrows Indicate Increasing Values of the Parameter)

Table 4

SUMMARY OF DATA ON MULBERRY STUDIED
UNDER A FLOWING ELECTROLYTE

Wire Number	Electrolyte	$-E_1(1)$ (volts)	$-E_2(1)$ (volts)	$-E_3(1)$ (volts)	$-E_{max}(1)$ (volts)	S_B (ksi)	Comments
13	0.001 <u>N</u> KCl	0.250	0.250	0.250	0.62	33.5	
14	0.001 <u>N</u> KCl	0.240	0.575	0.775	> 1.2	82	Initial Load 9.1 ksi
6	0.01 <u>N</u> KCl	0.232	0.375	0.725	0.960	31	Initial Load 7 ksi
10	0.01 <u>N</u> KCl	0.30	0.43	0.80	1.40	12	
11	0.01 <u>N</u> KCl	0.320	0.720	0.825	1.20	36	Initial Load 9.1ksi, SHT's ⁽²⁾ Present
17	0.1 <u>N</u> KCl	0.30	0.36	0.85	~ 1.25	21	
15	0.1 <u>N</u> HCl	~ 0.25	~ 0.25	0.82	1.05	4.6	Breaks on Initial Loading
16	0.1 <u>N</u> HCl	~ 0.25	~ 0.25	0.85	1.0	3.5	Breaks on Initial Loading

(1) All potentials versus SCE, which is + 0.242 volt versus normal hydrogen electrode.

(2) Self-healing transients.

The potential that the wire assumed after breaking and after a decay time of five minutes is E_f . This decay back to a more positive potential should be a measure of oxide film formation. This parameter cannot be measured using the first method, but can be with the cell described later. Table 4 summarizes the parameters for each wire studied by the flowing electrolyte method.

Figures 71 and 72 show the broken ends of Wires 3 and 5. These broken ends are typical of Mulberry wires broken in this manner and show two fracture modes: (1) intergranular stress-corrosion attack, and (2) dimple overload rupture.

Table 5 shows the relationship between the electrolyte, the load at time of breaking, and the percent of intergranular attack. If there were no compositional variations or flaws, and if the velocity of the intergranular stress-corrosion cracking were small compared with the dimple overload fracture, then the yield stress should be inversely proportional to the percent intergranular attack. Since the Mulberry was arc melted, the presence of compositional variations cannot be ruled out. Therefore, any observed scatter in an S_B versus percent intergranular attack plot should not be surprising.

Uranium-Niobium Binary Alloy Wires - Several wires of nominal uranium-6 weight percent niobium and uranium-8.5 weight percent niobium composition were studied. These wires were exposed to 0.01 N KCl solutions which were purged with argon and oxygen. The cell in which this and most subsequent studies were done may be seen in an exploded view in Figure 73 and assembled in place in Figure 67.

The cell has three compartments, each with its own bubbler. One end compartment held the SCE, the middle held the stressed wire, and the other end compartment held the platinum counter electrode. The top of the center compartment was sealed with a Teflon plate machined with concentric ridges for alignment and a hole in the center through which the wire is passed. A loosely fitting chamber, which could be purged with a gas, was located on top of the Teflon plate. The wire was sealed at the bottom, with epoxy, into a 5-mil-thick Teflon diaphragm. The whole assembly was then bolted together and filled with solution. Electropolishing these wires was carried out in the same manner as the Mulberry wires. Polishing currents were of the same magnitude.

The behavior of these binary alloy wires with respect to stress in the presence of an electrolyte was much the same as the Mulberry wires. The same generalized curve (Figure 70) and parameters may be used to describe them. Values of these parameters are listed in Table 6.

Table 7 gives the averaged values of the parameters of Table 6. The clear trend of more positive potentials in the case of oxygen purging compared with argon purging may be seen in this table. The differential values (argon values minus oxygen values) are reported in Table 8. There seems to be a clear correlation between changes in the purge gas composition and the potential. Similar behavior was reported by Funk.⁽¹¹⁾

Fractographic examination of Wires 1a, 2a, 1b, and 2b, listed in Table 9, showed the typical intergranular fracture plus dimple overload. The percentages of intergranular fracture for

(a) At 3,000X SM-11051

(b) At 1,000X SM-11052

(c) At 300X SM-11053

(d) At 100X SM-11054

Figure 71. SCANNING ELECTRON MICROGRAPHS OF ONE AREA ON A TYPICAL FRACTURE SURFACE DUE TO STRESSED CORROSION CRACKING IN MULBERRY WIRE 3. (This Area Shows Typical Intergranularity with Some Cleavage)

(a) At 1,000X SM-11082

(b) At 300X SM-11083

(c) At 100X SM-11084

Figure 72. SCANNING ELECTRON MICROGRAPHS OF AN AREA ON A FRACTURE SURFACE DUE TO STRESSED CORROSION CRACKING IN MULBERRY WIRE 5. (This Area Shows Intergranular Fracture Changing Over to a Ductile Dimple Rupture)

Table 5

PERCENT INTERGRANULAR ATTACK FOR MULBERRY
WIRE IN VARIOUS ELECTROLYTES

Wire Number	Electrolyte	Intergranular Attack ⁽¹⁾ (%)	S _B (ksi)
13	0.001 N KCl	59	33.5
14	0.001 N KCl	60	82
6	0.01 N KCl	76	31
10	0.01 N KCl	95	12
11	0.01 N KCl	67	36
17	0.1 N KCl	59	21
15	0.1 N HCl	100	4.6
16	0.1 N HCl	95	3.5

(1) Determined by measuring areas with a planimeter.

