214
29-75
1

Dr-1141

Y-1965

VARIABLES WHICH INFLUENCE THE STRESS-
CORROSION CRACKING OF URANIUM-7.5
NIOBIUM-2.5 ZIRCONIUM ALLOY

J. W. Koger

MASTER

January 1975

UNION
CARBIDE

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

*prepared for the U.S. ATOMIC ENERGY COMMISSION
under U.S. GOVERNMENT Contract W-7405 eng 26*

DISTRIBUTION OF THIS DOCUMENT UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Reference to a company or product name does not imply approval or recommendation of the product by Union Carbide Corporation or the U.S. Atomic Energy Commission to the exclusion of others that may meet specifications.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$2.25

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Date of Issue: January 28, 1974
Distribution Category: UC-25

Report Number: Y-1965

**VARIABLES WHICH INFLUENCE THE STRESS-CORROSION CRACKING
OF URANIUM-7.5 NIOBIUM-2.5 ZIRCONIUM ALLOY**

J. W. Koger

Metallurgical Development Department
Y-12 Development Division

Oak Ridge Y-12 Plant

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

Prepared for the U.S. Atomic Energy Commission
Under U.S. Government Contract W-7405-eng-26

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT UNLIMITED

Py

ABSTRACT

More positive electric potentials, lower pHs, increasing chloride content, and increasing stresses decrease the time to failure of uranium-7.5 wt % niobium-2.5 wt % zirconium alloy (mulberry). Increasing amounts of chlorides increase the general corrosion rate of mulberry. In chloride solutions and above the yield stress, all failure times are short regardless of the chloride content, pH, or potential.

CONTENTS

SUMMARY	4
INTRODUCTION	5
VARIABLES WHICH INFLUENCE THE STRESS-CORROSION CRACKING OF MULBERRY.....	6
Experimental Work	6
Experimental Results	7
Fully Recrystallized Alloys	7
Unrecrystallized Alloys	14
Discussion	14
Conclusions	16
REFERENCES	18
ACKNOWLEDGEMENTS	19

SUMMARY

More positive electric potentials, lower pHs, increasing chloride content, and increasing stresses decrease the time to failure of uranium-7.5 wt % niobium-2.5 wt % zirconium alloy (mulberry). Increasing amounts of chlorides increase the general corrosion rate of mulberry. In chloride solutions and above the yield stress, all failure times are short regardless of the chloride content, pH, or potential. Crack growth was discontinuous and failure was intergranular. Sodium nitrate inhibited crack growth but did not prevent it. Pitting occurred in chloride-containing solutions of 50 ppm or more and pHs from 2 to 9. Passivation can occur in chloride solutions at a pH of 12. Electropolished mulberry is more resistant to cracking than machined-surface mulberry in solutions of low chloride concentration, but not in solutions of high chloride concentration. Unrecrystallized mulberry showed more resistance to cracking than the fully recrystallized alloy at 34 ksi (234 MPa). At stresses above yield, no differences were seen.

INTRODUCTION

Single-phase, gamma-quenched uranium-7.5 wt % niobium-2.5 wt % zirconium (mulberry) is susceptible to stress-corrosion cracking in aqueous chloride-containing solutions.^(1 - 10) It was the purpose of this investigation, conducted at the Oak Ridge Y-12 Plant,^(a) to systematically determine the time to failure of the alloy as a function of stress, applied potential, pH, and chloride content, and to assess the effect of each on stress-corrosion cracking. Inhibition and pitting were also studied. Fully recrystallized, unrecrystallized, partially recrystallized, and electropolished alloys were to be tested.

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

VARIABLES WHICH INFLUENCE THE STRESS-CORROSION CRACKING OF MULBERRY

EXPERIMENTAL WORK

The mulberry used in this experiment was double arc melted, hot forged, hot rolled, and vacuum-water quenched from 800° C. The alloy was then aged at 150° C for one hour and machined into the various specimens. Some of the specimens were further worked and water quenched to provide alloys which were not fully recrystallized. Various mechanical properties are given in Table 1. All these specimens had machined surfaces with naturally formed oxide. Some of the standard specimens were electropolished in a mixture of concentrated phosphoric acid and 3% chromic acid heated to 120° C. Before test, all specimens were degreased with acetone and rinsed with ethanol.

