

INFORMAL REPORT

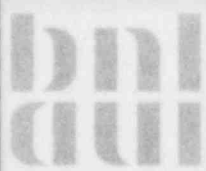
STRESS CORROSION CRACKING, GALVANIC  
CORROSION, AND SELECTIVE LEACHING DATA REQUIREMENTS  
FOR TiCode-12 HIGH LEVEL WASTE CONTAINERS

DRAFT REPORT

J. SHAO

MANUSCRIPT COMPLETED AUGUST 1982

NUCLEAR WASTE MANAGEMENT DIVISION  
DEPARTMENT OF NUCLEAR ENERGY BROOKHAVEN NATIONAL LABORATORY  
UPTON, NEW YORK 11973



Prepared for the U.S. Nuclear Regulatory Commission  
Office of Nuclear Materials Safety and Safeguards  
Contract No. DE-AC02-76CH00016

BNL-NUREG-31771  
INFORMAL REPORT  
Limited Distribution

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Prepared for the U.S. Nuclear Regulatory Commission  
Office of Nuclear Materials Safety and Safeguards  
Contract No. DE-AC02-76CH00016  
FIN No. A-3164

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PQR

*NRC Research and/or Technical Assistance Report*

Accession No. \_\_\_\_\_

**Contract Program or Project Title:** Assessment of DOE Waste Package Programs  
Subtask 1.1 National Waste Package Program.

**Subject of this Document:** STRESS CORROSION CRACKING, GALVANIC CORROSION, AND  
SELECTIVE LEACHING DATA REQUIREMENTS FOR TiCode-12 HIGH LEVEL WASTE CONTAINERS.  
DRAFT REPORT.

**Type of Document:** Interim Report

**Author(s):** J. Shao

**Date of Document:** August 1982

**Responsible NRC Individual**

**and NRC Office or Division:** Mr. Everett A. Wick  
High Level Waste Licensing Management Branch  
Division of Waste Management  
U. S. Nuclear Regulatory Commission  
Washington, DC 20555

This document was prepared primarily for preliminary or internal use. It has not received full review and approval. Since there may be substantive changes, this document should not be considered final.

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for the  
U.S. Department of Energy

Prepared for  
U.S. Nuclear Regulatory Commission  
Washington, D.C. 20555  
Under Interagency Agreement DE-AC02-76CH00016  
FIN A-3164

## ABSTRACT

This is one of a series of studies which evaluates the possible chemical failure modes of TiCode-12 high level waste containers and describes the anticipated data required to characterize them for waste package licensing. This report specifically addresses the galvanic corrosion, selective leaching, and stress corrosion cracking (SCC) behavior of TiCode-12 in salt and basalt repository environments.

The available data on titanium and titanium alloys suggest that galvanic corrosion and selective leaching are unlikely to be significant failure modes. However, the lack of sufficient data pertaining specifically to TiCode-12 behavior under repository conditions prevents, at present, a guarantee that a container lifetime will be on the order of one thousand years.

Galvanic corrosion will occur if TiCode-12 contacts some other metallic component of the waste package. Further studies are required to quantify the effects of possible hydrogen evolution, cathode to anode ratios, and galvanically induced accelerated degradation.

Very little is known regarding selective leaching behavior of TiCode-12. Further testing which includes surface analyses and long term uniform corrosion studies is recommended.

TiCode-12 appears to be highly resistant to SCC under the conditions tested. However, microscopic examinations have revealed signs of embrittlement in specimens fractured in brine. Both real time and accelerated testing should be continued to characterize SCC behavior of TiCode-12. This includes the long term testing of statically loaded specimens under expected repository conditions.

CONTENTS

ABSTRACT . . . . . iii  
TABLES . . . . . vi  
ACKNOWLEDGMENTS. . . . . vii

1. INTRODUCTION . . . . . 1

2. GALVANIC CORROSION . . . . . 2

    2.1 Introduction. . . . . 2

    2.2 Background - General Description of Galvanic Corrosion. . . . . 2

    2.3 Galvanic Corrosion Data Available to Characterize  
        TiCode-12 Corrosion Behavior in High Level  
        Waste Repositories. . . . . 3

    2.4 Additional Data Requirements for Characterization  
        of TiCode-12 Galvanic Corrosion Behavior. . . . . 10

    2.5 Summary and Conclusions . . . . . 13

    2.6 References. . . . . 14

3. SELECTIVE LEACHING . . . . . 16

    3.1 Introduction. . . . . 16

    3.2 Background -General Description of Selected Leaching. . . . . 16

    3.3 Selective Leaching Data Available to Characterize  
        TiCode-12 Corrosion Behavior in High Level  
        Waste Repositories. . . . . 16

    3.4 Additional Data Requirements for Characterization  
        of TiCode-12 Selective Leaching Behavior. . . . . 18

    3.5 Summary and Conclusions . . . . . 19

    3.6 References. . . . . 20

4. STRESS CORROSION CRACKING. . . . . 22

    4.1 Introduction. . . . . 22

    4.2 Background - General Description of  
        Stress Corrosion Cracking . . . . . 22

    4.3 Stress Corrosion Cracking Data Available to Characterize  
        Titanium and TiCode-12 Corrosion Behavior in High Level  
        Waste Repositories. . . . . 23

    4.4 Additional Data Requirements for the Characterization of  
        TiCode-12 Stress Corrosion Cracking Behavior. . . . . 27

    4.5 Summary and Conclusions . . . . . 28

    4.6 References. . . . . 29

TABLES

2.1	Galvanic Series of Some Commercial Metals and Alloys in Seawater. . . . .	5
2.2	Galvanic Series in Seawater . . . . .	6
2.3	Galvanic Couple Tests, Titanium, and Other Metals in Three-Percent Sodium Chloride Solution, Air, Specimens in Motion. . . .	7
2.4	Total Corrosion Rate Acceleration Factors Due to Dissimilar Metal Coupling as 1:1 Area Ratio in Flowing Seawater. . . . .	9
2.5	A Galvanic Series of Selected Materials in Ocean Water at 25°C . . . . .	10
2.6	Corrosion Potentials Before ( $\phi_{\text{corr}}^e$ ) and After ( $\phi_{\text{corr}}^e$ ) Galvanic Couple Test, 3.5% NaCl, 22 $\pm$ 1°C . . . . .	11
2.7	Summary of Galvanic Current Data in 3.5% NaCl . . . . .	12

## ACKNOWLEDGMENTS

The author gratefully acknowledges the assistance of Dr. P. Soo in the preparation of this report. The typing and preparation of the manuscript by Sharon M. Moore and Grace F. Searles are also appreciated.



## 1. GENERAL INTRODUCTION

The definition and functions of a high level waste package have been outlined in the proposed Nuclear Regulatory Commission (NRC) criteria and standards. A primary function of the waste package is the containment of all radionuclides for a period on the order of one thousand years after closure of the geologic repository. The titanium alloy, TiCode-12, is a current candidate to be a principal component of the waste package for meeting this containment criterion.

In the selection of a metal as a waste package component, corrosion resistance of the metal under repository conditions is of prime importance. At present, bedded or domed salt and basalt are among the primary host rocks being considered for repositories. A detailed evaluation of container corrosion must therefore be made to determine those conditions which may cause a loss of container integrity and subsequent radionuclide release from the waste package. This current work is one of a series which evaluates the various potential failure modes and describes anticipated data requirements to characterize them for the licensing process.

This report will briefly review and outline the available data on the galvanic corrosion, selective leaching, and stress corrosion cracking behaviors of TiCode-12 in brine and basalt groundwaters. Although titanium and other titanium alloys are not reference materials, they will also be considered in this report because of their basic similarities to TiCode-12 and the availability of data. The additional data required for characterization of these forms of corrosion and licensing activities will then be specified and outlined.

## 2. GALVANIC CORROSION

### 2.1 Introduction

The use of a multibarrier system has been proposed for the disposal of high level radioactive wastes in geologic repositories. If a discrete backfill is not used, it is possible that the container will be in contact with a metallic emplacement sleeve. For backfill designs, it is still possible for metal-on-metal contact to occur between the container and other engineered barriers if the backfill has low positional stability. In both cases, galvanic corrosion can lead to the accelerated degradation of the components. This report will briefly review and outline the possible effects of galvanic corrosion interactions between TiCode-12 and other waste package components. As there is little available data pertaining to TiCode-12, titanium and other titanium alloys are considered and discussed because of their basic similarities to TiCode-12. The report will then address the licensing data required to fully characterize this potential failure mode.

