MAY 23 1967

MASTER

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
NUCLEAR DIVISION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL - TM - 1834

COPY NO. - 20

DATE - April 28, 1967

ELECTROCHEMICAL MEASUREMENTS ON CRYSTAL-BAR ZIRCONIUM
IN OXYGENATED 0.05 M K_2SO_4 SOLUTIONS,
BETWEEN 200° AND 240°C

H. S. Gadiyar

NOTICE This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

THIS DOCUMENT HAS BEEN REVIEWED,
NO INVENTIONS OF PATENT INTEREST
TO THE AEC ARE DISCLOSED THEREIN.

282
5-24-67 DISTRIBUTION OF THIS DOCUMENT IS 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.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Neither the United States nor the Commission, nor any person acting on behalf of the Commission, makes any warranty, representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor, prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

CFSTI PRICES

H.C. \$3.00; MN 65

ELECTROCHEMICAL MEASUREMENTS ON CRYSTAL-BAR ZIRCONIUM
IN OXYGENATED 0.05 M K_2SO_4 SOLUTIONS,
BETWEEN 200° and 240°C

H. S. Gadiyar

ABSTRACT

Electrochemical measurements on crystal-bar zirconium in oxygenated 0.05 M K_2SO_4 solution have been made between 200 and 240°C, to measure the rates of corrosion and film growth at different temperatures. The rate-time plots obtained thus have been analyzed for kinetics of film growth. This work was done by A. L. Bacarella, H. S. Gadiyar and A. L. Sutton. The purpose of this report is to record and make available the data obtained. Interpretations are incomplete and will be included in other reports.

INTRODUCTION

Zirconium and its alloys have extensive use in high temperature, high pressure, water and steam cooled reactor systems. Electrochemical techniques are being used, in recent years,^{1-6,8-10} to obtain information on the corrosion of Zr and its alloys. Several investigations on this film formation and anodic film growth on Zr, Ta^{13,14} and other valve metals¹³ by electrochemical and electrical methods have been reported in literature. In the current series, experiments on electrochemical measurements on crystal-bar zirconium have been made between 200° and 240°C in oxygenated 0.05 M K_2SO_4 solution. This is an extension of work previously carried out by Bacarella and Sutton,³⁻⁵

in the same equipment, but in different solutions. This work was done by A. L. Bacarella, H. S. Gadiyar and A. L. Sutton. The purpose of this report is to record and make available the data obtained. Interpretations are incomplete and will be included in other reports.

EXPERIMENTAL

Specimen Preparation:

Cylindrical type specimens fabricated from crystal-bar zirconium were used and were of approximate size 2.2" (long) x 0.112" (dia.); total surface area being 5 to 6 cm². The specimen was first polished on 600 grit emery paper, washed with soap and distilled water, degreased in methanol and then chemically treated in solution containing 5 vol. per cent HF (48%), 45 vol. per cent HNO₃ (conc.) and 50 vol per cent H₂O for 60 sec. It was then washed in triple distilled water, immersed in boiling triple distilled water for 5 min and then once again washed in triple distilled water before being introduced into the cell.

The water used for preparing the solution was carefully purified by triple distillation to eliminate oxidizing impurities that may interfere in the reaction. Analar grade potassium sulphate (Formula wt 176.27) was used and the solution was prepared by dissolving 87.1 gm of K₂SO₄ in 10 liters of triple distilled water.

The electrochemical cell used for measurements has been designed and described by Bacarella.⁴ The schematic diagram of the cell arrangement has been shown in Fig. 1. A 20 liter stainless steel autoclave reservoir is used for holding the stock solution and the solution