Table 1
MECHANICAL PROPERTIES OF MULBERRY

	Ultimate Tensile Strength		Yield Strength ⁽¹⁾		Elongation ⁽²⁾
	(ksi)	(MPa)	(ksi)	(MPa)	(%)
Aged 150°C - 1 hr (completely recrystallized)	125.0	861.3	75.0	516.8	25.0
Very Little Recrystallization	139.0	957.7	80.0	551.2	25.0
Partially Recrystallized (over 50%)	125.5	864.7	67.0	461.6	25.0

(1) At 0.2% offset.

(2) In one inch.

Solutions used were prepared from laboratory reagent chemicals and deionized water. The buffers used to fix the pHs included acetic acid, potassium hydrogen phthalate, and sodium hydroxide. Polarization measurements were made on specimens in water containing only the buffers to assess the effect of the buffers. No corrosive or inhibitive effects were noted.

The electrochemical cells were either glass or polyethylene. Platinum was used as the counter electrode. Potentials were measured using an Ag/AgCl or calomel reference electrode. The electronic potentiostat used was designed and built at the Oak Ridge National Laboratory.

The test method used to determine the stress-corrosion-cracking (SCC) characteristics of a particular system involved exposing bent specimens, to which a potential was applied, to chloride solutions. The specimens were stressed in constant-deflection, four-point bend fixtures made of Plexiglas. Several fixtures which could provide a variety of strains were available. The strains provided by the fixtures were calculated and the values obtained compared favorably to strain-gage measurements on specimens held in the fixtures. The stress-corrosion specimens were 5 inches (127 mm) long by 0.5 inch (13 mm) wide by 0.0625 inch (2 mm) thick. The reproducibility of data for a specimen of this size was quite good. An acoustic emission detector was also attached to the specimen during SCC tests. The detector was an AEROTECH piezoelectric transducer. The acoustic pulse was amplified with a 60 db, 1 Hz-to-1 MHz amplifier and was high-pass filtered at 5000 kHz to remove

extraneous background pickup. The number of acoustic pulses passing above a 0.2-volt threshold each second was recorded. Along with the acoustic pulses, the current resulting from the applied potential, the time of the first appearance of a visible surface crack, and the time for complete failure were noted and recorded. After test, specimens were subsequently examined both by optical and scanning electron microscopy.

The open-circuit potential (initial corrosion potential) was obtained for each system before applying a potential. The open-circuit potential was monitored up to 30 minutes, by which time it was normally constant. Polarization curves were obtained for unstressed specimens in the various chloride systems. The potential was varied from - 900 to + 900 mV vs the Ag/AgCl standard electrode and the change in current monitored. The scanning rate was about 4 v/hr.

EXPERIMENTAL RESULTS

Fully Recrystallized Alloys

Machined Surface - It was first noted that the open-circuit potentials obtained during the measurement of polarization curves or before applying a potential to the stressed specimens became more positive as the chloride content was lowered. More positive values generally reflect lower dissolution rates, so increasing amounts of chlorides apparently promote increasing general dissolution of the alloy. This effect becomes more obvious as the pH is lowered.

The time to failure at a given potential for specimens stressed to 34 ksi (234 MPa) for various chloride concentrations and pHs is given in Figure 1. At more positive potentials, lower pHs, and higher chloride concentrations, the time to failure decreases. Increasing the potential had the same effect as adding oxidizers to the solution. Figure 2 shows times to failure in various solutions and applied potentials as a function of the applied stress. As expected, the time to failure increased with decreasing stress. The increase was less in the more aggressive solutions. The effect of applied potential and chloride concentration can also be seen in this figure. At 34 ksi (234 MPa), failure occurred in 195 minutes in a 1-ppm chloride solution of a pH of 4 and an applied potential of + 700 mV vs Ag/AgCl. Also, at 34 ksi (234 MPa), failure occurred in deionized water (< 1 ppm chloride) at an applied potential of + 1500 mV vs Ag/AgCl in 10 hours. At stresses above yield; for example, 1.5% strain [$\sim$ 110 ksi (760 MPa)], specimens would fail in about five minutes at any chloride concentration, pH, or potential.