### 2.2 Background - General Description of Galvanic Corrosion

The following discussion of galvanic corrosion has been adapted from Fontana and Greene<sup>1</sup> and Macki and Kochen.<sup>2</sup>

When two dissimilar metals are placed in contact or electrically connected and immersed in a corrosive or conductive solution, a galvanic current flows between the two metals. Galvanic corrosion occurs as the less corrosion resistant metal experiences increased attack while the corrosion of the more resistant metal is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal cathodic. Usually the cathode or cathodic metal corrodes very little or not at all in this type of couple.

The driving force for the current flow is the potential difference between the two dissimilar metals. When other parameters are held constant, the extent of galvanic corrosion is usually proportional to the potential difference between the anodic and cathodic members of the couple.

A galvanic series is a list of metals and alloys arranged in order of the potentials generated when electrodes of each material are compared with one another in a specific environment. Since the sequence of the potentials assumed by the materials can vary with the environment, a galvanic series obtained in one environment is not necessarily valid for another. Ideally, galvanic series for metals and alloys in all environments at various temperatures are needed, but this would require an almost infinite number of tests. To reduce the number of tests, the galvanic series in seawater is used for most applications and additional galvanic series have been determined only for a few selected environments.

A galvanic series is different from a standard EMF series. The galvanic series is based on the potentials generated by corroding electrodes in a specific environment. The standard EMF series is based on the potentials

generated by pure metals exposed to solutions containing one gram atomic weight of their respective ions (unit activity). However, in actual corrosion situations, galvanic coupling between pure metals in equilibrium with their ions rarely occurs. Most galvanic corrosion results from the electrical connection of two corroding metals. An EMF series cannot be used to determine the severity of galvanic corrosion or predict the corrosion rate since it refers only to reversible thermodynamic conditions.

The relative positions of two materials in a galvanic series (potential differences) are not final indicators of galvanic corrosion because of polarization effects. Polarization refers to the change in potential of an electrode resulting from current flow. The effect of polarization is usually to alter the potential assumed by the cathode in the direction of the anode, and the potential of the anode in the cathodic direction. The net result of polarization is to decrease the potential difference and thereby decrease the galvanic current and galvanic corrosion.<sup>2</sup> It is the polarization of the reduction reaction (cathodic polarization) which usually predominates. For example, titanium is very noble in seawater, yet galvanic corrosion on less resistant metals when coupled to titanium is usually not accelerated as much as would be anticipated because the titanium cathodically polarizes readily in seawater.

Another important factor in galvanic corrosion is the ratio of the cathodic to anodic areas. When the galvanic current is under cathodic control, the amount of galvanic current, and hence the degree of galvanic corrosion at the anode, is proportional to the area of the cathode. An unfavorable area ratio consists of a large cathode and a small anode since for a given current flow in the cell, the current density is greater for a small electrode than for a larger one.

Titanium and its alloys are active-passive metals which can produce unusual effects under certain conditions in a galvanic couple. The general rule is that the corrosion rate of the metal with the most active corrosion potential is accelerated when galvanically coupled. Titanium, however, will sometimes spontaneously passivate and show a decreased corrosion rate upon coupling to a more noble metal such as platinum in an acid solution.<sup>1</sup> This unusual behavior occurs because the passive region of the metal begins at a potential more active than the reversible potential of the redox system.

In saline environments, titanium is cathodic to most other metals. If the titanium area is large compared with the metal to which it is coupled, the second metal may corrode severely. Hydrogen may also migrate to titanium when it is coupled to an active metal.<sup>3</sup> This is of concern since titanium is capable of adsorbing hydrogen and becoming embrittled. This effect will be discussed more fully in another part of this program

### 2.3 Galvanic Corrosion Data Available to Characterize TiCode-12 Corrosion Behavior in High Level Waste Repositories.

Because galvanic series are extremely environment dependent and metal specific, it is important to develop a series which includes TiCode-12 and all

possible metallic waste package components in both basalt groundwater and brines. Data of this specific nature is not available as of yet. Both electrode potential measurements and corrosion rate tests would be useful in obtaining this information. Though there exists no series with TiCode-12 in the repository groundwaters and brines, there are plenty of data for titanium and other titanium alloys in seawater and sodium chloride solutions. TiCode-12 will behave somewhat differently than these metals, but because of their similarities these data are presented to yield an indication of what one may expect.

In the Pacific Northwest Laboratory (PNL) program for the development of structural barriers for high level nuclear waste packages, Westerman and others<sup>4</sup> utilized galvanic couples with titanium and iron in some of their corrosion tests. No evidence of galvanically enhanced corrosion was reported in the titanium-iron couples exposed for a one-month period at 250°C in simulated Hanford basalt groundwater.

As mentioned previously, a galvanic series is an arrangement of metals and alloys in accord with their actual measured potentials in a given environment. The potentials which determine the position of a metal in a series may include steady-state values in addition to reversible values, and hence alloys and passive metals may be listed.

Table 2.1, from Fontana and Greene,<sup>1</sup> is based on potential measurements and galvanic corrosion tests in unpolluted seawater conducted by the International Nickel Company at Harbor Island, North Carolina. In general, the positions of metals and alloys in the galvanic series agree closely with their constituent elements in the EMF series. The passive states of the alloys occupy more noble positions as compared with the lower positions of these materials when in the active condition. The brackets indicate that the alloys grouped in a given bracket are close together in the series and the potentials generated by couples of these metals are not great. The potential generated is greater for metals which are further apart in the series.

The potential generated by a galvanic cell consisting of dissimilar metals can change with time as polarization occurs. The potential difference of the polarized electrodes and the conductivity of the corrosive environment determines how much current flows between them and the extent of corrosion.

It can be seen from Table 2.1 that of the metals listed, only platinum, gold, and graphite are cathodic to titanium in seawater. TiCode-12 is likely to behave similarly to titanium and would probably be cathodic in most galvanic couples. In these cases, the primary concern would be the accelerated corrosion of the anodic metal and possible hydrogen embrittlement of the TiCode-12 as a result of the cathodic reduction reaction.

In the literature there are several other galvanic series given in seawater. The differences among them may be due to variations in the tests such as slight variations in the environments or measuring procedures. Table 2.2 is a galvanic series in which the passive forms of two stainless steels, type 304 and 316, are listed as cathodic to titanium.<sup>5</sup> If any of these steels

Table 2.1

Galvanic Series of Some Commercial  
Metals and Alloys in Seawater<sup>1</sup>

↑	
Noble or Cathodic	<p>Platinum</p> <p>Gold</p> <p>Graphite</p> <p>Titanium</p> <p>Silver</p> <p>Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)</p> <p>Hastelloy C (62 Ni, 17 Cr, 15 Mo)</p> <p>18-8 Mo stainless steel (passive)</p> <p>18-8 Stainless steel (passive)</p> <p>Chromium stainless steel 11-30% Cr (passive)</p> <p>Inconel (passive) (80 Ni, 13 Cr, 7 Fe)</p> <p>Nickel (passive)</p> <p>Silver Solder</p> <p>Monel (70 Ni, 30 Cu)</p> <p>Cupronickels (60-90 Cu, 40-10 Ni)</p> <p>Bronzes (Cu-Sn)</p> <p>Copper</p> <p>Brasses (Cu-Zn)</p> <p>Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)</p> <p>Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)</p> <p>Inconel (active)</p> <p>Nickel (active)</p> <p>Tin</p> <p>Lead</p> <p>Lead-tin solders</p> <p>18-8 Mo stainless steel (active)</p> <p>18-8 stainless steel (active)</p> <p>Ni-Resist (high Ni cast iron)</p> <p>Chromium stainless steel, 13% Cr (active)</p> <p>Cast iron</p> <p>Steel or iron</p> <p>2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)</p> <p>Cadmium</p> <p>Commercially pure aluminum (1100)</p> <p>Zinc</p> <p>Magnesium and magnesium alloys</p>
↓	
Active or Anodic	

Table 2.2

Galvanic Series in Seawater<sup>5</sup>

---

Active (read down)	
Magnesium	18-8 stainless steel, type 304 (active)
Magnesium alloys	18-8, 3% Mo stainless steel, type 316 (active)
Zinc	Lead
	Tin
Aluminum 5052H	Muntz metal
Aluminum 3004	Manganese bronze
Aluminum 3003	Naval brass
Aluminum 1100	
Aluminum 6053T	Nickel (active)
Alclad	76% Ni-16% Cr-7% Fe (Inconel) (active)
	Yellow brass
Cadmium	Aluminum bronze
	Red brass
Aluminum 2017T	Copper
	Silicon bronze
Aluminum 2024T	5% Zn-20% Ni, Bal. Cu (Ambrac)
	70% Cu-20% Ni
Mild steel	88% Cu-2% Zn-10% Sn (composition G-bronze)
Wrought iron	88% Cu-3% Zn-6.5% Sn-1.5% Pb (comp. M-bronze)
Cast iron	Nickel (passive)
Ni-Resist	76% Ni-16% Cr-7% Fe (Inconel) (passive)
13% Chromium stainless steel, type 410 (active)	70% Ni-30% Cu (Monel)
50-50 lead-tin solder	Titanium
(Continued in next column)	18-8 stainless steel, type 304 (passive)
	18-8, 3% Mo stainless steel, type 316 (passive)
	Noble (read up)

---

are to be used as a component in the HLW package, accelerated corrosion of the TiCode-12 may need to be considered as a possibility.