drawn from the reservoir passes first through a preheater before entering the reaction cell. A split resistance furnace is used for heating the cell. The cell could be rapidly cooled if necessary by means of an air blast. The cell temperature is controlled within $\pm 0.5^{\circ}\text{C}$ by means of three thermocouples located near the heating furnace, outside the reaction cell and inside the reaction cell into the thermocouple well. The reaction cell is made up of Ti metal and is capable of holding about 175 cc of the solution. The cell contains five ports, four on the top and one on the bottom portion (Fig. 2). A Ti rod welded to the reaction cell acted as the auxiliary electrode. To one of the ports, an extended Ti tube was welded and a Pt reference electrode was placed inside this by means of a Teflon cone, sleeve and a pressure nut. The other three ports provided positions for a thermocouple well, solution outlet flow and the Zr test electrode. The test electrode was isolated from the autoclave again by means of a Teflon cone and a Teflon sleeve. The solution to the cell entered through the bottom port. The Pt reference electrode was positioned entirely in the air-cooled portion of the Ti tube extension, giving a "reference" potential independent of temperature changes in the reaction cell (see Fig. 3).

The entire assembly was first rinsed with distilled water and 12 liters of the solution was aspirated into the reservoir autoclave; it was then saturated with 250 psig of oxygen gas with a Magne Dasher. A super pressure of 950 psig of the gas was used to maintain the O_2 and steam in solution at the operating temperatures; this also provided the pressure differential for solution flow through the reaction cell. The flow of the solution through the cell was adjusted to 0.5 to 1 cc/min

by means of a stainless steel valve.

The pre-heater temperature while starting the experiment was kept about 20°C higher than the operating temperature. To attain temperature of the cell within about 3 min, the split furnace heated previously to the reaction temperature was brought into position around the reaction cell and the exit valve was fully opened; the hot solution from the pre-heater fills the cell and the temperature is then attained to the desired experimental value. The hot solution flowing out from the cell during this heating operation was passed through a water cooled Ti tube coil, before being let off. The solution flow was adjusted to about 0.5 cc/min when the experimental temperature is attained.

The potentials were measured with a modified L&N model pH meter, used as a potentiometer. The signal from the L&N meter was fed into a 10 mv Brown Recorder. Polarizing currents were obtained by selecting voltage from a series of 22.5-45 v batteries connected in series across a chosen resistance from 10 to 10^9 ohms provided by a series of decade switches. The currents were measured by recording the voltage drop across precision resistors connected in series with the decade switches in the polarizing circuit. (Fig. 3a). An electronic potentiostat was used for making potentiostatic measurements and the anodic currents were measured by recording the voltage drop across precision resistors in series in the polarizing circuit.⁵ The capacitance of the film was measured using galvanostatic pulse technique. Current densities of about 5×10^{-3} amp/cm² were pulsed through the electrode for about 3 milliseconds, and the slope of the voltage-time trace during the first 5-10 μ seconds was obtained with the capacitance $c = i/dV/dT$. The

values of the film thicknesses were calculated by integration of the anodic current based on an estimate of $1 \text{ amp.min/cm}^2 = 4.8 \times 10^3 \mu\text{g O}_2/\text{cm}^2$ and $1 \mu\text{g O}_2/\text{cm}^2 = 67.3 \text{ \AA}$. An initial thickness $x_0 = 100 \text{ \AA}$ was also assumed. (see Appendix I).

The measurements included (1) the current-voltage and capacitance between $200^\circ\text{--}240^\circ\text{C}$ as a function of film thickness, (2) the rate of film growth as a function of time at constant anodic potential of 0.00V (vs Pt/O_2) between 200 and 240°C and (3) activation energy determination at different thicknesses between 175° and 240°C .

RESULTS

The current voltage measurements made galvanostatically at 238°C as a function of time have been plotted in Figs. 4(a) to 4(f); Fig. 5 is a plot made at 204°C ; the $i\text{--}v$ plot presented in Fig. (6) corresponds to a potentiostatic measurement made after growing the film at 204°C for 10,000 minutes ($x_T \sim 850 \text{ \AA}$) at constant anodic potential of 0.00V vs Pt/O_2 electrode, made over a wide range of potentials, -1.4 v to 8.0 v vs Pt O_2 . The values of the sum of the transfer coefficients change more rapidly during the initial stages of exposure until the first 300 minutes and then remain in the region of about 0.3 to 0.5; the $\alpha_a z_a$ values decreased gradually from 0.455 (at 30 min) to about 0.1 after 24 hr exposure, further decreased to a steady value ranging from 0.04 to 0.05 after about 3,000 minutes of corrosion; the $\alpha_c z_c$ values increased from 0.28 during the initial stages to about 0.3 to 0.35 after about 3,000 minutes. The $\alpha_a z_a$ values appear to be higher at lower temperature and vice versa for $\alpha_c z_c$ values at the same period of

corrosion.