The specimens of Curve 2 (Figure 2) were exposed to the same solution as the specimens of Curve 1, but applied electrical potential was different. This 50-mV difference about doubled the time to failure at the lower stresses. For the given test conditions, the specimens of Curves 2 and 3 could be stressed about 40% more than the specimens of Curve 1 to obtain equal times to failure. It is interesting to compare Curves 2 and 3, which are about identical. The specimens of Curve 3 were exposed to less chloride, which increases the time to failure; but were in a solution of lower pH and had a higher applied electrical potential, which decreases the time to failure. These effects essentially balanced out. From a comparison of the longer times to failure of the specimens of Curve 3 to those of Curve 1, it is obvious that the change in chloride content from 355 to 50 ppm, which increases the time to failure, had more effect than the decrease in pH from 8 to 4, which decreases the time to failure.

Likewise, in comparing the specimens of Curves 3 and 4, the decrease in chloride content had a much greater effect than the increase in applied electrical potential of 700 mV. In a practical sense, these results show that changes in the oxidizing potential of the medium

Figure 1. TIME TO FAILURE VERSUS THE POTENTIAL. (Mulberry in Sodium Chloride Solutions as a Function of the pH for Mulberry that was Stressed at 34 ksi (234 MPa))

Figure 2. TIME TO FAILURE OF MULBERRY VERSUS THE APPLIED STRESS. (All Potentials vs Ag/AgCl Standard Electrode)

(applied electrical potential) and pH are more easily tolerated than changes in chloride concentration.

The effect of each of the variables (applied potential, chloride concentration, stress, and pH) on the time to failure, while holding the others constant, is quite interesting and sometimes rather dramatic. The effect of the variables for pHs of 4 and 9 are given in Table 2. At certain potentials, pHs, and stresses, mulberry did not fail after 1000 minutes in 50-ppm chloride solutions, but would fail in a very short time in 0.1 M (3550-ppm) chloride solutions. A stress increase from 34 to 55 ksi (234 to 379 MPa) at a constant pH, chloride concentration, and potential, or a pH change from 9 to 4 at constant stress, chloride concentration, and potential, greatly decreased the time to failure.

Table 2

EFFECT OF STRESS-CORROSION-CRACKING VARIABLES ON THE TIME TO FAILURE OF MULBERRY IN SODIUM CHLORIDE SOLUTIONS

Applied Potential vs Ag/AgCl Electrode (mV)	Chloride Concentration	Applied Stress		pH	Time to Failure (min)
		(ksi)	(MPa)		
<u>Effect of Cl⁻ Concentration</u>					
0	0.1 M	34	234	9	20
0	0.1 M	34	234	9	64
0	50 ppm	34	234	9	(1)
0	0.1 M	34	234	4	4
0	50 ppm	34	234	4	(1)
-100	0.1 M	34	234	9	60
-100	50 ppm	34	234	9	(1)
<u>Effect of Stress</u>					
0	0.1 M	34	234	9	20
0	0.1 M	55	379	9	10
-100	0.1 M	34	234	4	27
-100	0.1 M	55	379	4	3
0	50 ppm	34	234	4	(1)
0	50 ppm	55	379	4	42
+200	50 ppm	34	234	4	56
+200	50 ppm	110	758	4	4
<u>Effect of Applied Potential</u>					
0	0.1 M	34	234	9	20
-100	0.1 M	34	234	9	60
0	0.1 M	34	234	4	4
-100	0.1 M	34	234	4	27
0	50 ppm	34	234	4	(1)
+200	50 ppm	34	234	4	56
<u>Effect of pH</u>					
0	0.1 M	34	234	9	20
0	0.1 M	34	234	4	4
-100	0.1 M	34	234	9	60
-100	0.1 M	34	234	4	27

(1) None failed in 1000 min.

The acoustic pulses generated during the time-to-failure experiments were discrete; and, in solutions of 0.1 and 0.01 *M* NaCl, did not occur until about five minutes before complete failure. An example is given in Figure 3. This discontinuous emission is characteristic of crack propagation or twinning. It was observed that the first recorded pulse coincided with the first visible crack. On this basis, the crack velocity was calculated and found to be ~ 0.1 in/min (0.04 mm/sec) in 0.1 and 0.01 *M* NaCl solutions. The crack growth was discontinuous—stopping and starting until failure occurred. An example of the acoustic pulse behavior for a low-chloride (< 1 ppm) solution is given in Table 3. Crack velocities varied with the applied stress. The first acoustic pulse represented the initiation of the crack, while the onset of the series of discrete pulses represented the crack growth. The crack-growth rate was much slower than that seen in the more concentrated solutions.