Schlain<sup>6</sup> had conducted an investigation of the galvanic corrosion behavior of titanium in three percent sodium chloride solution in open beakers. In the setup, two identical specimens were attached to a rotating holder with each pair being coupled through a calibrated resistance of 0.62 ohms. The coupled strips were held 5.7 cm apart in parallel positions with 26 cm<sup>2</sup> of submerged surface. One and one-half liters of fresh solution was used in each test with air being passed through the solution for one hour before the specimens were placed in it and continuously during the test. Voltage readings were taken across the calibrated resistance for use in estimating the size of the galvanic current. The results of the tests are given in Table 2.3

Table 2.3

Galvanic Couple Tests, Titanium, and Other Metals in Three-Percent Sodium Chloride Solution, Air, Specimens in Motion<sup>6</sup>

Second Metal			Loss in Weight, Milligrams per Day				
Metal	Electrode Potential Volts	Length of Test, Hour	Estimated Galvanic Current, ma.	Total (Coupled)	Chemical (Uncoupled)	Galvanic (Calc. from Current)	Increased Chemical
Mg	-1.35	20.3	11.0	441.0	148.0	120.0	173.
Zn	-0.80	21.4	1.6	495.0	185.0	45.6	264.
Al	-0.58	17.4	2.1	60.4	0.69	16.8	43.
Fe	-0.39	41.5	0.9	213.0	185.0	19.2	9.
Cu	0.06	90.6	0.06	27.4	20.4	1.7	5.3
Stainless steel	0.10	118.9	0.0	0.14	0.12	0.0	--

Linear velocities of specimens: magnesium, zinc, and aluminum 75 feet per minute; iron and stainless steel 69 feet per minute; copper 23 feet per minute.

The total and chemical weight losses listed are based upon the weight losses of the coupled and uncoupled specimens, respectively. The current measured in the couple was used to calculate the galvanic weight loss and the increased chemical loss in weight was obtained by subtracting the sum of the chemical and galvanic losses from the total. The galvanic and increased chemical losses must be considered to be rough approximations, since they were based upon a voltage that varied considerably in magnitude during most tests and of which only a few readings were taken.

No chemical or galvanic corrosion of titanium was reported for the galvanic couple tests. However, magnesium, zinc, aluminum, iron, and copper corroded as a result of being coupled with titanium. The stainless steel, whose composition was not given, did not corrode by galvanic action when in contact with the titanium. The steady state electrode potential of titanium in solution was measured at 0.44 volts indicating the stainless steel to be slightly more anodic.

The current which flows between two members of a bimetallic couple rather than their potential difference, provides a more realistic measure of the degree of corrosion involved. Using zero-resistance ammeters, the galvanic hazard involved when a range of materials of construction used in marine engineering are coupled in seawater has been investigated. A summary of results is provided in Table 2.4 in which the degree of acceleration of corrosion is expressed by means of a numerical factor which should be compared with the uncoupled rate of corrosion of each metal or alloy in seawater, which is obtained under the same experimental condition.<sup>7</sup> All of the alloys listed in the table experience accelerated corrosion when coupled to titanium. It should be noted that these data are for flowing seawater which invariably brings about an increase in the rate of galvanic corrosion.<sup>6</sup>

Shalaby<sup>8</sup> studied the galvanic coupling of Ti with Admiralty brass, Cu-Ni and Al-Mg alloys in 32.7% NaCl solutions at ambient and 90°C. The following results were presented:

- Ti is highly resistant to corrosion and its corrosion resistance is not affected by contact with other alloys.
- Admiralty brass, Al-brass, and Cu-Ni alloys can be galvanically coupled with Ti even at higher temperatures with no galvanic effects resulting upon these alloys. The galvanic coupling of a Cu-Ni alloy with relatively large areas of Ti causes pitting corrosion of the alloy.
- Galvanic coupling of Ti with Al-Mg alloy diminishes the corrosion of the latter alloy in the case of equal areas. Coupling with relatively larger areas of Ti is deleterious as it increases the corrosion of the coupled Al-Mg alloy.

Macki and Kochen<sup>2</sup> studied the behavior of several alloys in hydrochloric acid and ocean water. They measured the gravimetric corrosion rate of



Table 2.4

Total Corrosion Rate Acceleration Factors Due to  
Dissimilar Metal Coupling as 1:1 Area Ratio in Flowing Seawater  
(Mean Flow Rate About 1-2 m/s)<sup>7</sup>

Coupled Metal (Wrought Form)	Uncoupled Corrosion Rate <sup>b</sup> (mm/y)	Acceleration Factor <sup>a</sup> Due to Dissimilar Metal Coupl- ing With Titanium
Zinc	0.05	4
SiC aluminum	0.008	30
Mild steel	0.15	2
Lead	0.01	3
2% aluminum brass	0.01	3
10% aluminum bronze	0.02	3
Nickel aluminum bronze	0.015	1
Copper	0.03	6
90/10 cupro-nickel (1% Fe)	0.02	3
Monel 400	0.005	2
Stainless steel type 316	0.005	2

<sup>a</sup>Accelerated factors quoted for coupled metal corroding.

<sup>b</sup>Corrosion rates relate to general corrosion only and are average rates obtained over about one year's exposure.

galvanically coupled specimens and have constructed a galvanic series for each environment from electrode potential measurements. Based on the electrode potential measurements in oxygen saturated ocean water at 25°C, the 304 steel (passive) was noble with respect to the titanium alloy. The 4340 steel measured a more active potential as shown in Table 2.5. In 0.1 N HCl solution at 25 and 70°C, the position of the titanium alloy in the galvanic series differed. This was attributed to the different degrees of cathodic polarization experienced by the titanium in each environment.

The galvanic corrosion behavior of titanium and its alloys can be affected by surface treatments which thicken and toughen the oxide film. When galvanically coupled in synthetic seawater to more active metals, greater galvanic currents were found for thermally oxidized titanium as compared to anodized and pickled titanium.<sup>9</sup> This has been attributed to the more noble rest potential of the thermally oxidized titanium which provides a greater driving force for corrosion. This may not be applicable for long term behavior or for the case of TiCode-12. An exception could be for welded material if significant oxidation is present. In the same study, protective effects of the different surface treatments to general corrosion found for titanium were not found for TiCode-12. However, in an acidic environment, the result did show some short term protective behavior in TiCode-12.

Table 2.5

A Galvanic Series of Selected Materials  
in Ocean Water<sup>a</sup> at 25°C<sup>2</sup>

Alloy <sup>b</sup>	Electrode Potential (Millivolts) <sup>c</sup>	
	Air-Equilibrated	Oxygen-Saturated
4340 steel	540	480
Ti-6 Al-5 V	350	390
304 steel <sup>d</sup>	250	225

<sup>a</sup>The ocean water was prepared according to ASTM designation D-1141-52.

<sup>b</sup>The alloys are listed in order of the increasing nobility from top to bottom as determined by the electrode potentials in oxygen-saturated ocean water.

<sup>c</sup>All electrode potentials are negative with respect to the saturated calomel electrode.

<sup>d</sup>Passive.

Ti-6Al-4V has been included in many galvanic studies. The results of two such studies<sup>10,11</sup> are shown in Tables 2.6 and 2.7. Table 2.6 shows that many alloys may have a nobler potential than Ti-6Al-4V. Specifically, many stainless steels, copper, and nickel which are commonly used metals can be cathodic. However, the corrosion potential can change with time and reversals of galvanic current sign have been observed.

#### 2.4 Additional Data Requirements for Characterization of TiCode-12 Galvanic Corrosion Behavior

The additional data required to characterize TiCode-12 galvanic corrosion behavior are very specific to the Department of Energy's waste package design. The corrosive environment is of primary importance and testing should be done under the expected repository conditions. TiCode-12 and all other adjacent metallic candidate waste package components should be included in this testing. The two scenarios of obvious concern are: (1) TiCode-12 is compromised, thereby exposing any cast iron, steel, or other metallic component underneath and (2) the waste package design does not include a discrete backfill or the backfill has low positional stability, which will result in a galvanic couple between the TiCode-12 and emplacement sleeve.