The corrosion rate of the specimen can be read at various time intervals at the intersection of the anodic and cathodic curves. The rates have also been determined at various periods by polarization resistance measurements using the equation

$$I_{\text{corr}} = \left(\frac{dI}{dE} \right)_{E \rightarrow E_0} \times \frac{RT}{F} \times \frac{1}{\alpha_a z_a + \alpha_c z_c}, \quad (1)$$

where I_{corr} = corrosion rate in amp/cm², $\alpha_a z_a$ and $\alpha_c z_c$ are the transfer coefficients obtained from the tafel slopes $\beta = dE/d\log I$ for the anodic and cathodic reactions respectively where $\alpha z = 2.3 RT/F \times 1/\beta$. The rates determined by this method have been tabulated in Table 1. However, the rates may be within 10 to 15% of the error due to variations in the αz values. The capacitance measured by pulse technique (which is a function of film thickness) at 238°C have been presented in Table 2 as a function of time. A linear relationship plotted in Fig. (7) has been observed between $(1/c)^2$ vs time. This shows a parabolic kinetics of film growth on Zr at open potential measurements studied at 238°C.

Below oxygen evolution potential, the film growth in the anodic region is produced with 100% efficiency, and the thickness can then be calculated by integration of the anodic current. The rate of film growth at constant anodic potential 0.00V vs Pt/O₂ (55°C) vs time at three different temperatures 204°, 226° and 242°C have been plotted in Fig. (8). Fig. 9a, b, c shows the plot of reciprocal capacitance vs film thickness at these temperatures; the linear relationship has been obtained from these results; the dielectric constants calculated from the slope of x_T vs A/cm^2 is also presented.

$$[\epsilon = \frac{\Delta x_T}{\Delta A/c} \times \frac{1}{8.85 \times 10^{-8}}]$$

where A is the area of the specimen. The dielectric constants obtained from capacitance measurements have been shown against temperature in Fig. (10).

The rate of passive film growth in aqueous systems generally decreases as the film thickness increases and is complicated by the presence of two interfaces viz metal/oxide and oxide/solution, at which transfer processes occur. Numerous rate laws have been proposed for the film growth reaction and mechanisms have been postulated on the basis of the fit into these laws. It is observed that the slope of the log rate vs log time in Fig. (8) for anodic film growth give values between -0.6 and -0.7. Cubic growth⁴ is expected as per this slope, which can be stated in the form,

$$\left(\frac{1}{r}\right)^{3/2} = k_1 t + k_2 \dots \quad (2)$$

where $r = dx/dt =$ rate, t is time in minutes and k_1 and k_2 are constants. The above relation can also be written in the form (Appendix II)

$$\left(\frac{1}{r}\right)^{1/2} = \frac{k_1 x_T}{3} - \frac{k_1 k_3}{3} \dots \quad (3)$$

where k_3 is another constant. In Fig. 11, are plotted $(1/r)^{1/2}$ vs x_T for three temperatures 204°, 226° and 242°C.*

*Note: Bacarella⁵ on his measurements of film growth on zirconium in oxygenated 0.05 M H₂SO₄ at temperatures from 174 to 284°C has represented the anodic film growth by an hyperbolic sine function relating the film growth current to the field strength by an expression

$$i = i_o \left[\exp\left(\frac{BV}{x}\right) - \exp\left(-\frac{BV}{x}\right) \right] = 2 i_o \sinh \frac{BV}{x}$$

where B is the field coefficient and $\frac{V}{x}$ is the field strength. Polling and Charlesby⁹ in their studies on oxidation of Zr have predicted the relation between oxide thickness and time depends upon the value of

$$\frac{BV}{x} = z = \frac{qa}{x} \frac{V}{RT}$$

where $\frac{V}{x}$ is the electric field, q , is ion charge and "a" barrier width; at high temperatures when the value of z is about equal to one, the growth should be approximately cubic. It has been observed that the value of z is nearly equal to unity for film thicknesses around 1000 to 1500 Å in these studies, thereby justifying the cubic growth as shown in Fig. 11.