134998

Figure 73. EXPLODED VIEW OF THE THREE-COMPARTMENT ELECTROLYTIC CELL USED IN THE STRESSED-WIRE EXPERIMENTS. (All Three Compartments were Equipped with Argon Bubblers)

these samples are also listed in Table 9. Some deep cracking perpendicular to the crack face (parallel to the stress) was seen. All of the broken ends of the wires were measured with a micrometer, and the maximum deviation from the nominal 40-mil diameter was 0.6 mil.

Table 6

SUMMARY OF DATA ON URANIUM-NIOBIUM BINARY ALLOY WIRES STUDIED IN THE LARGE CELL UNDER 0.01 N KCl

Wire Number	Composition (wt % Nb)	Purge Gas	- E ₁ ⁽¹⁾ (volts)	- E ₂ ⁽¹⁾ (volts)	- E ₃ ⁽¹⁾ (volts)	- E _{max} ⁽¹⁾ (volts)	- E _f ^(1,2) (volts)	S _B (ksi)	Comments
1b	6	Ar	0.274 ⁽³⁾	0.280	0.555	0.645	-	20.2	-
4b	6	Ar	0.507 ⁽⁴⁾	0.507	0.605	0.825	-	48	-
6b	6	Ar	0.261 ⁽⁵⁾	0.240	0.460	0.465	0.344	29.5	SHT ⁽⁶⁾ at 25.5 ksi
2b	6	O ₂	0.390	0.282	0.520	0.528	0.355	29.4	-
3b	6	O ₂	0.305	0.310	0.460	0.684	-	23.7	-
5b	6	O ₂	0.204	0.254	0.398	0.398	0.262	29.4	SHT ⁽⁶⁾ at 25.5 ksi
1a	8.5	Ar	0.348	0.360	0.580	0.617	0.542	29.4	-
3a	8.5	Ar	0.326	0.381	0.554	0.654	0.621	25.5	SHT's ⁽⁶⁾ at 20.2 and 22.0 ksi
6a	8.5	Ar	0.335	0.344	0.494	0.495	0.407	29.4	-
2a	8.5	O ₂	0.412	0.361	0.468	0.484	0.425	25.5	-
4a	8.5	O ₂	0.181 ⁽⁷⁾	0.231	0.403	0.433	0.258	16.2	SHT's ⁽⁶⁾ at 11.0 and 14.5 ksi
5a	8.5	O ₂	0.245	0.288	0.415	0.432	0.348	38.7	-

(1) All potentials versus SCE, which is + 0.242 volt versus the normal hydrogen electrode.

(2) Taken five minutes after break.

(3) Immediately after electrolyte added E₁ = 0.32.

(4) Immediately after electrolyte added E₁ = 0.395.

(5) Immediately after electrolyte added E₁ = 0.298.

(6) Self-healing transients.

(7) At start of oxygen bubbling = 0.342; this sample soaked overnight in an oxygen-purged solution.

Table 7

AVERAGED VALUES OF THE PARAMETERS SHOWN IN TABLE 6

Composition (wt % Nb)	Purge Gas	- E ₁ (volts)	- E ₂ (volts)	- E ₃ (volts)	- E _{max} (volts)	- E _f (volts)	S _B (ksi)
6	Ar	0.347	0.342	0.540	0.645	0.344	32.6
6	O ₂	0.300	0.282	0.459	0.537	0.309	27.5
8.5	Ar	0.336	0.362	0.543	0.589	0.523	38.1
8.5	O ₂	0.279	0.293	0.429	0.450	0.344	26.8

Table 8

DIFFERENTIAL VALUES OF THE PARAMETERS OF TABLE 7

Composition (wt % Nb)	[- E ₁ (Ar)] - [- E ₁ (O ₂)] (volts)	[- E ₂ (Ar)] - [- E ₂ (O ₂)] (volts)	[- E ₃ (Ar)] - [- E ₃ (O ₂)] (volts)	[- E _{max} (Ar)] - [- E _{max} (O ₂)] (volts)	[- E _f (Ar)] - [- E _f (O ₂)] (volts)
6	0.047	0.060	0.081	0.108	0.035
8.5	0.057	0.069	0.114	0.139	0.179

Low-Stress-Rate Experiments

Experimental - Experiments were performed wherein Mulberry wires were subjected to stress initially at 5 ksi and increased at the rate of + 5 ksi/day. The wires were prepared as previously described. The wires in all cases had along their length several bright spots on their surfaces. In performing this series of experiments, the wires were masked off over their entire length except for an approximate 2-mm length. This unmasked area was chosen to be one of the shiny spots, since scanning electron microscopy had shown that they were generally smoother and more uniform than the matte areas.