The additional data to be determined in these tests should include a measure of the extent of galvanic corrosion on both couple components which includes the determination of dissolution and film growth rates. Since there

Table 2.6

Corrosion Potentials Before ( $\phi^s_{\text{corr}}$ ) and After ( $\phi^e_{\text{corr}}$ )  
Galvanic Couple Test, 3.5% NaCl, 22  $\pm$  1° C<sup>10</sup>

	$\phi^s_{\text{corr}}$ (mV)		$\phi^e_{\text{corr}}$ (mV)	
SS A286	0.53	+ 25	0.221	+ 17
SS 304	0.56	+ 21	0.224	+ 38
PH 13-8 Mo	0.60	+ 23	0.274	+ 51
Ag	0.69	+ 31	0.82	+ 7
SS 347	0.76	+ 17	0.155	+ 32
SS 301	0.85	+ 15	0.219	+ 38
Inco 718	0.151	+ 20	0.222	+ 13
Ni 270	0.223	+ 55	0.235	+ 34
Cu	0.237	+ 10	0.230	+ 3
Haynes 188	0.278	+ 59	0.292	+ 37
Ti-6-4	0.352	+ 32	0.275	+ 35
Sn	0.522	+ 79	0.494	+ 26
4130	0.598	+ 3	0.659	+ 7
Al 2219	0.724	+ 6	0.756	+ 20
Al 2024	0.733	+ 4	0.796	+ 32
Al 6061	0.756	+ 28	0.863	+ 33
Al 1100	0.765	+ 39	0.874	+ 57
Cd	0.808	+ 5	0.762	+ 15
Al 7075	0.813	+ 18	0.902	+ 27
Zn	0.1064	+ 8	0.1088	+ 7

Table 2.7

Summary of Galvanic Current Data in 3.5% NaCl  
 $i_g$  ( $\mu\text{A}/\text{cm}^2$ ),  $\phi_{\text{corr}}$  (mV vs SCE)<sup>11</sup>

	SS 304L	Ni 270	Cu	Ti-6-4	Sn	Steel 4130	Cd	Zn
SS 304L $\phi_{\text{corr}} = -79 \pm 57$ mV	--	-0.017	-0.17	-0.013	-2.34	-9.53	-13.9	-15.9
Ni 270 $\phi_{\text{corr}} = -221 \pm 41$ mV	+0.017	--	-0.94	+0.016	-5.62	-30.0	-15.3	-70.3
Cu $\phi_{\text{corr}} = -237 \pm 10$ mV	+0.18	+0.89	--	+0.19	-14.9	-28.8	-48.5	-72.5
Ti-6Al-4V $\phi_{\text{corr}} = -352 \pm 32$ mV	+0.013	-0.019	-0.19	--	-1.91	-6.66	-2.11	-21.3
Sn $\phi_{\text{corr}} = -572 \pm 39$ mV	+2.47	+5.65	+15.8	+2.02	--	-10.5	-3.83	-23.0
4130 Steel $\phi_{\text{corr}} = -591 \pm 19$ mV	+9.57	+27.3	+27.4	+6.31	+9.71	--	-30.4	-71.7
Cd $\phi_{\text{corr}} = -806 \pm 9$ mV	+14.8	+14.6	+49.2	+2.11	+3.66	+32.6	--	-41.3
Zn $\phi_{\text{corr}} = -1058 \pm 4$ mV	+16.6	+67.4	+72.9	+21.3	+21.8	+72.4	+40.9	--

exists the possibility of hydrogen evolution due to the coupling, it is desirable to determine the amounts and effects of any hydrogen produced. The cathode to anode ratio effect is dependent upon the corrosion mechanism. This should be studied as it will be useful in the estimation of the extent of galvanic corrosion and perhaps determination of the mechanisms involved. A galvanic series in brine and basalt groundwaters for TiCode-12 and the other waste package components should be constructed to complete the characterization of the galvanic effect.

## 2.5 Summary and Conclusions

TiCode-12 is likely to interact with other components of a HLW package in a waste repository. One such interaction is galvanic corrosion which leads to the degradation of the components involved. This form of corrosion is metal and environment specific yet there exist little data pertaining to galvanic corrosion of TiCode-12 in repository environments. The available data suggest that galvanic corrosion is unlikely to be a major degradation mode for TiCode-12. However, it is still desirable to address this problem and characterize any galvanic effects if long term containment is to be guaranteed.

In a metallic couple, TiCode-12 may be either cathodic or anodic depending upon the other metal component and the specific environment. In the former case, the factors to consider are:

- Titanium is very noble and therefore will be cathodic in the majority of cases.
- A prime concern is the accelerated corrosion experienced by the anodic material. The extent of damage will depend upon the second metal selected, the corrosiveness and conductivity of the environment, and the cathode-to-anode-area ratio. The cathodic polarization of TiCode-12 will likely lessen the severity of the galvanic effect.
- A possible scenario for severe corrosion of anodic material can occur if a pit or crack occurs in a TiCode-12 overpack exposing a small area of underlying active metal. The large cathode-to-anode-area ratio could greatly enhance the anodic corrosion rate.
- Another major concern is the production of hydrogen from the reduction (cathodic) reaction. This may lead to hydrogen adsorption and embrittlement of TiCode-12.

In the case where TiCode-12 is anodic the concerns are:

- Accelerated corrosion of TiCode-12 may result when coupled to a nobler metal.
- Many stainless steels have been shown to be cathodic to titanium. Copper and nickel have shown nobler potentials than Ti-6Al-4V. There are insufficient data pertaining to the position TiCode-12 in a

galvanic series, but there might be problems if it behaved similarly to titanium or Ti-6 Al-4V and was in contact with these metals.

- The galvanic effects on titanium and Ti-6Al-4V when they are anodic appear to be small. It is possible that TiCode-12 may even be moved into a passivated state.

There are insufficient data to characterize the galvanic corrosion behavior of TiCode-12 under repository conditions. In order to eliminate guesswork and assumptions, it is necessary to conduct galvanic corrosion studies and to determine a galvanic series. The conditions (solution chemistries, temperatures, pH, Eh, etc.) to test under should be similar to those considered for general corrosion.<sup>12,13</sup> The information to be determined is:

- Measurements of the extent of galvanic corrosion on both anode and cathode. This includes determination of dissolution and film growth rates and the amount and effects of hydrogen production due to galvanic coupling.
- The cathode-to-anode ratio effect which is dependent upon the corrosion mechanisms.
- An actual galvanic series which includes TiCode-12 and other waste package components in brine and basalt groundwaters.

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### 3. SELECTIVE LEACHING

#### 3.1 Introduction

Molybdenum and nickel are the main alloying additions in TiCode-12 which are believed to be responsible for its superior corrosion resistance when compared to titanium under expected high level waste repository conditions. The actual roles played by nickel and molybdenum in the corrosion mechanisms have not yet been established and are currently under investigation. However, depletion or enhancement of one or both of these elements can lead to possible accelerated corrosion and selective leaching must, therefore, be evaluated as a potential failure mode. This report will briefly review and outline the available data pertinent to this phenomenon in TiCode-12. The report will then address the data needs required to fully characterize this failure mode.

#### 3.2 Background - General Description of Selective Leaching

Selective leaching is the removal of one element from a solid alloy by corrosion processes.<sup>1</sup> Generally, this form of corrosion leaves the size and shape of the structure undergoing attack basically unaltered. The term selective leaching will be used loosely in this report to include all mechanisms which can lead to the depletion or enhancement of an element in an alloy. This will include selective microstructural attack or the presence of composition gradients which may lead to a depletion through the removal of higher concentration layers by corrosion.