In Figs. 12a, b, c are plotted $\alpha_a z_a$ values as a function of film thicknesses at three different temperatures. The values decrease continuously but gradually from 0.0975 to 0.0498 as the film thickness increases from 185 Å to 968 Å at 204°C; the decrease is more rapid at higher temperatures.

Figures 13a, b, c, d shows the activation energy plots made at different temperatures and at various film thicknesses, the film being grown at constant anodic potential 0.00 volts. The values range between 30 kcal/mole to 26 kcal/mole at studied thicknesses. Figure 14 is another activation energy plot, for the film grown at open potential at 238°C, with the value 27 kcal/mole.

ACKNOWLEDGEMENT:

The kind encouragement and helpful discussions from time to time from Dr. G. H. Jenks is greatly appreciated.

APPENDIX I

10^5 coulombs $\equiv$ 1 equivalent of reacting O_2 .

$\equiv$ 8 units

$$\frac{1 \text{ amp}}{\text{cm}^2} = \frac{1 \text{ coulomb}}{\text{sec. cm}^2} = \frac{10^{-5} \text{ equivalent}}{\text{sec. cm}^2}$$

$$\equiv \frac{8 \times 10^{-5} \text{ gm}}{\text{sec. cm}^2}$$

[1 equivalent was substituted by 8 gm for O_2]

$$\equiv \frac{60 \times 8 \times 10^{-5} \times 10^6}{\text{min. cm}^2} \mu\text{gm of } \text{O}_2$$

$$\equiv \frac{4.8 \times 10^3}{\text{min. cm}^2} \mu\text{g } \text{O}_2$$

$$\therefore \frac{1 \text{ amp min}}{\text{cm}^2} = \frac{4.8 \times 10^3}{\text{cm}^2} \mu\text{gm } \text{O}_2$$

$$91.2/x = 32/1 \mu\text{g } \text{O}_2$$

$$x = \frac{91.2 \times 1}{32} = 2.85 \mu\text{gm Zr for } 1 \mu\text{gm } \text{O}_2$$

$$2.85 \mu\text{gm Zr} + 1 \mu\text{gm } \text{O}_2 \quad 3.85 \mu\text{gm ZrO}_2$$

$$\text{density of ZrO}_2 = 5.71 \text{ g/cm}^3$$

$$\therefore \frac{1 \mu\text{g } \text{O}_2}{\text{cm}^2} = \frac{3.85 \times 10^{-6}}{5.71} = 67.3 \text{ \AA (ZrO}_2 \text{ film)}$$

APPENDIX-2

$$\left(\frac{1}{r}\right)^{3/2} = k_1 t + k_2$$

$$\left(\frac{1}{r}\right) = (k_1 t + k_2)^{2/3}$$

$$\frac{dx}{dt} = r = (k_1 t + k_2)^{-2/3}$$

$$dx = (k_1 t + k_2)^{-2/3} dt$$

$$\text{Let } y = k_1 t + k_2$$

$$dy = k_1 dt$$

$$dt = \frac{dy}{k_1}$$

$$dx = y^{-2/3} \cdot \frac{dy}{k_1}$$

$$x = \frac{3}{k_1} y^{1/3} + k_3$$

$$x = \frac{3}{k_1} (k_1 t + k_2)^{1/3} + k_3$$

$$(x - k_3)^{-2} = \left(\frac{3}{k_1}\right)^{-2} (k_1 t + k_2)^{-2/3}$$

$$\text{or } (k_1 t + k_2)^{-2/3} = \left(\frac{3}{k_1}\right)^2 / (x - k_3)^2$$

$$\text{Therefore, } \frac{dx}{dt} = \left(\frac{3}{k_1}\right)^2 / (x - k_3)^2$$

$$1/dx/dt = (x - k_3)^2 / \left(\frac{3}{k_1}\right)^2$$

ie,

$$\left(\frac{1}{r}\right)^{1/2} = \frac{x - k_3}{3/k_1} = \frac{k_1 x_T}{3} - \frac{k_1 k_3}{3}$$

crystal bar Zr (chromium plated)