Optical and scanning electron micrographs (Figure 4) of all the failures showed intergranular attack with few, if any, signs of ductile behavior.

Inhibition - It was previously reported that nitrate ions inhibit crack growth in mulberry. (6,11) Ten grams per liter appeared to be sufficient to prevent or delay the cracking of mulberry in 8.6×10^{-3} *M* sodium chloride.

In order to further quantify the nitrate-inhibition effect, an accelerated SCC test was conducted on mulberry in chloride solutions containing varying amounts of sodium nitrate. The acoustic-emission device was connected to the specimens to monitor the cracking. The results are given in Table 4. With increased amounts of sodium nitrate, the time to failure did increase several times. In all but the last case (12.5 g/l NaNO₃), few, if any, acoustic-emission signals were detected until 2 to 8 minutes before failure. In the last case, signals (cracks) were detected five minutes after the start of the test and continued until failure. The sodium nitrate did inhibit the crack growth but did not cause passivation or eliminate the failure.

Figure 3. ACOUSTIC EMISSION EVENTS PRECEDING THE FAILURE OF MULBERRY IN A STRESS-CORROSION-CRACKING TEST.

Table 3
AVERAGE CRACK VELOCITY VERSUS THE APPLIED STRESS
FOR MULBERRY IN LOW-CHLORIDE WATER

Applied Stress		Time (min)			Average Crack Velocity	
(ksi)	(MPa)	First Acoustic Pulse	Series of Discrete Pulses	Failure	(in/min)	(mm/min)
34	234	140	160	195	0.014	0.36
35	379	45	75	95	0.025	0.64
72	496	25	44	56	0.042	1.07

(a) Optical Micrograph. (100X)

MS-73-0989-4

10,000X

SM-40003

3000X

SM-40004

1000X

SM-40005

300X

SM-40006

(b) Scanning Electron Micrograph at Various Magnifications.

Figure 4. MICROGRAPHS OF THE STRESS-CORROSION-CRACKING FRACTURE SURFACE OF MULBERRY EXPOSED TO A SODIUM CHLORIDE SOLUTION.

Pitting - In chloride-containing solutions (50 ppm and more), of pH 2 to 9, pitting of mulberry occurred at all potentials above the rest potential. The anodic polarization curve for the alloy in these solutions showed increasing current densities (corrosion rates) as the potentials increased, and the curves for stressed and unstressed specimens were identical. There was no evidence of an active-to-passive transition. Conditions that produced short failure times in stressed specimens produced visible pits in short times. An active/passive transition was noted in 0.1 M NaOH (pH, 12.7) with essentially no chloride and with 355-ppm chloride. No transition was seen in 0.1 M NaOH with 3550-ppm chloride, although the transition may occur at other scan rates. Figure 5 presents the anodic polarization curves. With the addition of the 355-ppm chloride, the current density where passivation starts, i_c , increased, and pitting occurred at +620 mV vs Ag/AgCl. The critical potential, E_c , at which passivity ended, decreased 80 mV with the addition of 355-ppm chloride. In the NaOH solution containing 3550-ppm chloride, pitting occurred rapidly at -20 mV. Cracking of the alloy stressed to 34 ksi (234 MPa) occurred in the 0.1 M NaOH solutions with 355-ppm chloride only at potentials above +620 mV vs Ag/AgCl. At +1400 mV vs Ag/AgCl, a sample failed in 46 minutes. In 0.1 M NaOH solution containing 3550-ppm chloride, failure will occur at almost any potential above the open circuit corrosion potential. No cracking was noted in the cathodic regions.