A commonly quoted mechanism for selective leaching is the selective dissolution of one metal leaving a residual mass of the other metal. However, a more commonly accepted proposed mechanism involves the simultaneous dissolution of both elements followed by the subsequent redeposition of one element at favorable sites.<sup>2,3</sup> Some observers conclude that both mechanisms may exist, depending on various external influences. The term selective texture corrosion has been used to describe the numerous observations that in two-phase or duplex alloys there is a definite tendency for one phase to dealloy before the other or for localized corrosion to start in solute rich areas such as grain boundaries in single-phase alloys.<sup>2</sup>

The most common example of selective leaching is the selective removal of zinc in brass alloys which is called dezincification. Other alloy systems experience similar processes in which aluminum, iron, cobalt, chromium, and other elements are removed. Sometimes selective corrosion of one element in an alloy may be beneficial. Enrichment of silicon observed in the oxide film on stainless steels results in better passivity and resistance to pitting.<sup>1</sup>

#### 3.3 Selective Leaching Data Available to Characterize TiCode-12 Corrosion Behavior in High Level Waste Repositories

There exists very little data regarding the selective leaching behavior of TiCode-12. There is a present effort at Sandia<sup>4</sup> to study the role played by nickel and molybdenum alloying additions to titanium in TiCode-12 in the



corrosion mechanisms. As part of this study, an Auger depth profile was performed on TiCode-12 which had been immersed in pH = 1 concentrated NaCl brine at 200°C for three weeks. Figure 3.1 shows that in the oxide film there is an enhancement of nickel relative to the bulk metal value. Molybdenum enhancement or depletion was not detectable due to a lack of sensitivity.

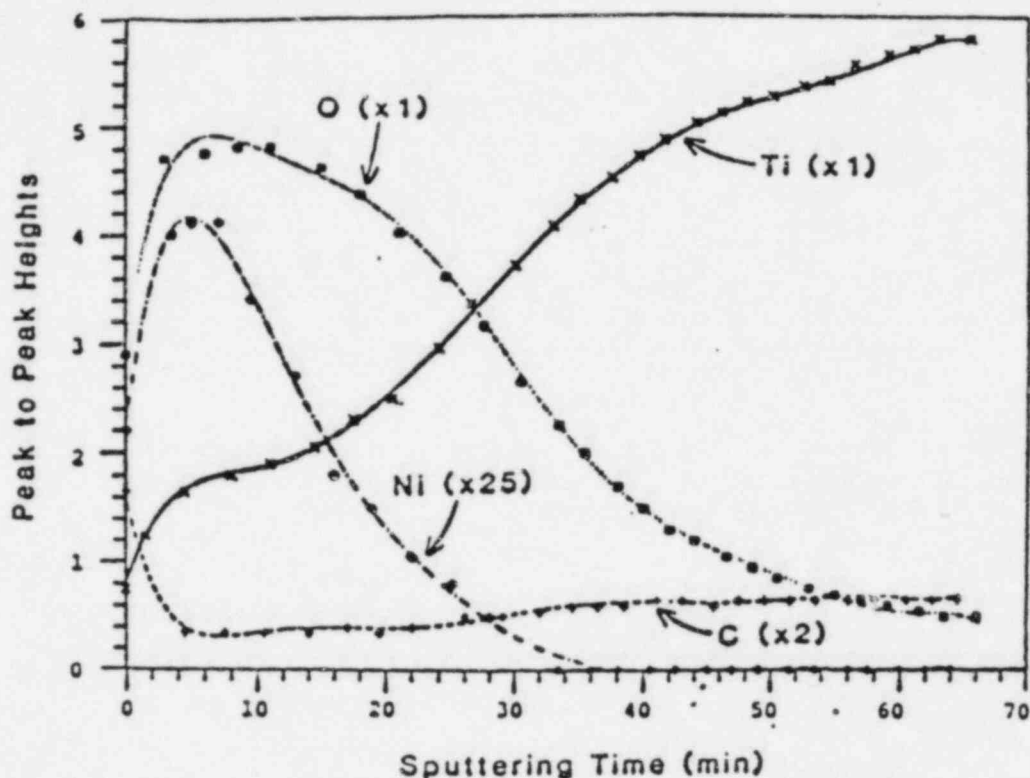


Figure 3.1 Auger depth profile of TiCode-12 oxidized in pH = 1 Brine at 200°C.<sup>4</sup>

The phenomenon of nickel enhancement has been observed or suggested in other titanium alloys<sup>5,6</sup>. Green and Kotval<sup>6</sup> exposed the welded regions of a titanium-2% nickel alloy to boiling acidic chloride solutions to examine their corrosion behavior. Optical microscopy indicated that the microstructure close to the weld bead was martensitic. Farther away from the weld area, the microstructure showed a partially recrystallized alpha and alpha + Ti<sub>2</sub>Ni eutectoid. Potentiometric studies were conducted to examine the anodic and cathodic polarization characteristics of quenched (martensitic) and furnace cooled (eutectoid) microstructures in boiling acidic chloride solutions. (See Figure 3.2.) It was observed that the cathodic kinetics were not influenced by the variation of the microstructure. In the anodic study, slightly higher current densities were obtained at equivalent potentials for the furnace cooled structure when compared to the quenched structure. At the highest noble potentials (>1.6 V vs SCE) the quenched material exhibited some

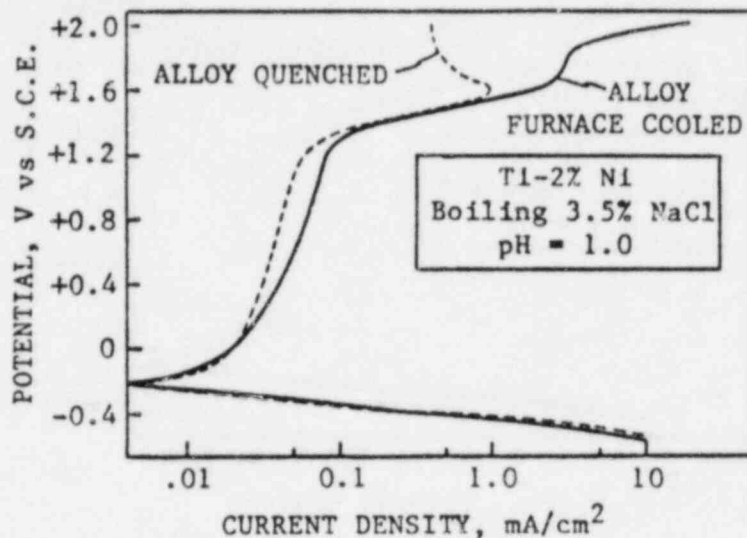


Figure 3.2 The influence of heat treatment on the potentiostatic polarization characteristics of Ti-2% Ni exposed to boiling, acidic, chloride-containing solutions.<sup>6</sup>

tendency to passivate whereas the furnace cooled material did not. It was suggested that this difference may be attributed to the more uneven distribution of the nickel bearing intermetallic  $Ti_2Ni$  in the furnace cooled material.

The corrosion behavior of the alloy Ti-15% Mo in 40%  $H_2SO_4$  at 90°C was studied by Tomashov and others.<sup>7</sup> It was observed that during the corrosion of two phased alloys, the surface is enriched with the more stable phase. In the active region of potentials, the  $\beta$ -phase (which contains greater amounts of Mo) accumulated on the surface while the  $\alpha$ -phase dissolved. At transpassivation, the  $\beta$ -phase dissolved preferentially, resulting in a depletion of Mo.

Martin<sup>8</sup> conducted an electron microprobe analysis of the alloy Ti-8Al-1V-1Mo in a study of the stress corrosion mechanism. Examination of the alloy, both in the unexposed condition and also after exposure under a salt coating to which failure occurred after 4000 hours at 650°F (343°C), revealed a distinct concentration of molybdenum in the areas adjoining the crack. He suggested that the segregation phenomena within the titanium alloy was possibly responsible for the stress corrosion susceptibility.

#### 3.4 Additional Data Requirements for Characterization of TiCode-12 Selective Leaching Behavior

In order to characterize TiCode-12 selective leaching behavior, further testing should be conducted under expected repository conditions.<sup>9,10</sup> The mechanisms leading to the enrichment or depletion of the alloying additions and the resultant effects on the corrosion resistance need to be clarified to evaluate very long term behavior.

Further studies such as those at Sandia National Laboratory may provide greater insight on this corrosion mode. It should be determined if the Ni enrichment observed is a result of Ni segregation by diffusion out of the bulk alloy or some kind of Ti depletion at the surface or other phenomenon. The structure of the TiCode-12 oxide scale must also be determined to find if there is some local clustering or formation of intermetallics such as  $Ti_2Ni$ . If possible, the same type of information should be obtained for the Mo.

The study on Ti-15% Mo was done in a very acidic solution and may not be indicative of TiCode-12 behavior under repository conditions. However, since TiCode-12 is likely to have a two-phase microstructure, selective texture corrosion should be studied further. The extent of Ni and Mo enrichment or depletion should be determined along with their effects on the corrosion rate. Longer term tests must also be conducted to determine if the mechanisms change with time as enrichment or depletion proceed. It is also possible that this type of corrosion can lead to some sort of localized corrosion such as intergranular attack.