Corrosion rates at open potential in 0.05 M K_2SO_4 + 250 ppm O_2

Temperature = 238°C; Total surface area = 4.51 cm²

G 122

TABLE-1

Time	Open Potential E_o (vs SCE)	$E - E_o$ $= \Delta E$	I ($\mu A/cm^2$)	$\frac{\Delta E}{I}$	$Z \times Z$	$\frac{RT}{F}$	I_{corr} $= (RT/F)$	$\frac{0.046}{\Delta E \times Z \times Z}$
10 min	-1.06V	10.0	1.1×10^{-6}	9.1×10^3	0.74	0.044	6.54×10^{-6}	
14 min	-1.06V	11.0	1.15×10^{-6}	9.56×10^3	0.74	0.044	6.22×10^{-6}	
20 min	-1.07V	14.0	1.15×10^{-6}	12.17×10^3	0.74	0.044	4.89×10^{-6}	
30 min	-1.00V	9.5	0.575×10^{-6}	16.5×10^3	0.74	0.044	3.61×10^{-6}	
44 min	-1.16V	10.0	0.375×10^{-6}	17.4×10^3	0.74	0.044	3.42×10^{-6}	
58 min	-1.165V	11.0	0.575×10^{-6}	19.12×10^3	0.74	0.044	3.14×10^{-6}	
70 min	-1.16V	8.5	0.375×10^{-6}	22.7×10^3	0.74	0.044	2.64×10^{-6}	
85 min	-1.155V	8.75	0.375×10^{-6}	23.32×10^3	0.74	0.044	2.55×10^{-6}	
100 min	-1.152V	9.0	0.378×10^{-6}	23.8×10^3	0.75	0.044	2.47×10^{-6}	
120 min	-1.154V	11.0	0.470×10^{-6}	23.4×10^3	0.79	0.044	2.38×10^{-6}	
140 min	-1.160V	9.0	0.425×10^{-6}	21.6×10^3	0.79	0.044	2.32×10^{-6}	
160 min	-1.174V	9.5	0.425×10^{-6}	22.4×10^3	0.79	0.044	2.46×10^{-6}	
182 min	-1.190V	9.5	0.420×10^{-6}	22.9×10^3	0.75	0.044	2.51×10^{-6}	
520 min	-1.154V	10.0	0.425×10^{-6}	23.5×10^3	0.65	0.044	2.62×10^{-6}	
815 min	-1.068V	11.0	0.425×10^{-6}	25.9×10^3	0.60	0.044	2.81×10^{-6}	
1160 min	-1.042V	13.0	0.425×10^{-6}	30.6×10^3	0.55	0.044	2.61×10^{-6}	
1370 min	-0.990V	14.0	0.45×10^{-6}	31.1×10^3	0.55	0.044	2.57×10^{-6}	
1640 min	-0.995V	15.0	0.45×10^{-6}	33.3×10^3	0.55	0.044	2.40×10^{-6}	
4260 min	-1.029V	22.0	0.46×10^{-6}	47.8×10^3	0.40	0.044	2.19×10^{-6}	
5530 min	-1.01V	25.0	0.385×10^{-6}	65.0×10^3	0.40	0.044	1.62×10^{-6}	
6040 min	-1.005V	28.0	0.385×10^{-6}	72.7×10^3	0.40	0.044	1.52×10^{-6}	
7060 min	-1.008V	23.0	0.285×10^{-6}	80.7×10^3	0.40	0.044	1.36×10^{-6}	
... PTD								

TABLE 1 (contd).