Table 4
TIME TO FAILURE OF STRESSED MULBERRY IN 0.1M
SODIUM CHLORIDE (pH, 5) AS A FUNCTION OF THE
SODIUM NITRATE CONCENTRATION [Applied
Potential = +50 mV; Ag/AgCl Standard
Electrode; Stress = 32 ksi
(0.35% strain, 220 MPa)]

NaNO ₃ Concentration (kg/m ³)	Average Time to Failure (min)
0	2
2.5	6
5.0	12
7.5	30 - 79(1)
10.0	24 - 59(1)
12.5	156

(1) Average value meaningless because of a large scatter.

Figure 5. ANODIC POLARIZATION CURVES OF MULBERRY EXPOSED TO 0.1 M NaOH CONTAINING VARYING AMOUNTS OF CHLORIDE.

In the solutions without chloride, the faster the scan rate the greater the current density (corrosion rate) at any given potential above the passive region. Table 5 provides an example for + 2000 mV vs the standard calomel electrode (SCE). The regions of passivity were unaffected by the scan rate; therefore, at the slower scan rates, the alloy remained in the passive region longer, which possibly allowed more passive film buildup. Assuming that less passive-film formation is associated with higher corrosion rates above the passive region, the results show that the time spent by the alloy in the passive region is directly connected to the amount of passive-film formation.

Table 5
SCAN RATE VERSUS CURRENT DENSITY FOR
MULBERRY IN 0.1 M SODIUM HYDROXIDE

Scan Rate (mV/min)	Current Density ⁽¹⁾ (mA/cm ²)	
	0-ppm Cl ⁻	355-ppm Cl ⁻
500	1.34	1.65
250	0.97	1.16
100	0.54	2.31
50	-	2.24
16.7	0.34	6.3

(1) At 2000 mV versus the standard calomel electrode.

Addition of 355-ppm chloride increased the corrosion rate at each scan rate (Table 5). The pattern followed by mulberry in the solutions without chloride was adhered to only in the two fastest scan rates. Thereafter, the slower the scan, the higher the corrosion rate. In the competition between passive-film formation and breakdown by chlorides, the film breakdown is apparently favored as time increases, at least for 355-ppm chloride.

Electropolished Surface - In order to evaluate the effect of surface treatment, stress-corrosion tests were run on electropolished and machined surface mulberry. The results are compared in Table 6. Under highly corrosive conditions [0.1 M NaCl (pH, 4) and at 34 ksi (234 MPa)], the electropolished samples showed less resistance to cracking. In pH 4 solutions containing 50-ppm and 1-ppm chloride, the machined-surface specimens showed less resistance to cracking. No differences were seen at higher strains except at very low concentrations of chloride.

Table 6
COMPARISON OF TIME TO FAILURE BETWEEN ELECTROPOLISHED
AND MACHINED SURFACE MULBERRY

Chloride Concentration pH of 4 (ppm)	Stress		Applied Potential vs Ag/AgCl (mV)	Time to Failure (min)	
	ksi	MPa		Surface Electropolished	Machined
3550	34	234	-200	40	90
3550	34	234	-100	10	28
3550	55	379	-200	5	5
50	34	234	+200	No Failure in 17 hr	80
50	55	379	+200	6	5
1	34	234	+700	No Failure in 90 hr	195
1	55	379	+700	150	95
1	110	758	+700	110	56

Unrecrystallized Alloys

Time to failure of the alloys with almost no recrystallization and about 50% recrystallization was determined in chloride solutions and is reported in Table 7 along with comparative data for the recrystallized alloy. Both special alloys showed more resistance to cracking than the fully recrystallized alloy at 34 ksi (234 MPa). The alloy with the least recrystallization showed the best behavior. At stresses above yield, no differences were seen. Acoustic pulses were noted at intervals in the tests where no failure occurred. An optical micrograph of such a specimen is seen in Figure 6. Note the very shallow surface cracks.

Table 7

TIME TO FAILURE OF GAMMA-QUENCHED MULBERRY
IN VARIOUS STAGES OF RECRYSTALLIZATION

Alloy Treatment	Applied Stress		Test Conditions	Time to Failure (min)
	(ksi)	(MPa)		
150°C for 1 Hour	34	234	A ⁽¹⁾	62 C ⁽²⁾
	34	234	B	56 C
	110	758	B	4C
Partially Recrystallized (50%)	34	234	A	97 D
	34	234	B	nf E
	110	758	B	5 C
Very Little Recrystallization	34	234	A	nf E
	34	234	B	nf E
	110	758	B	5 C

(1) A - 0.1 M NaCl, pH of 4, -200 mV vs Ag/AgCl Standard Electrode

B - 50-ppm chloride, pH of 4, +200 mV vs Ag/AgCl Standard Electrode

(2) C - All specimens failed.