Table 9

PERCENT INTERGRANULAR ATTACK FOR
URANIUM-NIOBIUM BINARY WIRES
IN 0.01 N KCl SOLUTIONS

Wire Number	Composition (wt % Nb)	Intergranular Attack ⁽¹⁾ (%)	S _B (ksi)
1a	8.5	82	29.4
2a	8.5	90	25.5
1b	6	87	20.2
2b	6	87	29.4

(1) Determined by measuring areas with a planimeter.

On a 40-mil-diameter wire, a load of 2,850 grams corresponds almost exactly to a 5-ksi stress. Therefore, each addition of 2,850 grams, as shown on the succeeding figures, corresponds to a change in stress of + 5 ksi.

Results - Figures 74 through 83 show the behavior of the potential of the wires with time for the various solutions used. Figures 74 through 78 show a series of wires exposed to a Cl⁻ concentration of 1 N, at pH's of 2, 4, 7, 10, and 12, respectively. Figures 79 and 80 show wires exposed to a Cl⁻ concentration of 0.01 N, at pH's of 2 and 12; Figure 80 is a composite of two runs under the same conditions. Figures 81 through 83 show wires

Figure 74. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRE 41 IN A 0.01 N HCl-1 N KCl SOLUTION (OXYGENATED).

Figure 75. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRE 43 IN A 0.0001 N HCl-1 N KCl SOLUTION (OXYGENATED).

Figure 76. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRE 45 IN A 1 N KCl SOLUTION (OXYGENATED).

Figure 77. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRE 44 IN A 1 N KCl-0.0001 N KOH SOLUTION (OXYGENATED).

Figure 78. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRE 42 IN A 0.01 N KOH-1 N KCl SOLUTION (OXYGENATED).

Figure 79. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRE 39 IN A 0.01 N HCl SOLUTION (OXYGENATED).

Figure 80. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRES 37 and 38 IN A 0.01 N KOH-0.01 N KCl (OXYGENATED).

Figure 81. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRE 40 IN A 0.01 N HClO₄-0.0001 N HCl SOLUTION (OXYGENATED).

exposed to 0.0001 N Cl^- at pH's of 2, 7, and 12; Figure 83 is a composite of three runs under the same conditions. Other than qualitative observations of the frequency of excursion, the parameters observed in this study were: (1) the mean peak potential, defined as the arithmetic mean of the five highest negative excursions, excluding any very large excursions which would be out of the range of error of the five; (2) the base potential, defined as the most positive potential reached during the experiment (as decay from the excursion ideally approaches a positive limit); and (3) the stress on the wire at breaking. Figures 84 through 87 show the surfaces of wires electropolished using four different solutions.

Figures 88 and 89 show contour maps of the mean peak potentials and breaking stresses, respectively. These are plotted on a pH-log $[\text{Cl}^-]$ field. Figure 90 is a similarly plotted contour map of rest potentials observed in the spinning-electrode experiments reported in Table 3. Table 10 gives the analyses of the solutions used in the long-term stressed-wire experiments, before and after exposure. Figures 91 through 96 are scanning electron micrographs (SEM) which include a representative sample of the wires used in this study.

Figure 82. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRE 48 IN A 0.0001 N KCl SOLUTION (OXYGENATED).

Figure 83. POTENTIAL AS A FUNCTION OF TIME FOR MULBERRY WIRES 46, 47, AND 49 IN A 0.01 N KOH-0.0001 N KCl SOLUTION (OXYGENATED).

The micrographs show the fractured ends of the wires and the portions of the wire surfaces that were exposed to the electrolyte. These views are presented for their intrinsic interest without further comment.

The behavior of the potential of the wires in Figures 74 through 83 generally is as follows: The freshly electropolished wire inserted in the oxygenated solution changed potential, somewhat asymptotically approaching a positive (more noble) limit. This shift was probably due to the oxide film thickening and/or becoming more enriched in oxygen. At some point this change was interrupted by an excursion in the negative direction, representing an anodic process on the surface; ie, a process whereby surface material gave up electrons to the underlying metal. This action could be accomplished in two ways: (1) the surface oxide, probably $\text{UO}_2 + x$ (with U in the +4 state), is further oxidized to the +5 or +6 state; or (2) an interruption of the oxide film exposes base metal, which is then oxidized. This process, or processes, is then overshadowed by the reformation of the protective oxide film which again carries the potential toward an asymptotic limit. This behavior is then repeated *ad fracturum*.

This idealized behavior seems to be the most accurate description of the wires in solutions that are more concentrated in the Cl^- ion. It is a good description of the 1 N Cl^- case, a fair description of the 0.01 N Cl^- case, and an occasional description of the 0.0001 N Cl^- case.

Figures 84 through 87 show that intergranular surface etching was not obtained as a result of electropolishing in four different solutions, including the one used in the experiments, and shows (at least on a 3,000X scale) that the initial surface of the wires used was smooth.

Figure 88 shows the behavior of the mean peak potential versus the SCE on a pH-log $[\text{Cl}^-]$ field. The pH and chloride ion concentration were determined by analyzing the solutions after the experiment. The observed behavior was fairly complex. Over most of the field there was a negative trend in potential as the $[\text{Cl}^-]$ was increased at a constant pH. At a constant $[\text{Cl}^-]$, increasing the pH from zero resulted in a negative trend followed by a positive trend in the potential. The effect is that of having a set of bowl-shaped contours concave in the direction of a high $[\text{Cl}^-]$ with the minimum being in the pH range from 4 to 7.