Time	E_0	$E - E_0$ $= \Delta E$ (mV)	I (amp)	$\frac{\Delta E}{I}$	$\epsilon \alpha z$	$\frac{RT}{F}$	I_{conv} ($\frac{0.044}{\Delta E \times \epsilon \alpha z}$)		
7490mV	-1.005V	24.0	0.285×10^{-6}	84.2×10^3	0.40	0.044	1.31×10^{-6}		
8450mV	-1.005V	25.0	0.228×10^{-6}	109.0×10^3	0.40	0.044	1.01×10^{-6}		
8950mV	-1.000V	11.5	0.11×10^{-6}	104.5×10^3	0.40	0.044	1.05×10^{-6}		
9900mV	-0.974V	15.0	0.11×10^{-6}	136.4×10^3	0.40	0.044	8.1×10^{-7}		
11,240mV	-0.970V	16.5	0.11×10^{-6}	150.0×10^3	0.40	0.044	7.33×10^{-7}		
11,690mV	-0.960V	17.0	0.11×10^{-6}	154.5×10^3	0.385	0.044	7.38×10^{-7}		
12,980mV	-0.962V	19.0	0.11×10^{-6}	172.7×10^3	0.382	0.044	6.67×10^{-7}		
14,360mV	-0.955V	21.5	0.11×10^{-6}	195.5×10^3	0.382	0.044	5.88×10^{-7}		
15,580mV	-0.938V	24.0	0.11×10^{-6}	218.0×10^3	0.382	0.044	5.28×10^{-7}		

(B-182)

Capacitance measured by pulse technique at various time intervals
for crystal bar Zr Corroded in 0.05 M K_2SO_4 + 250 ppm O_2 at $238^\circ C$

TABLE 2. at open potential

Surface Area of the Specimen = 4.51 cm^2

Time	C (farads)	$\frac{1}{C} \propto X_T$	$(\frac{1}{C})^2$							
30 min	11.0×10^{-6}	9.09×10^4	82.6×10^8							
85 min	10.1×10^{-6}	9.9×10^4	98.0×10^8							
140 min	9.73×10^{-6}	10.3×10^4	1.06×10^9							
210 min	9.03×10^{-6}	11.1×10^4	1.23×10^9							
1160 min	3.75×10^{-6}	26.7×10^4	7.13×10^{10}							
1640 min	2.85×10^{-6}	35.1×10^4	12.3×10^{10}							
4260 min	1.93×10^{-6}	51.8×10^4	26.8×10^{10}							
5530 min	1.80×10^{-6}	55.6×10^4	30.9×10^{10}							
6040 min	1.73×10^{-6}	57.8×10^4	33.4×10^{10}							
7060 min	1.63×10^{-6}	61.2×10^4	37.4×10^{10}							
7490 min	1.57×10^{-6}	63.7×10^4	40.6×10^{10}							
8460 min	1.46×10^{-6}	68.5×10^4	47.0×10^{10}							
8950 min	1.405×10^{-6}	71.1×10^4	50.5×10^{10}							
9900 min	1.32×10^{-6}	75.8×10^4	57.5×10^{10}							
11,240 min	1.275×10^{-6}	78.4×10^4	61.5×10^{10}							
11,690 min	1.227×10^{-6}	81.5×10^4	66.5×10^{10}							
12,980 min	1.14×10^{-6}	86.2×10^4	74.4×10^{10}							
14,360 min	1.125×10^{-6}	88.9×10^4	79.0×10^{10}							
15,580 min	1.07×10^{-6}	93.4×10^4	87.2×10^{10}

Fig. 1. Equipment for Electrochemical Measurements at High Temperature and Pressure.

ORNL-DWG 63-4910

Fig. 2. Titanium Reaction Cell.

ORNL-DWG 63-4911

Fig. 3.

Galvanostat or Potentiostat can be connected at A,B,C.