D - Some specimens did not fail.

E - At least 1000 minutes.

DISCUSSION

Fully recrystallized, single-phase-machined-surface mulberry will stress-corrosion crack in chloride solutions. The time to failure of the alloy is a function of the applied potential, stress, pH, and chloride concentration. Stress is a mechanical effect, while the others are chemical effects which affect the dissolution rate. An increase in stress, chloride concentration, applied potential, or a change in pH from basic to acidic can decrease the time to failure.

It is obvious that, for a system whose anodic polarization curve shows no active/passive transition (ie, the current density increases as the potential increases), an increase in potential merely increases the dissolution rate. Thus, the time to failure of a stressed specimen would decrease as the potential is increased, reaching a limit at high potentials. For mulberry, the dissolution rate is higher at low pHs and high chloride concentrations. Thus, times to failure decrease as the pHs are lowered and chloride concentrations increased.

In anodic regions, the only conditions which prevent cracking are those which would place the system in the passive condition. For mulberry, these conditions are high pHs (around 12) and low chloride concentrations.

J339

Figure 6. OPTICAL MICROGRAPH OF UNRECRYSTALLIZED MULBERRY AFTER EXPOSURE TO AQUEOUS CHLORIDE SOLUTIONS. (Stress-Corrosion Cracking did not Occur; ~ 8X)

The crack path for stress-corrosion cracking (SCC) of recrystallized mulberry in chloride solutions is intergranular, and the crack-growth rate is quite rapid. Partially recrystallized mulberry is less susceptible to failure at lower stresses. The same amount of pitting (almost always in grain boundaries) occurred in fully and partially recrystallized mulberry in a given time. The main difference in the samples was the irregular grain-boundary structure of the partially recrystallized specimen which apparently made crack propagation more difficult. Bullock and Condon⁽⁶⁾ suggest that since cracks avoid the cold-worked areas, the grain boundaries of the cold-worked areas lack the proper chemical composition to allow the anodic action needed in SCC. Cold working does increase the number of point defects and increases the strain and should decrease any compositional differences between the grain matrix and the grain boundary. No attempt was made to determine if compositional differences were a factor. At higher stresses, the driving force for propagation is still sufficient to cause failure regardless of the grain structure.

The electropolished alloy is superior to the machined-surface alloy in solutions of low chloride concentration, but is not in solutions of high chloride concentration. The oxide layer on the machined surface apparently promotes cracking at a low chloride concentration (50 ppm) and acts as somewhat of a deterrent or has little effect at higher chloride concentrations (3550 ppm).

Additions of NaNO_3 to salt solutions increases the time to failure of the alloy but does not cause passivation or eliminate the failure. The NaNO_3 apparently complexes the chloride ions, making fewer of them available for attack. The times to failure of the alloy in 0.1 M NaCl (pH, 5) at NaNO_3 concentrations of 7.5 - 12.5 g/l, correspond to failure times found in 50-ppm-and-lower chloride solutions.

The findings reported here compliment those of several workers in the field of the SCC of mulberry. Bullock and Condon⁽⁶⁾ and Stephenson⁽⁴⁾ found cracking in anodic regions and not in cathodic regions, and found that strong bases retarded crack initiation. These authors, along with Zehr,⁽⁵⁾ showed that cold work inhibits cracking. Weirick and Scheonfelder⁽¹⁰⁾ showed that no cracks were initiated in stressed [77 ksi (530 MPa)] mulberry specimens that were exposed to 100% rh, with no appreciable chloride and significant amounts of oxygen, or where chloride was present and oxygen was excluded. This work shows that there are conditions where cracking can occur in solutions of low chloride and oxygen content.