Figure 89 shows the stress on the wires at the breaking point plotted on a pH-log $[\text{Cl}^-]$ field. The breaking stress is also described by bowl-shaped contours having a minimum in the pH range from 3 to 5.

Figure 90 shows that the general behavior of the potentials measured, using the spinning-electrode technique, follows that of the stressed-wire potentials and breaking stresses with a minimum at a pH of 7.

It is postulated that the process occurring during cracking is similar to the bare metal-solution reactions taking place at the spinning electrode, since both had similar pH-log Cl^- dependence. The difference in the observed minima (pH = 4 - 7 for the stressed wires versus a pH of ≈ 7 for the spinning electrode) could have been due to the relative integrities of the oxide film. These films would have retarded the reaction except at lower pH values. This retardation would be due to the onset of passivity at higher pH values as already postulated for the spinning electrode. This onset of passivity would have required a higher pH for the case where abrasion was interfering (spinning electrode) as opposed to the case where there was no abrasion (stressed wires).

(a) At 3,000X SM-14331

(b) At 1,000X SM-14332

(c) At 300X SM-14333

(d) At 100X SM-14334

Figure 84. SCANNING ELECTRON MICROGRAPHS OF AN AREA ON A MULBERRY WIRE THAT WAS ELECTROPOLISHED USING CONCENTRATED PHOSPHORIC ACID.

(a) At 3,000X SM-14192

(b) At 1,000X SM-14193

(c) At 300X SM-14194

(d) At 100X SM-14195

Figure 85. SCANNING ELECTRON MICROGRAPHS OF AN AREA ON A MULBERRY WIRE THAT WAS ELECTROPOLISHED USING CONCENTRATED PHOSPHORIC ACID SATURATED WITH POTASSIUM CHROMATE.

(a) At 3,000X SM-14323

(b) At 1,000X SM-14324

(c) At 300X SM-14325

(d) At 100X SM-14326

Figure 86. SCANNING ELECTRON MICROGRAPHS OF AN AREA ON A MULBERRY WIRE THAT WAS ELECTROPOLISHED USING A 75 VOLUME PERCENT CONCENTRATED PHOSPHORIC ACID-25 VOLUME PERCENT CONCENTRATED NITRIC ACID SOLUTION.

(a) At 3,000X SM-14205

(b) At 1,000X SM-14206

(c) 300X SM-14207

(d) 100X SM-14208

Figure 87. SCANNING ELECTRON MICROGRAPHS OF AN AREA ON A MULBERRY WIRE THAT WAS ELECTROPOLISHED USING FIVE VOLUME PERCENT PERCHLORIC ACID IN MENTHANOL.

*Average of two points.

**Average of three points.

***This wire exhibited two different regions which individually yielded different MPP's. Since the more negative value (- 0.432) seemed to be anomalous, the lower value was used.

Figure 88. CONTOUR MAP OF A MEAN PEAK POTENTIAL ON A pH-LOG $[Cl^-]$ FIELD. (Potential Expressed in Volts with Respect to SCE)

Figure 89. CONTOUR MAP OF A BREAKING STRESS ON A pH-LOG $[Cl^-]$ FIELD. (Stress Expressed in ksi)

Figure 90. CONTOUR MAP OF A SPINNING ELECTRODE REST POTENTIAL ON A pH-LOG $[Cl^-]$ FIELD.
(Potential Expressed in Volts with Respect to NHE)

Table 10

ANALYSES OF SOLUTIONS EXPOSED TO STRESSED MULBERRY WIRES

Nominal Solution	Wire Number	Pre-Analysis		Post-Analysis	
		pH	log $[Cl^-]$	pH	Log $[Cl^-]$
pH 2, 1 $N [Cl^-]$	41	2.09	-0.012	2.14	0.034
pH 2, 0.01 $N [Cl^-]$	39	2.23	-1.983	2.13	-1.963
pH 2, 0.0001 $N [Cl^-]$	40	2.09	-2.646	2.05	-5.686
	51	2.09	-2.646	2.44	-4.646
pH 4, 1 $N [Cl^-]$	43	-	-	-	-
pH 4, 0.01 $N [Cl^-]$	52	3.97	-1.613	4.08	-2.939
	53	3.97	-1.613	4.00	-2.917
pH 4, 0.0001 $N [Cl^-]$	54	3.91	-3.031	3.72	-4.772
	55	3.91	-3.031	3.87	-4.706
	62	3.91	-3.031	3.62	-5.629
pH 7, 1 $N [Cl^-]$	45	-	-	6.12	-2.975
pH 7, 0.01 $N [Cl^-]$	-	-	-	-	-
pH 7, 0.0001 $N [Cl^-]$	64	5.58	-2.367	5.08	-5.979
	48	5.58	-2.367	6.27	-2.306
	61	5.58	-2.367	4.88	-4.369
pH 10, 1 $N [Cl^-]$	44	-	-	6.54	0.008
pH 10, 0.01 $N [Cl^-]$	58	8.48	-3.011	6.61	-2.867
	59	8.48	-3.011	6.57	-2.780
pH 10, 0.0001 $N [Cl^-]$	56	7.53	-3.249	6.60	-4.073
	57	7.53	-3.249	6.33	-4.646
pH 12, 1 $N [Cl^-]$	42	-	-	-	-
pH 12, 0.01 $N [Cl^-]$	37	12.32	-2.176	11.72	-1.879
	50	12.32	-2.176	10.75	-1.833
pH 12, 0.0001 $N [Cl^-]$	46	12.29	-2.395	11.12	-2.031