### 3.5 Summary and Conclusions

A review of the available data and literature indicates there is little known about the selective leaching behavior of TiCode-12. Previous studies on TiCode-12 and relevant titanium alloys such as Ti-2% Ni and Ti-15% Mo have shown there exist some types of alloy-addition segregation which can lead to the enrichment or depletion of Ni or Mo. The extent and consequences of these processes are not known.

TiCode-12 is likely to have a multiphase structure, i.e., a combination of  $\alpha$ ,  $\beta$  and possibly  $\omega$  phases, especially in weld affected regions. This may result in selected texture attack similar to that found in Ti-15% Mo which can alter the Mo concentration. There also appears to be a higher concentration of Ni near the surface than in the bulk which may be a form of, or will result in, selective leaching corrosion.

So far, the available data do not indicate that selective leaching of TiCode-12 is likely to be a major failure mode. Uncertainties still exist, however, and therefore further investigation is recommended. The occurrence of selective leaching and its effects should become manifest and detectable during routine long term uniform corrosion testing.

The additional data required to characterize TiCode-12 selective leaching behavior under waste repository conditions are the following:

- The range of conditions under which TiCode-12 will be prone to selective leaching has to be defined. There are insufficient data pertaining to this at present.
- Further analyses such as Auger depth profiles should be conducted to determine the concentration gradients of the alloying components. This should be done before and after exposure of the alloy to expected repository conditions to determine corrosion effects, if any.

- The microstructure must be defined, and testing performed, to evaluate the extent of selected texture attack. Long term phase stabilities should also be examined, e.g., precipitation of an intermetallic or component segregation can lead to intergranular attack.
- The mechanisms which lead to composition gradients such as that of Ni should be established. They may be a result of or may lead to selective leaching attack.
- The consequences of component enrichment or depletion must be examined. It must be determined whether it is detrimental or beneficial to the overall corrosion resistance.
- Longer term testing of both base metal and welds should be conducted to determine how the mechanisms of corrosion change with time as enrichment or depletion of the components proceeds.

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## 4. STRESS CORROSION CRACKING

### 4.1 Introduction

Stress corrosion cracking (SCC) behavior in titanium and its alloys has been known to occur in a number of different environments, although the number of failures that have occurred under service conditions is very small. The characterization of the SCC behavior of TiCode-12 is of primary concern since susceptibility to this corrosion form can lead to catastrophic failure. This report will briefly review and outline the current available data pertaining to SCC in TiCode-12 under waste repository conditions. The report will then address the additional data needs required to fully characterize this failure mode.

### 4.2 Background - General Description of Stress Corrosion Cracking

The occurrence of stress corrosion in a susceptible material requires the conjoint action of an applied stress and a corrosion process. For nuclear waste containment applications the two forms of SCC of importance are SCC in aqueous solutions and hot salt cracking. Cracking in gaseous environments is also of interest and is currently being evaluated by Ahn<sup>1</sup> in a separate BNL report as it relates to hydrogen embrittlement of TiCode-12. Hydrogen is also often thought to play an active role in the mechanisms of SCC in aqueous solutions and hot salt cracking.

The susceptibility of titanium alloys to SCC in aqueous environments is influenced by several factors such as the species in solution, the concentration, pH, temperature and viscosity of the solution, and the electrical potential.<sup>2</sup> Addition of the halide ions  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  increases susceptibility and crack velocity in these alloys. On the other hand,  $\text{F}^-$  does not cause failure and may instead inhibit crack propagation.<sup>2,3,4</sup> Cations less noble than titanium, such as Na, Li, and K have no influence on SCC behavior<sup>5</sup> while some cations more noble than titanium, e.g.,  $\text{Cu}^{+2}$ , reduce or prevent cracking.<sup>4</sup>

Increasing the pH of water or very dilute  $\text{Cl}^-$  solution decreases or suppresses susceptibility to SCC. Decreasing the pH by the addition of HCl results in increased susceptibility and crack velocity. This effect is complicated by the increase in  $\text{Cl}^-$  concentration necessary to reduce the pH. However, the susceptibility of cathodically polarized specimens in  $\text{H}_2\text{SO}_4$  is also increased by reducing the pH.<sup>2</sup>

In neutral and acid  $\text{Cl}^-$  solutions, the susceptibility is hardly affected by temperature, but crack velocity increases with increasing temperature over the range 249-366°K (-24 to 93°C). Increasing the temperature also lowers the viscosity. The increase of crack velocity with temperature can therefore be attributed to either increasing the anodic reaction rate or facilitating mass transport, or both.<sup>2</sup>

There are also metallurgical variables which can influence SCC susceptibility and these are the alloy composition; interstitial content; slip character; and the structure, morphology, and grain size of the alloy phases. Oxygen, iron, and aluminum have been singled out for their adverse effects on the SCC resistance of titanium.<sup>6</sup> Oxygen and iron are difficult to remove from titanium and exist as major impurities in the metal. Aluminum is a prominent alloy element in titanium alloys but is not present in TiCode-12 or unalloyed titanium.

The exact mechanism of stress corrosion cracking in titanium alloys is unknown. There are two popular environmental models to describe the mechanism of SCC. A number of workers consider hydrogen and its embrittlement effect to be central to the issue, while others support an electrochemical mass transport kinetic model or anodic dissolution mechanism.<sup>7</sup>

Beck<sup>8,9</sup> proposed the mass transport kinetic mechanism which attempts to explain the phenomenon as occurring from the result of a high concentration of  $Cl^-$  ions at the tip of the crack which results in the formation of a layer or layers of titanium chloride. This initiates a cleavage crack in the alloy lattice under the influence of the acting tensile stress component.

The hydrogen embrittlement mechanism<sup>9</sup> involves the discharge of hydrogen on unfiled or thin film surfaces at the crack tip. The entry of hydrogen into the deforming volume of metal in front of the crack tip results in a plastically induced slow strain rate hydrogen embrittlement. Scully<sup>10,11</sup> and others<sup>12</sup> suggested that cleavage initiated from hydrides precipitated on slip planes near the crack tip in addition to transgranular cleavage attributed to anodic dissolution.

The experimental results of Rideout, Louthan, and Selby<sup>13</sup> have been interpreted to support a hydrogen embrittlement mechanism in hot salt cracking. Also, substantial increases in hydrogen content have been measured by Gray<sup>14</sup> in the vicinity of the fracture surfaces of embrittled specimens of Ti-8Al-1Mo-1V after hot salt exposure.

It is clear that a single SCC model has not been developed which can explain all of the basic aspects of SCC in titanium and titanium alloys. It is well known, however, that the primary factors which determine the nature of stress corrosion failure in titanium alloys are hydrogen, halide ions, certain alloying addition, microstructure, and stress intensification.<sup>7</sup>

#### 4.3 Stress Corrosion Cracking Data Available to Characterize Titanium and TiCode-12 Corrosion Behavior in High Level Waste Repositories

Current efforts to characterize titanium and TiCode-12 SCC behavior under high level waste repository conditions are under way at Pacific Northwest Laboratory (PNL), Sandia National Laboratory (SNL), and Brookhaven National Laboratory (BNL). The data and results of testing that have been completed will be summarized below. Details of the experimental setups and techniques used are discussed in a separate BNL report.<sup>15</sup>

Initial tests at PNL<sup>16</sup> used two types of specimens to evaluate Grade 2 and 12 titanium susceptibility to SCC. Wedge-opening load (WOL) and residual stress specimens were loaded and exposed in autoclaves for 89 days at 250°C to a simulated Hanford basaltic groundwater. The WOL specimens, which were loaded to about 50 Ksi  $\sqrt{in}$ , showed no surface cracking during exposure. The residual stress specimens were visually examined following exposure and no cracks were found.

The PNL program is currently emphasizing the accelerated testing of these alloys for environmentally induced fracture.<sup>17,18</sup> The two experimental methods that were used were the slow strain rate (SSR) and fatigue crack growth rate (FCGR) tests.

The SSR tests were conducted at 250°C in a simulated Hanford basaltic groundwater. Both the titanium Grade 2 and 12 lost some ductility with a decrease in strain rate. The ductility diminution, however, was about the same when the tests were conducted in presumably inert air as when they were conducted in Hanford groundwater. The fracture surfaces of specimens strained to failure at  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$ , and  $2 \times 10^{-7}$ /sec were examined for signs of environmentally enhanced cracking and it was determined that the fracture modes in all cases were by microvoid coalescence. It was suggested that the embrittlement mechanism was other than SCC, possibly dynamic strain aging.