Weirick⁽⁹⁾ has recently studied the effect of heat treatment upon the SCC of mulberry. In this, he shows, as was done here, an increase in the time to initiation and failure with decreasing stress and strain in 0.001 M KCl. He explains his findings with Zehr's explanation that the grain boundaries are depleted in niobium, thus making them anodic with respect to the grain interior, and thus causing the grain boundaries to corrode selectively. Zehr⁽⁵⁾ proposed that propagation consisted of alternating stages—an anodic reaction at the crack tip and mechanical failure of the partially reacted metal and niobium oxide corrosion product.

In this work, the electrochemical processes for both pitting and SCC were found to be identical. The current-density potential curves were identical for stressed or unstressed specimens. Pits formed on each at about the same time, and pitting always preceded SCC. A possible explanation for the cracking found in the experiments reported here is that areas around pits (which formed preferentially on grain boundaries) are embrittled by the hydrogen that results from the corrosion process. These embrittled areas crack, due to the strain imposed on the specimen, and the crack proceeds to other embrittled areas in the grain boundaries, thus becoming intergranular in nature. Anodic dissolution still occurs during the cracking process. Bullock and Condon⁽⁶⁾ have cracked mulberry which had not pitted and conclude that a pitting mechanism is not necessary for SCC in mulberry. Mechanisms they propose are preferential etching, grain-boundary separation due to expansion from a chemical reaction, a surface-tension lowering at the grain boundaries, and possibly hydrogen embrittlement.

CONCLUSIONS

The following conclusions can be stated as a result of this study:

1. Increasing amounts of chlorides increases the general corrosion rate of mulberry.
2. At more positive electric potentials, lower pHs, increasing chloride concentrations, and increasing stresses, the time to failure decreases.
3. Above the yield stress, all failure times are short, regardless of chloride concentration, pH, or potential.

4. Crack growth is discontinuous and failure is intergranular.
5. Sodium nitrate inhibits crack growth.
6. Pitting occurs in chloride-containing solutions of 50 ppm and more and pHs from 2 to 9.
7. Passivation can occur in chloride solutions having a pH of 12.
8. Electropolished mulberry is superior to machined-surface mulberry in solutions of low chloride concentration, but not in solutions of a high chloride concentration.
9. Unrecrystallized mulberry shows more resistance to cracking than the fully recrystallized alloy at 34 ksi (234 MPa). At stresses above yield, no differences are seen.

REFERENCES

- (1) Whitlow, G. A.; *Stress Corrosion of Uranium Alloys*, AWRE 0-49 (1966).
- (2) Magnani, N. J.; *The Effect of Chloride Ions on the Susceptibility of Stress Corrosion Cracking of Mulberry and U-4-1/2% Nb*, SC-RR-70-860 (1970).
- (3) Magnani, N. J., Romero, H., and Miglionico, C. J.; *A Study of the Stress Corrosion Cracking Behavior of Mulberry (U-7.5 wt % Nb-2.5 wt % Zr)*, SC-RR-70-371 (1970).
- (4) Stephenson, L. L.; *A Survey of Factors Which Influence Stress Corrosion Crack Initiation in Several Uranium Base Alloys*, SC-DR-70-71-8 (1970).
- (5) Zehr, S. W.; "A Study of the Intergranular Cracking of Mulberry in Aqueous Chloride Solutions", *Corrosion*, 28, p 196 (1972).
- (6) Bullock, J. S., IV and Condon, J. B.; *Electrochemical and Other Studies of A Uranium Alloy Exhibiting Stress Corrosion Cracking*, Y-1821; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee (1972).
- (7) Peterson, C. A. W. and Steele, W. J.; *Delayed Cracking Study in U-7.5 wt % Nb-2.5 wt %*, UCID-15256 (1967).
- (8) Adolphson, D. R. and Johnson, D. R.; *The Oxidation and Stress Corrosion of Mulberry*, AWRE, Paper A4.2 (1968).
- (9) Weirick, L. J.; *The Effect of Heat Treatment Upon the Stress Corrosion Cracking of Mulberry (U-7.5 Nb-2.5 Zr)*, SLL-73-5015 (1973).
- (10) Weirick, L. J. and Schoenfelder, C. W.; *The Effect of Oxygen Chloride, Ion, and Water Vapor on Crack Initiation in U-7-1/2 wt % Nb-2-1/2 wt % Zr (Mulberry)*, SCL-DC-720103 (1973).
- (11) Winslow, F. R.; Personal Communication.