(a) At 3,000X (cracked surface)

SM-15446

(b) At 1,000X (cracked surface)

SM-15447

(c) At 3,000X (exposed surface)

SM-15455

(d) At 1,000X (exposed surface)

SM-15456

Figure 91. SCANNING ELECTRON MICROGRAPHS OF MULBERRY WIRE 43 THAT WAS EXPOSED TO A NOMINAL 0.0001 $\underline{N}$ HCl-1 $\underline{N}$ KCl SOLUTION. (Intergranular Cracking and Slight Surface Intergranular Etching are Shown)

(a) At 3,000X (cracked surface)

SM-15465

(b) At 1,000X (cracked surface)

SM-15466

(c) At 3,000X (exposed surface)

SM-15476

(d) At 1,000X (exposed surface)

SM-15477

Figure 92. SCANNING ELECTRON MICROGRAPHS OF MULBERRY WIRE 44 THAT WAS EXPOSED TO A pH = 6.54-pCl = 0.008 SOLUTION. (Etch Pits and Mud Cracking on the Surface are Shown)

(a) At 3,000X

SM-15442

(b) At 1,000X

SM-15443

(c) At 3,000X (exposed surface)

SM-15434

(d) At 1,000X (exposed surface)

SM-15435

Figure 93. SCANNING ELECTRON MICROGRAPHS OF MULBERRY WIRE 42 THAT WAS EXPOSED TO A NOMINALLY $\text{pH} = 12$ - $\text{pCl} = 0$ SOLUTION. (A Probable Crack Initiation Site and Surface Intergranular Etching are Shown)

(a) At 3,000X (cracked surface)

SM-15390

(b) At 1,000X (cracked surface)

SM-15391

(c) At 3,000X (cracked surface)

SM-15392

(d) At 3,000X (cracked surface; etch pit)

SM-15394

Figure 94. SCANNING ELECTRON MICROGRAPHS OF MULBERRY WIRE 39 THAT WAS EXPOSED TO A $\text{pH} = 2.13$ - $\text{pCl} = 1.963$ SOLUTION. (A Transition Area between Intergranular Cracking and a Dimple Rupture, and also a Large Etch Pit are Shown)

(a) At 10,000X (cracked surface)

SM-15423

(b) At 1,000X (cracked surface)

SM-15425

(c) At 3,000X (cracked surface)

SM-15419

(d) At 3,000X (exposed surface)

SM-15414

Figure 95. SCANNING ELECTRON MICROGRAPHS OF MULBERRY WIRE 40 THAT WAS EXPOSED TO A pH = 2.05-pCl = 5.686 (ORIGINALLY pCl=2.646) SOLUTION. (Spherical Corrosion Product and Cleavage are Shown)

(a) At 3,000X (exposed surface)

SM-18536

(b) At 1,000X (exposed surface)

SM-18537

(c) At 300X (exposed surface)

SM-18538

Figure 96. SCANNING ELECTRON MICROGRAPHS OF MULBERRY WIRE 56 THAT WAS EXPOSED TO A pH = 6.60-pCl = 4.073 SOLUTION. (Deep Intergranular Etching Next to the Crack is Shown)

RELATIONSHIP OF PITTING AND STRESS-CORROSION CRACKING

Rationale

The lower limit of the anodic current needed for crack propagation has not been determined, but current densities of less than 1×10^{-6} amp/cm² in halide solutions were found to be sufficient under most conditions. Pitting of Mulberry samples was observed in many instances when the anodic current was very high. Polarization studies have also revealed a potential region of high pitting activity.

From polarization studies it seemed apparent that pitting occurred at much higher potentials than the region of small anodic current densities. However, the argument could not be ignored that pitting was not observed due to the short length of time of the experiments, and that cracking did proceed by the same mechanism as pitting. Long-term pitting studies were initiated to see if, given a sufficient length of time, pitting could be accomplished under the same conditions that cracking occurred.

There are several pitting mechanisms which have been proposed which differ in details, the most recent being by F. A. Posey.⁽¹²⁾ All the mechanisms rely on metal dissolution followed by precipitation of a basic salt. This, in turn, lowers the pH of the solution and makes oxide passivation difficult. The pitting occurs since this mechanism requires restricted geometry to inhibit ionic transport. The object of this study was not to be specific as to the details of the pitting mechanism of Mulberry but to check to see if any pitting mechanism could apply to Mulberry stress-corrosion cracking.