The FCGR tests were performed to detect environmentally assisted cracking, not to simulate expected loading or environmental conditions in a repository. This type of test forces cracking by fatigue and allows time for environmental damage to occur at the crack tip. These tests were performed in Hanford basaltic groundwater, fluoride-ion enhanced Hanford groundwater (220 ppm F<sup>-</sup>) and high-purity water at 90°C.

The FCGRs of titanium Grade 2 and 12 were not affected relative to air or high purity water by any of the environments used in the study, and no frequency dependence was observed. It was tentatively concluded that no environmental cracking mechanism relative to a Hanford basalt repository is significantly operative under the conditions of high oxygen fugacity and a temperature of 90°C.

At SNL, Braithwaite, Magnani, and Munford<sup>19</sup> conducted several SSR tests under a wide range of environmental conditions. The SSR results for TiCode-12 at 250°C in air, dry salt, and saturated brine are plotted in Figure 4.1 as a reduction in area vs strain rate. The data showed that for the strain rates tested ( $1 \times 10^{-4}$  to  $5 \times 10^{-7}$  sec<sup>-1</sup>), the effect of environment on the ductility of TiCode-12 was not significant. Additional tests, all at  $1 \times 10^{-5}$  sec<sup>-1</sup> and 250°C in oxygenated brine (~500 ppm O<sub>2</sub>), deoxygenated dry salt and dry salt plus 2% H<sub>2</sub>O resulted in similar reduction in area values of 43 to 52%.

SSR tests were conducted at room temperature in laboratory air on irradiated specimens of TiCode-12 which were exposed to Brine A and  $10^7$  rad/hr



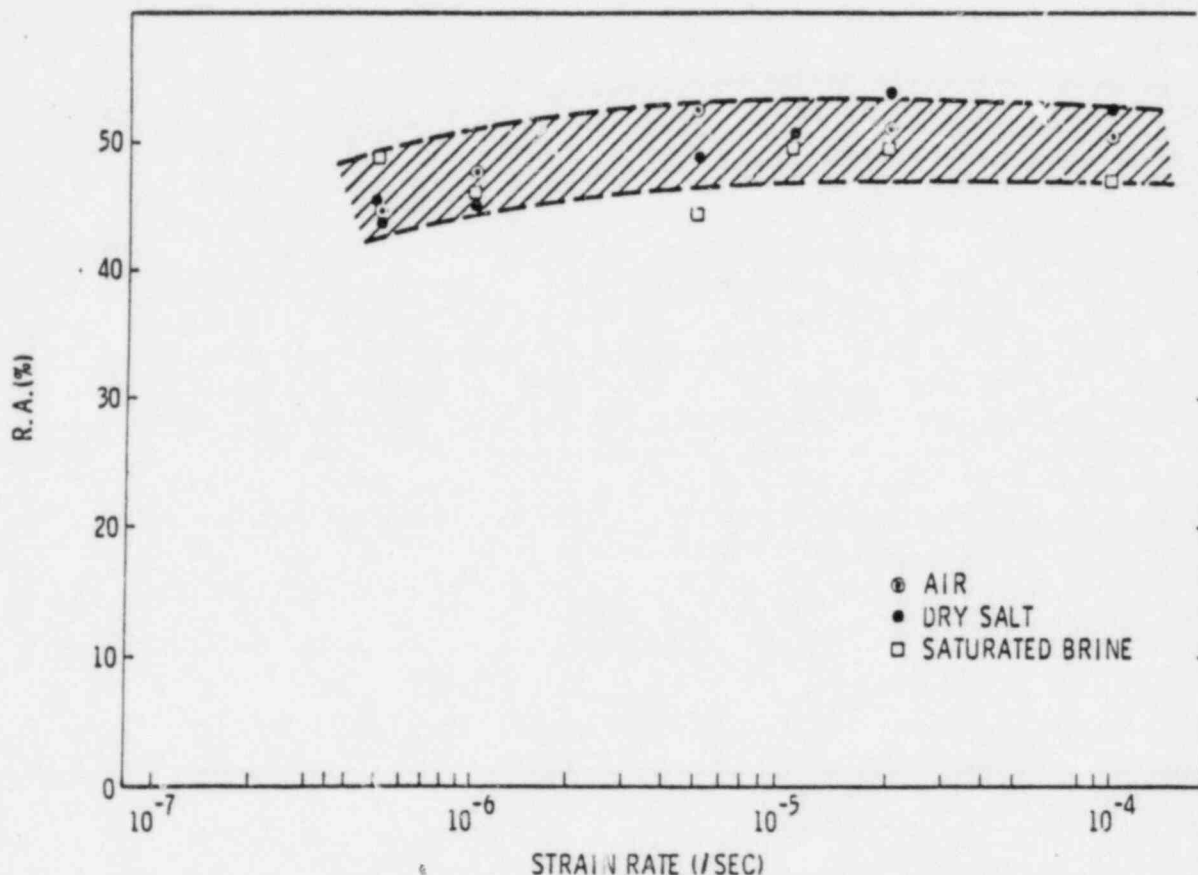


Figure 4.1 The relationship between the reduction of area (RA) and strain rate for TiCode-12 tested in air, dry salt, and saturated brine at 250°C.<sup>19</sup>

for 31 days prior to testing. It was concluded that ductility was not significantly affected by this radiation exposure.

Fractographic examinations were conducted to determine if environmental effects on the fracture behavior were on a scale too fine to be detected by ductility measurements. It was found that while a ductile fracture morphology was typical of TiCode-12 exposed to dry salt and brines, the specimens exposed to high temperature oxygenated brine and irradiated brine exhibited atypical regions. These regions were localized at the edges of the specimen and characteristic of a less ductile fracture mechanism such as quasi-cleavage.

A number of fracture mechanics specimens were tested to determine the stress corrosion crack propagation behavior of TiCode-12. There was no indication of subcritical crack growth found during room temperature tests using fatigue pre-cracked specimens. The tests were conducted in brine and dry salt (100% relative humidity) at stress intensities as high as 90% of overload (37 MN/m<sup>3/2</sup>) for times greater than 1000 hours.

Others at SNL<sup>20,21,22</sup> have studied the susceptibility of TiCode-12 to SCC. SSR tests at constant strain rates ( $10^{-4}$  to  $10^{-7}$   $\text{sec}^{-1}$ ) were used with environmental test variables which included temperature (30 to 250°C), solution (air as reference vs Brine A, Brine B, or seawater), pH (1 to 6.5), and dissolved oxygen content (static deoxygenated conditions as well as flowing oxygen saturated conditions). Other test variables included prior gamma irradiation in brine, heat treatment, and the presence of welds.

Figure 4.2 is a representative sample of some of the results in these studies. The absence of SCC is suggested by the ratios of measurements in environment to measurements in air near unity. In all cases so far, no macroscopic evidence of SCC in TiCode-12 has been observed. However, fractographic observations have suggested that some environmental degradation may have occurred particularly at the slowest strain rate examined which was  $10^{-7}$   $\text{sec}^{-1}$ . At this rate, the fracture mode changed from quasi-cleavage to dimple rupture with increasing distance from the sample edge. Fractography also revealed some evidence of embrittlement in the outer 50 micrometers of samples strained after gamma irradiation in brine.