If switch D is closed ($\pm$ polarity) and relay E is closed, then part of potentiostat current will flow thru pulse circuit, demanding more current for polarization of Z_r to proper potential.

$$(E_{Z_r} - E'_{pt}) - E_{Ref.} = \epsilon \sim 0.0 \text{ Volts}$$

Fig. 3a.

G-122

Fig 4(a) Current-voltage measurements for crystal bar Zr (Corrosion temperature 238°C)

Corroded in 0.05M K_2SO_4 + 250 psig O_2 at open potential

(Galvanostatic Measurement)

○ Exptl cathodic current

◇ Calculated — do —

□ Exptl Anodic current

△ Calculated — do —

Corrosion Time = 30 minutes

Specimen }
Surface Area } = 4.5 cm²

G-122

ORNL DWG. 67-4454

Fig 4(b) Current-Voltage measurements for crystal bar Zr (Corrosion Temp 238°C)

Corroded in 0.05M K_2SO_4 + 250psig O_2 at open Potential

(Corrosion Time 120 minutes)

(Galvanostatic Measurement)

AREA = 4.5 cm²

(5129)

Fig 4(c) Current-Voltage measurements for crystal bar Zn (Corrosion Temperature = 238°C)

Corroded in 0.05M K_2SO_4 + 150 psig O_2 at open Potential
(Galvanostatic Measurement)

○ Experimental Cathodic Current

⊖ Calculated Cathodic Current

□ Experimental Anodic Current

⊕ Calculated Anodic Current

Corrosion Time 1150 minutes

AREA = 4.5 cm²

(6-122)

ORNL DWG. 67-4457

(G-122)

Fig 44

ORNL DWG. 67-4458

Fig(5)

Current-voltage curve for crystal bar Zn in (0.05M $\text{H}_2\text{SO}_4 + 0.05\text{M O}_2$) at 20°C (galvanostatic Measurement)

ORNL DWG. 67-4459

6-107

Current-Voltage curve for crystal bar Zn in $(0.05 \text{ M K}_2\text{SO}_4 + 0.05 \text{ M O}_2)$ at 204°C . (potentiostatic measurement)
 [After corroding at a constant potential of 0.00 V vs Pt/O_2 electrode in the same solution at 55°C for 10,000 minutes;

Fig 6

- Exptl Cathodic Current
- — — anodic current
- Relatd Cathodic Current
- — — Anodic Current

x (Total Thickness of the film $\sim 850 \text{ \AA}$)

ORNL DMC 67-4460

[Anodic Polarization studied upto 8.0 V vs Pt/O_2 (45°C)

α_{Zn} up to 0.7 V vs $\text{Pt}/\text{O}_2 = 0.052$

α_{Zn} from 0.7 V to 4.0 V vs $\text{Pt}/\text{O}_2 = 0.039$

α_{Zn} from 4.0 V to 8.0 V vs $\text{Pt}/\text{O}_2 = 0.031$

G-1230

Crystalline Zn, corroded in 0.05M K_2SO_4 + 250 psig O_2 at 238°C (OPEN POTENTIAL)

Fig 7

$(\frac{1}{2})^2$ Vs Time (minutes) ; Surface area of the Specimen = 4.51 cm²

ORNL DWG. 67-4461

ORNL DWG. 67-4462

Corrosion Rate (v) Vs time (t)

Crystalline Zn in 0.05M K_2SO_4 Solution + 250 psig O_2 Film growth is at Constant anodic Potential 0.00V, Vs Pt/ O_2

• At 20°C
 • At 22°C
 • At 24°C

Fig 8

6-104

Fig 9(a) crystal bar zr Corroded in 0.05 M K_2SO_4 + 250 psi O_2
 at constant anodic Potential 0.00V vs Pt/ O_2 (SSCC)
 (Total thickness x_T vs Reciprocal Capacitance)

(G-114)

Fig. 9(4)

ORNL DWG. 67-4464

(G₂-115)

ORNL DWG. 67-4465

Fig: 10

Dielectric constant vs Temperature
crystal lean Zn film grown in 0.05M K_2SO_4 at constant anodic potential 0.00V vs Pt/O_2 .