The experiment was designed to place unstressed Mulberry specimens in conditions which would assuredly crack a stressed sample but which would not lead to observable pitting. It was hypothesized that pitting occurs only under highly anodic conditions and is mostly determined by the potential of the sample. It had already been determined (see **Polarization Studies in Aqueous Chloride Solutions**, Page 30) that the pitting region was at least above +0.5 volt with respect to the standard hydrogen electrode for most solutions. A "critical pitting potential"^(c) has not been determined due to experimental difficulties.

The conditions, therefore, chosen to carry out the long-term test were a 0.01 N HCl solution with an anodic current density of 2×10^{-6} amp/cm². These conditions would cause complete failure (stress cracking) of a bend specimen in a matter of minutes. The 0.01 N HCl does not attack Mulberry at the rest potential on a short-term basis. Pitting, however, can be initiated more easily in this solution than in most other solutions so far studied. A voltage of only +0.25 volt and a current density of 2×10^{-5} amp/cm² are sufficient to initiate short-term pitting. Furthermore, once initiated, a lower voltage is

(c) Definition of "critical pitting potential" is, at present, in dispute. The latest definition accepted is the potential obtained when the potential is swept negative from the pitting conditions to the oxide passivation. The potential of cessation of pitting is then designated as the "critical pitting potential", E_{pc} . For Mulberry, however, in some solutions the pitting stops when the sample becomes cathodic and never passes through the passivation step. The E_{pc} will be highly dependent on the type of solution used. Theoretically, it is assumed that, given enough time, the sample would pit if its potential were above the E_{pc} .

required to stop pitting in this solution compared to the other solutions studied. The voltage had to be dropped below + 0.05 volt to stop the pitting if it were in process. It is reasonable to assume that if no pitting were to occur in this solution at 2×10^{-6} amp/cm², it would not occur in any of the other solutions studied.

Experimental

The Mulberry samples were selected from well-characterized skull-cast material. The material was cut in 1/4-inch cubes, mounted in epoxy resin, and mechanically polished. The final polishing of the samples was done only a few hours before admission to the electrolytic cell and the start of the experiment. A 1/8-inch hole was drilled in the back of the sample mount to permit an ohmic contact by a platinum wire. The wire and press screw were coated with lacquer for insulation. The polished surface of the Mulberry sample was, therefore, the only locus of the anodic current.

Each sample was contained in a separate cell to avoid possible uncertainty in the polarization current due to geometry or sample interaction. The counter electrodes were of platinum, consisting of 30-gauge wire and a half-inch square of platinum mesh. Each cell was provided with a calomel electrode. These electrodes were checked after the long-term experiment to see if any damage had been done due to a back flow of solution into the electrode. All electrodes checked within one millivolt except one which had a cloudy appearance and was off by + 0.55 volt. The voltage measurements of that sample were discounted.

Included in the cell design was an argon bubbler to sweep out the oxygen in solution before and during the experiment. This argon was first purified over uranium chips at 700° C and then saturated with water in a bubbler to prevent evaporation of the electrolyte.

A constant current was maintained by using a constant-voltage DC power supply and dropping the voltage (20 volts) across a 10-megohm resistor and the cell in series. Small variations in the EMF due to sample and counter electrode overvoltages were insignificant compared to the IR drop of the resistor. A record of the potentials of the samples versus the reference electrodes was maintained with the aid of a 12-point strip-chart recorder.

Results

Two samples each were run for 1, 2, 4 1/2, 8, 16, and 32 days with a constant current density of 2×10^{-6} amp/cm². For the 32-day samples, the bubbler was used only 16 days and the samples were allowed to equilibrate with air for the remaining 16 days. Samples were removed after the appropriate time and examined with a light microscope at a magnification of 1,000X. They were also examined with the aid of a scanning electron microscope with a magnification of 30,000X. Except for inclusions on the sample surface, the samples were featureless with no evidence of pitting, except for the 32-day sample whose micrograph at 30,000X revealed very small markings which were not identified but did not appear to be pits.

The potential of most of the samples initially became very negative for about 30 minutes, which might have been due to the recent mechanical polish. Most of the potentials settled to -0.05 ± 0.10 volt with respect to the NHE. Admission of air to the 32-day samples seemed to raise the potential slightly above this value. Transients of 0.025 volt were common, as typified in Figure 97. These transients were also common just before and during cracking of the bend specimens when constant current was applied, and may be characteristic of the

Figure 97. VOLTAGE TRANSIENTS ON AN UNSTRESSED MULBERRY SAMPLE IN A 0.01 N HCl SOLUTION WITH AN ANODIC CURRENT DENSITY OF 2 μ amps/cm². (Sample 11 after a 32-Day Exposure)

cracking process. In the case of cracking, these transients were followed by a crack opening and a large negative transient due to metal exposure. The possibility that these initial transients were due to oxide cracking and subsequent metal exposure is unlikely since the scanning electron microscope did not reveal a "mud cracking" or spalling effect, as might be expected. The electrical behavior of these samples was very similar to the bend samples which cracked under similar conditions.

It is concluded from these considerations and the absence of pits at 1,000X magnification on these samples that a pitting mechanism is not necessary for SCC in Mulberry, and some other mechanism predominates. Such mechanisms could be preferential etching, grain boundary separation due to expansion from a chemical reaction, a surface tension lowering at the grain boundaries, or possibly hydrogen embrittlement. Other mechanisms can be postulated. The pitting mechanism, however, is effectively eliminated.