ACKNOWLEDGEMENTS

Many helpful discussions are acknowledged that were conducted with J. S. Bullock, W. J. Hulsey, and J. L. Cadden.

Special thanks are given to S. A. Wallace for his assistance in setting up the acoustic emission equipment; to A. G. Dobbins for the metallography; to R. K. Bennett, Jr and A. D. Condry for the scanning microscopy; to P. I. Tinnel and R. L. Swain for thier assistance in conducting the tests; and to M. A. Russell who typed the manuscript.

Distribution**Atomic Energy Commission - Oak Ridge**

Hickman, H. D.
 Leed, R. E.
 Zachry, D. S., Jr

Dow - Rocky Flats

Jackson, R. J.
 Jiannetti, E.
 Karlson, R.
 Larson, D. T.
 Mah, R.
 Boland, J. F.

Lawrence Livermore Laboratory

Comenares, C.
 Perl, H.
 Rizzo, H. F.
 Roberts, L. W., Jr
 Rubin, B.
 Walker, F. E.
 Weiss, H.
 Wood, D. H.

Los Alamos Scientific Laboratory

Alire, R. M.
 Byers, D. H.
 Ellis, W. P.
 Peterson, C. L.
 Sandstrom, D.
 Taub, J. E.
 Kirby, R. S.

Oak Ridge Gaseous Diffusion Plant

Wilcox, W. J., Jr
 Winkcl, R. A.

Oak Ridge National Laboratory

Cathcart, J. W.
 Central Research Library
 DeVan, J. H.
 Griess, J. C., Jr
 Jenks, G. H.
 McHargue, C. J.
 Strehlow, R. A.

Vandemeer, R. A.
 Weir, J. R.

Oak Ridge Y-12 Plant

Alvey, H. E.
 Bennett, R. K.
 Bernander, N. K.
 Briscoe, O. W.
 Brown, A. D.
 Bullock, J. S.
 Durditt, R. B.
 Burkhardt, I. F.
 Cadden, J. L.
 Condon, J. B.
 Dobbins, A. G.
 Dodson, W. H.
 Ebert, T. H.
 Ellingson, R. D.
 Fraser, R. J.
 Gritzner, V. B.
 Harper, W. L.
 Haeusler, K. R.
 Hulse, W. J.
 Jackson, V. C.
 Jones, F. W.
 Kahl, K. G.
 Keith, A.
 Kite, H. T.
 Koger, J. W. (10)
 Lundin, M. I.
 Marrow, G. B.
 McIntyre, J. M.
 McLendon, J. D.
 Mills, J. M., Jr
 Phillips, L. R.
 Power, G. L.
 Schreyer, J. M.
 Sladky, R. E.
 Smith, H. R., Jr
 Smith, H. M.
 Smith, R. D.
 Stoner, H. H.
 Tench, F. M.
 Tewes, W. E.
 Tilson, F. V.

Townsend, A. B.
 Weathersby, W. E.
 Yaggi, W. J./Googin, J. M.
 Y-12 Central Files (5)
 Y-12 Central Files (master copy)
 Y-12 Central Files (route copy)
 Y-12 Central Files (Y-12RC)
 Zerby, C. D.

**US Army Materials and Mechanical
 Research Center - Watertown**

Burke, J. J.
 Greenspan, J. E.
 Levy, M.
 Seitz, D.
 Rizzitano, F. J.

Paducah Gaseous Diffusion Plant

Levin, R. W.

Sandia - Albuquerque

Berry, L.M.
 Davis, M. J.
 Dick, J. R.
 Magnani, N. J.
 Mattox, D. M.
 McLaughlin, B.
 Rohde, R. W.
 Sallach, R. A.
 Schwoebel, R. L.
 Stephenson, L. L.

Sandia - Livermore

Adolphson, D. R.
 Beeler, G. N.
 Brierly, J. M.
 Mote, M. W.
 Scholer, G. L.
 Swisher, J. H.
 Weirick, L.
 Zehr, S. W.

United Kingdom AWRE - Aldermaston

Horscroft, R. C.
 Orman, S.

In addition, this report is distributed in accordance with the category UC-25, *Materials*, as given in the *USAEC Standard Distribution Lists for Unclassified Scientific and Technical Reports*, TID-4500.