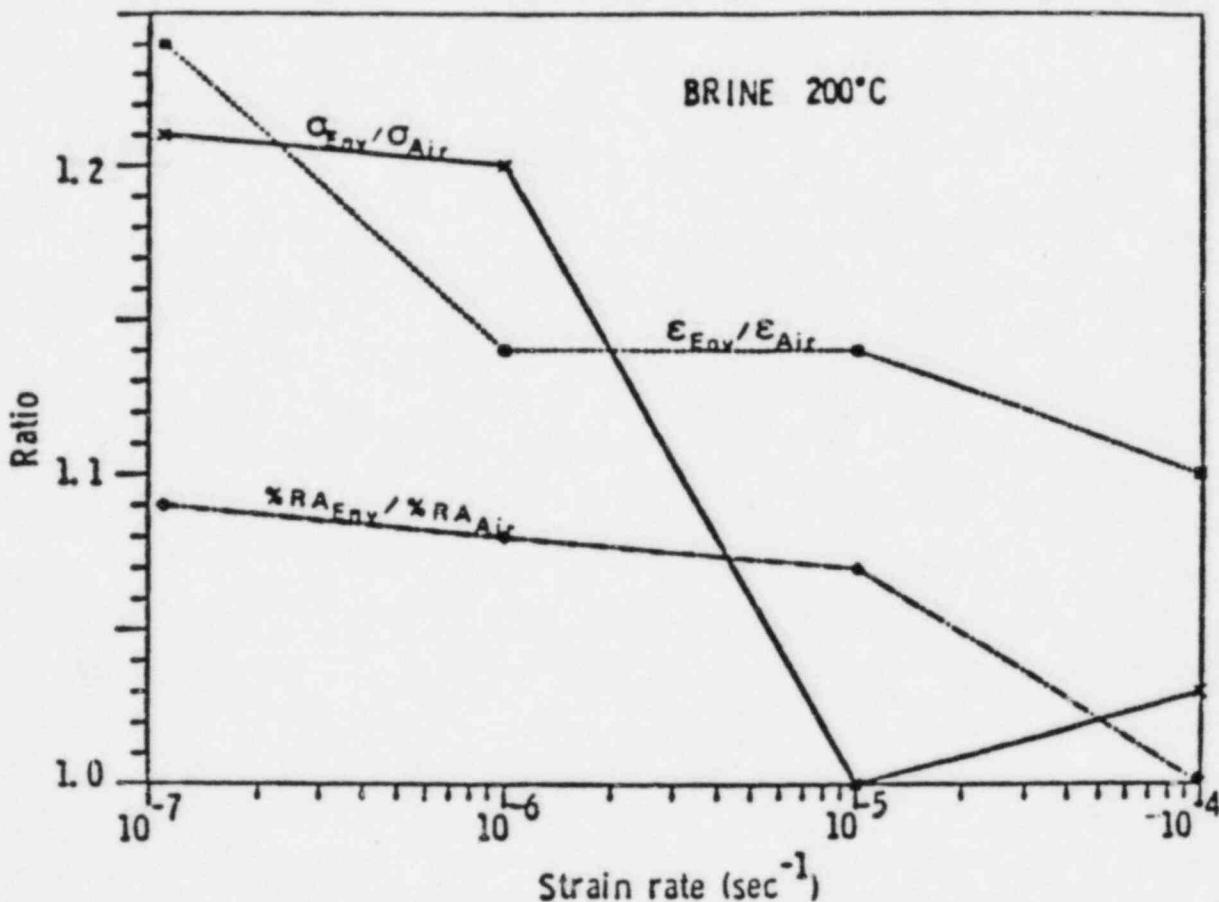


Figure 4.2 Influence of strain rate on the stress corrosion susceptibility of TiCode-12 in Brine A at 200°C as represented by ratios of (a) ultimate tensile strengths, (b) total strains to failure, and (c) reductions in area in brine and air.<sup>20,21</sup>

SCC testing of titanium and TiCode-12 has recently been initiated at BNL.<sup>23</sup> Notched and un-notched C-rings of titanium and TiCode-12 have been loaded and sealed in a capsule containing acidified Brine A at 150°C. Further testing and analyses to characterize SCC behavior is currently under way.

#### 4.4 Additional Data Requirements for the Characterization of TiCode-12 Stress Corrosion Cracking Behavior

Static and dynamic testing of TiCode-12 to determine SCC susceptibility have not revealed any effect on macroscopic properties by exposure to brine or basaltic water environments. However, microscopic examinations of specimens fractured during exposure indicate that the fracture mode may be sensitive to the environment.

There are several considerations when using laboratory data on SCC to predict the 1000-year behavior of TiCode-12 under repository conditions. These have already been discussed by a Materials Characterization Center (MCC) workshop and some main points are summarized below.<sup>24</sup>

There are basically two types of testing which are real-time and accelerated. In real-time testing, the corrosion test media simulates the actual expected environment as closely as possible. In accelerated testing, a parameter is varied in an attempt to accelerate the SCC process in order to study it. Real-time data are limited by experimental constraints, e.g., the length of time a test can be conducted, the constancy of steady-state crack growth rates, and the uncertainty in the threshold stress intensity. Parameters such as fracture thresholds are the most relevant data for ensuring the integrity of an engineered barrier over a specified time period, but the present experimental capability for measuring crack growth rates of  $10^{-8}$  mm/sec (about 300 mm/1000 years) is insufficient for 1000-year life predictions. In addition, changes in the fracture threshold with time must be considered for long term containment applications.

Results from accelerated testing are limited by confidence in the relationship between the SCC process and the parameter used to accelerate a material's susceptibility to SCC. The validity of extrapolating such accelerated data back to real-time conditions may be open to question if the accelerated SCC mechanism cannot be shown to be the same as the real-time SCC mechanism.<sup>15</sup>

Parameters which the MCC workshop have suggested to be suitable for isothermally accelerating SCC are pH, Eh, stress, strain rate, O<sub>2</sub> concentration, and halide concentration. Temperature was not considered to be a good parameter for accelerating SCC because it can introduce other mechanisms that may considerably change the material strength properties and the nature of the cracking phenomenon. Various testing methods and the types of useful information which can be obtained from them have been discussed in MCC<sup>24</sup> and BNL<sup>15</sup> reports.

It can be concluded from the above discussion that the absence of detectable degradation of macroscopic tensile properties in SCC testing to date does not guarantee non-susceptibility. Therefore, it is recommended that long term (several years) real-time testing of statically loaded specimens be performed under expected repository conditions.

Testing should continue to study the effects, if any, of variations of environmental parameters on SCC susceptibility. This includes the use of radiation fields, intermediate temperatures, and lower stress intensities and cyclic frequencies similar to those planned by PNL.<sup>17</sup> FCGR testing of TiCode-12 in brine solutions will also yield additional information regarding the influence of environment on the crack growth phenomenon in salt repositories.

The slow strain rate tests at Sandia in brine have indicated a change in fracture mode under microscopic examination. It had been suggested that this may possibly have been caused by an ingress of hydrogen into the alloys.<sup>21</sup> Further investigation of this phenomenon is recommended to determine the character, the extent, and any implications of the mechanisms involved.

No environmental cracking mechanism was found due to fluoride-ion enhanced Hanford groundwater.<sup>17</sup> The presence of fluorides may not necessarily promote SCC susceptibility<sup>2,3,4,12</sup> and it is therefore suggested that the influence of other halide concentrations be tested, e.g., chlorides, bromides, and iodides.

Hot salt SCC of titanium alloys is a function of temperature, stress, and time of exposure. In very general terms, hot salt SCC has not been observed below about 500°F (260°C),<sup>25</sup> however, some investigators have indicated some damage at temperatures slightly above 400°F (204°C).<sup>26</sup> Longer times at temperature also tend to reduce the threshold stress values. Though brine is expected to migrate towards the waste package and a backfill may be present between the container and host rock, it is still possible that the TiCode-12 can be exposed to hot dry salt. Further testing for longer time periods is recommended to investigate the possibility of hot salt SCC as the present available data in dry or moist salt are insufficient to dismiss it as a possible failure mode.

#### 4.5 Summary and Conclusions

The ultimate objective of SCC testing is to determine susceptibility and to quantify any crack initiation and propagation rates in order to predict a TiCode-12 lifetime. This problem is complicated by the many variables that can influence threshold stress intensity values and crack growth rates.

The available data indicate that apparently, TiCode-12 is highly resistant to SCC under the conditions tested. However, microscopic examination has revealed possible signs of embrittlement in specimens exposed to 250°C oxygenated brine, irradiated brine, and those fractured at slow strain rates in brine.

The additional data required to characterize TiCode-12 SCC susceptibility and/or behavior under waste repository conditions are the following:

- Both real-time and accelerated testing should be conducted to determine the ranges of conditions under which TiCode-12 base and weld structures are susceptible to crack initiation or crack growth. The various environmental test parameters include solution chemistries (e.g., brine and basaltic waters, pH, Eh, O<sub>2</sub> concentration, halide concentrations), stress, stress intensity factors, strain rate, cyclic frequencies, temperature, radiation levels, and time. A characterization of the local conditions at the crack tip will also aid in the understanding of the SCC mechanism.
- The development of predictive equations and models requires some determination of the failure mechanism, if indeed SCC exists. This understanding will also help in the interpretation of results from accelerated testing as the relationship between the accelerated parameters and mechanisms become known.
- The change in fracture mode reported by Sandia in slow strain rate tests should be investigated further. This phenomenon should be studied to determine the character, extent, and implications involved.
- Testing should continue in moist and dry salts as other titanium alloys are known to be susceptible to hot salt cracking and because longer times at temperature tend to reduce the threshold stress values.
- Long term real-time testing of statically loaded specimens under expected repository conditions should be conducted.
- The crack initiation period, crack growth rates, and fracture threshold values should be determined. Changes in the fracture threshold with time must also be determined.
- Microscopic examinations must accompany the macroscopic testing to characterize the fracture modes and mechanisms of any ductility degradation.

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