THE EFFECT OF TRACE AMOUNTS OF LANTHANUM

Rationale

One of the postulated mechanisms for stress-corrosion cracking of Mulberry assumed that an acidic product was produced in the advancing crack to produce an environment in which uranium was active. It was hoped that additions of small amounts of a metal which would create a basic solution in water would inhibit this action. For maximum effectiveness, this metal would have to prefer grain boundaries. Lanthanum was chosen because of its basic nature, its slight solubility in uranium, and its acceptable melting and boiling points. Other rare earths also appeared to be acceptable by these criteria.

Experimental Methods and Results

A small charge of Mulberry alloy was doped with a nominal 0.4 weight percent lanthanum and was swaged into wire that was 47.5 mils in diameter. It was observed during swaging that this alloy was more brittle than undoped Mulberry. An as-cast sample was examined metallographically (Figure 98) and was found to contain a dendritic structure in the grains, with large inclusions which were water soluble. It was assumed that these inclusions were lanthanum rich. With diamond-alcohol polishing, these inclusions were directly observable (Figure 99) and reacted in air, which supported this conclusion. The as-received wire samples had a certain amount of cold working. Metallographic examination (Figure 100) revealed an elongated grain structure with many inclusions.

There was a deep lap extending the full length of the wire, and when the wire was clamped into the wire-stressing apparatus, some splitting at this lap was observed. Prior to testing, the wires were electropolished in a $\text{H}_3\text{PO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ solution.

Three specimens of as-received wire were tested for resistance to SCC. Specimen 1 was exposed to 0.01 N HCl. This wire acquired a potential of - 0.26 volt versus the SCE and broke at about 53 ksi. Specimen 2 was exposed to 0.01 N HCl and acquired a potential of - 0.30 volt versus the SCE. This wire broke at about 64 ksi. Specimen 3 was exposed to a 0.01 N HCl-1.0 N KCl solution, acquired a potential of - 0.45 to - 0.46 volt versus the SCE, and broke at about 83 ksi. These results indicate a higher resistance to SCC than standard Mulberry; however, it had already been demonstrated that cold-worked Mulberry was resistant to stress-corrosion cracking. Scanning electron micrographs (SEM) of the cold-worked, doped Mulberry revealed purely mechanical fracture with no intergranularity.

This observation is in contrast to cold-worked Mulberry which is SCC resistant, but still fails intergranularly.

This same material was annealed at 800° C, water quenched, aged in oil at 150° C, and again exposed to chloride under stress. In this condition the wire cracked under about the same stress as the undoped Mulberry. The SEM (Figure 101) revealed complete intergranular fracturing with many etched areas and numerous small pits. Metallographic examination of this material (Figure 102) now showed normally shaped and well-defined grains and grain boundaries with many large inclusions in what appeared to be a linear array. This array resembled strongly the grain-boundary pattern of cold-worked material.

To detect if the lanthanum deposited in the grain boundaries and to determine any other possible segregations, samples of both the cold-worked and recrystallized material were analyzed by the electron microprobe. The microprobe analysis revealed a 0.3 weight percent lanthanum in the bulk of the metal and lanthanum-rich streaks where the cold-worked grain boundaries existed. In the unrecrystallized samples (Figure 103), streaks of 5 to 50 weight percent lanthanum-rich materials were detected; whereas, in the heat-treated sample (Figure 104), inclusions in linear arrays containing 5 to 80 weight percent lanthanum-rich material were present. It is apparent that the heat treatment was not adequate for the lanthanum to migrate with the grain boundaries as desired. Tests tried in 1 N KCl of pH 2 on as-cast material which was cut into bars have shown that this material is very susceptible to SCC. Heat treatment did not improve its resistance and may have made it more susceptible.

It appears that additions of lanthanum in 0.4 weight percent concentration did not improve the SCC resistance of Mulberry when the Mulberry was heat treated in the usual manner. However, the lanthanum did tend to concentrate at the grain boundaries. Due to its reactive nature in water, however, it may have leached out and weakened the integrity of the grain boundary.

H203a

Figure 98. AS-CAST LANTHANUM-DOPED MULBERRY. (Etched in 5% Oxalic Acid; 500X)

H203f

Figure 99. AS-CAST LANTHANUM-DOPED MULBERRY. (Diamond-Alcohol Polish and No Etch; 1,000X)

H113-2

Figure 100. METALLOGRAPH OF LANTHANUM-DOPED MULBERRY WIRE. (As Received; Longitudinal Section; 1,000X)

(a) At 3,000X

SM-19601

(b) At 1,000X

SM-19602

(c) At 300X

SM-19603

(d) At 100X

SM-19605

Figure 101. SCANNING ELECTRON MICROGRAPHS OF THE FRACTURED END OF A HEAT-TREATED, LANTHANUM-DOPED MULBERRY WIRE. (Intergranular Fracture and Etched Pits are Shown)

H113-4

Figure 102. METALLOGRAPH OF A LANTHANUM-DOPED MULBERRY WIRE AFTER HEAT TREATMENT. (Longitudinal Section; 1,000X)

(a) Backscattered Electron Videograph

(b) Uranium Characteristic X-Ray Videograph

(c) Niobium Characteristic X-Ray Videograph

(d) Zirconium Characteristic X-Ray Videograph

(e) Lanthanum Characteristic X-Ray Videograph

(f) Lanthanum Background X-Ray Videograph

Figure 103. MICROPROBE ANALYSIS OF AN AS-RECEIVED, LANTHANUM-DOPED MULBERRY WIRE. (Longitudinal Section; 1,000X)

(a) Backscattered Electron Videograph.