(That with this Zn film measured at 100Hz)

ORNL DWG. 67-4466

6-105 2042

current-voltage measurement as a function of film thickness

Crystal has Zr , $0.05 M K_2SO_4 + 2SDP$, gC_2
 film grown at constant anodic potential
 $2.20 V$ vs Pt/O_2

Fig 12 (a) Temperature $204^\circ C$
 Specimen Area = 5.0 cm^2

ORNL DWG. 67-4668

G-119

Fig. 12 (b) Temperature 22°C

Specimen Surface Area = 4.6 cm²

ORNL DWG. 67-4469

220°C

5-116-1007

Fig. 12 - (c) Temperature = 240°C

ORNL IMG. 67-4470

Fig 13(a)

Activation Energy Plots for crystal layer 2v corroded in 0.05M $K_2SO_4 + 250 \mu g/l$ at constant potential

Constant molar potential $\phi = 0.057$ V. Pfl.

ORNL DWG. 67-4471

6-105

Fig B(6)

ORNL DMG. 67-4472

G-105

Fig 13(e)

ORNL DWG. 67-4473

(Cn 122) Fig(14): Activation Energy plot for X-line Zn generated at open-circuiting

[After 13580 minutes]

ORNL DWG. 67-4475

REFERENCES

1. "Thin Film Formation on Zirconium," by R. E. Meyer, J. Electrochem. Soc., 106 (1959) p. 930.
2. "Cathodic Processes on Passive Zirconium," by R. E. Meyer, J. Electrochem. Soc., 107 (1960) p. 847.
3. "Electrochemical Measurements on Zr and Zr-2," A. L. Bacarella, J. Electrochem. Soc., 108 (1961) p. 331.
4. "Electrochemical Measurements on Zr and Zr-2," A. L. Bacarella, J. Electrochem. Soc., 112 (1965) p. 546.
5. "Anodic Film Growth on Zr at Temperatures from 200° to 300°C," A. L. Bacarella and A. L. Sutton, Electrochem. Tech., 4, (1966) p. 117.
6. "Reduction of Oxygen on Passive Zirconium," R. E. Meyer, J. Electrochem. Soc., 110 (1963) p. 167.
7. "Anodic Film Growth on Zr at Elevated Temperatures," A. L. Bacarella, H. S. Gadiyar and A. L. Sutton, ORNL-4076 (1967) p. 58.
8. "Ionic Currents in Thin Films on ZrO₂," A. Charlesby, Acta Metallurgica, 1, (1953) p. 340.
9. "The Influence of Anodic Oxide Films on the Thermal Oxidation of Zr," J. J. Polling and A. Charlesby, Acta Metallurgica, 2 (1954) p. 667.
10. "Analysis of the Formation Current in Electrolytic Oxidation of Zr," Proc. Phys. Soc. (London), 67B (1954) p. 201. J. J. Polling and A. Charlesby.
11. "Oxidation Potentials," W. M. Latimer, p. 271, Prentice-Hall, N. Y. (1952).
12. "Theory of Oxidation of Metals," N. Cabrera and N. F. Mott, Repts. Prog. Physics 12, (1948-49) p. 163.
13. "Anodic Oxide Films," L. Young, Academic Press, London, New York (1961).
14. "Steady-State Kinetics of Formation of Anodic Oxide Films on Ta in Sulfuric Acid," L. Young, Proc. Roy. Soc., Series A, 258 (1960) p. 496.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

DISTRIBUTION

1. A. L. Bacarella
2. E. G. Bohlmann
3. G. E. Boyd
- 4-6. H. S. Gadiyar
7. W. R. Grimes
8. G. H. Jenks
9. H. G. MacPherson
10. M. J. Skinner
- 11-12. Central Research Library, DC
13. Y-12 Technical Library, DC
- 14-18. Laboratory Records
19. Laboratory Records, ORNL-RC
- 20-34. DTIE, AEC
35. Div. Research and Development, ORO