(b) Uranium Characteristic X-Ray Videograph

(c) Niobium Characteristic X-Ray Videograph

(d) Zirconium Characteristic X-Ray Videograph

(e) Lanthanum Characteristic X-Ray Videograph

(f) Lanthanum Background X-Ray Videograph

Figure 104. MICROPROBE ANALYSIS OF HEAT-TREATED, LANTHANUM-DOPED MULBERRY WIRE. (Longitudinal Section; 1,000X)

CONCLUSIONS

Changing the oxide film thickness by thermal oxidation in air raised the rest potential of Mulberry, α, γ_3 Mulberry, and uranium in 1 N solutions of SO_4^{2-} , NO_3^- , OH^- , and ClO_4^- , but did not substantially change the rest potential in 1 N halide solutions. This result would seem to indicate some form of penetration of the oxide by halide ions.

Rest-potential differences observed across a sample of large-grained Mulberry that possibly contained α, γ_3 Mulberry were large enough to provide significant driving force for self-accelerated corrosion. The potential gradients found were more pronounced in the order: $\text{NH}_3(\text{aq}) < \text{KNO}_3 < \text{KCl} < \text{HCl}$.

Polarization under moisture films (presumably free from the chloride ion) also produced pitting. In these polarizations, the anodic branch had a higher current at a given overvoltage for the first sweep than for successive sweeps, possibly indicating the formation of an anodic film which was not subsequently reduced by the intervening cathodic polarization.

Polarization studies in hydroxide solution indicate the most consistent feature to be a Flade potential peak at +0.25 volt versus the NHE for uranium and +1.27 volts versus the NHE for Mulberry. A cathodic peak observed for Mulberry was determined not to be due to hydrogen charging. No differences larger than the experimental error were found for polarization curves measured for arc-melted and skull-cast Mulberry.

When polarization studies were carried out on Mulberry using chloride-containing solutions, small transient potential changes were observed at zero current, possibly indicating some pitting followed by self passivation. When the samples were anodically polarized into the active pitting region, the zero current potential in the following anodic-to-cathodic sweep was lowered considerably.

An abrading Mulberry electrode exposed to a variety of solutions exhibited a qualitatively similar behavior on the pH-pCl field as the transients and breaking stresses, but shifted on the pH axis. In nearly neutral solutions there is apparently participation by OH^- in the dissolution process, with passivation taking over at higher pH values.

Acoustic emission studies revealed that cracking could be inhibited by cathodic currents for all halides except F^- , and cracking was accelerated by anodic currents. During these studies it was also discovered that cold-worked areas were resistant to SCC, and that NO_3^- and CN^- would inhibit cracking in the presence of Cl^- .

High-stress-rate experiments on stressed wires showed that the potential of the wire is sensitive to the presence or absence of oxygen. This condition applies even to the fast transient observed when the wire catastrophically breaks.

Long-term stressed-wire experiments showed significant transients, apparently signifying cracking and/or pitting followed by passivation. These transients had amplitudes which could be as high as 0.5 volt. The potentials reached by the wires during these transients had a similar behavior regarding the pH-pCl field as did the breaking stress of the wires. Consumption of Cl^- from the solution was observed during these experiments.

It was shown, when using 0.01 N HCl, that anodic currents capable of causing immediate cracking of Mulberry would not cause pitting in the same environment, weakening support for a pit-related cracking mechanism.

The addition of 0.4 weight percent lanthanum to Mulberry was found to apparently further increase the resistance of cold-worked material to SCC, but to be ineffective in increasing the resistance of Mulberry given a subsequent heat treatment. In the cold-worked state, the lanthanum was apparently concentrated in the grain boundaries of the alloy. However, it did not follow the boundaries during a subsequent heat treatment.

Two mechanisms for SCC are deemed unlikely, namely:

1. Any mechanism that is purely dependent on a pitting model.
2. Any hydrogen charging or hydrogen embrittlement.

The stress-level contours obtained on the pH-pCl field are not favorable for the second mechanism. Furthermore, the absence of hydrogen charging in the cathodic region supports this contention. To counter the conclusions drawn from the pH-pCl field contours (by arguing that in low pH region the driving forces are eliminated due to more homogeneous potentials on the Mulberry surface) is not consistent with the potential gradients across the surface found with HCl solutions.

The simplest explanation for SCC of Mulberry would be preferential anodic dissolution of metal at the grain boundaries. This action is aided by possible complexing or oxide penetration by halide ions. Large ions such as NO_3^- and CN^- could interfere by competing surface adsorption.

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