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STUDIES ON THE ANODIC POLARIZATION OF
ZIRCONIUM—GROWTH RATES AND THICKNESSES
OF THE VERY THIN ANODIC OXIDE FILMS

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Studies on the Anodic Polarization of Zirconium -
Growth Rates and Thicknesses of the Very Thin Anodic Oxide Films

by

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Introduction

In a recent communication¹ the present authors have described the potential-time curve obtained with zirconium when this metal is anodized at constant current strength in certain aqueous electrolytes. This curve can be divided into three branches (Figure 1). With a freshly abraded specimen there is initially a rapid rise in potential with a rate of change which decreases until a constant value is reached (branch AB)⁺. This constant rate is then maintained until the potential has risen sufficiently for oxygen evolution to occur. At this time the rate drops abruptly to a very low value, which gradually increases over a long time interval (branch BC). During this period visible, localized gas evolution takes place. Finally, after an interval of time depending upon the current being passed, the potential rises at an accelerated rate and quickly attains a constant value, which is lower than that of branch AB; this rate is then maintained as the

⁺ The initial curvature in branch AB is apparent only at current densities of about $10\mu\text{A}/\text{cm}^2$ or less. Its significance has been explained previously.

potential climbs steadily to a hundred volts, or more (branch CD). The maximum voltage then attainable is limited only by the breakdown potential of the film.

With varying current density the potential-time curves change as shown in Figure 1; with very high current densities the flat branch is undetectable by our means of measurement, and with very low current densities the upper branch is not reached. The length of the branch BC and the slope of the branch CD are both highly dependent upon the oxygen concentration in the solution. Increasing concentrations of oxygen in the electrolyte shorten the flat branch and increase the slope of the upper branch but do not affect the slope of the lower branch. A change in the electrolyte does not affect the qualitative pattern of the curves, but may change certain parameters which can be quantitatively derived from them. An important exception is that of electrolytes containing halide ions in concentrations of .001 M or greater: in this case a stable horizontal branch occurs at a potential below that of the branch BC.

Previous workers have investigated the properties of the oxide film formed along this second steep branch of the curve, where both oxide film building and oxygen evolution occur together. The most recent work has been done by Charlesby² who determined the capacitance of the oxide film as a function of the formation voltage at constant current, the refractive index of the film, its optical thickness as a function of the formation voltage, and the voltage-time curves at constant current. From these measurements he was able to evaluate the formation field, the film thickness for a

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given formation voltage and the efficiency of the film building process. He showed that this efficiency never exceeds fifty percent for current densities up to 2 milliamp. per cm^2 , indicating that the electron current through the film giving rise to oxygen evolution was of the same order of magnitude as the ionic or film building current. This work confirmed that of Guntherschulze and Betz³ in showing that the anodic film growth follows the empirical law

$$I_+^0 = A_+ \exp(B_+ F) \quad (1)$$

between the true ionic current density I_+^0 and the electrostatic field F across the film. Charlesby re-evaluated the electrolytic parameters A_+ , and B_+ , and the field F , using a better value for the dielectric constant of the oxide than that employed by Guntherschulze and Betz. All of his work was done with oxide films sufficiently thick to show interference colors, the thicknesses varying from several hundreds, up to several thousands of Angstroms.

From simple kinetic considerations, Mott⁴ has obtained an equation of the form of (1) for the ionic current causing primary oxide film growth on metals, based upon the assumption that at high fields the rate determining step in the growth of the oxide film is the transfer of metal ions from the metal across a barrier existing at the metal-oxide interface into interstitial positions in the oxide. He assumes that at high fields equilibrium is not established for the movement of metal ions in the forward and reverse directions across the barrier, and the derivation is carried out on the premise that the

oxide film is so thin that the effect of any space charge built up by metal ions dissolving in the oxide film in the course of its formation is negligible. On this basis, the parameters A_+ and B_+ can be evaluated in terms of the barrier height and of certain physical properties of the metal and oxide. This film building mechanism should be valid for the primary growth of oxides on metals in air resulting from the field set up across the oxide film due to acceptor levels created by the adsorption of oxygen on the oxide-air interface, as well as for the growth of thin oxide films formed by anodization in an electrolyte. Below a certain critical temperature, the oxidation of the metal in air or in an aqueous electrolyte, due to this intrinsic field, will proceed only until a limiting oxide film thickness, generally of less than 100 Angstroms["], has been built up; it will effectively stop when the intrinsic field has been decreased sufficiently to raise the effective barrier height, thereby greatly reducing further passage of metal ions across the metal-oxide interface.

It would thus seem that, in order properly to evaluate the electrolytic parameters A_+ and B_+ and their variation with temperature as a test of the Mott theory or for the purpose of studying the early stages of the oxidation process, it would be preferable to work with oxide films which are less than 100 Angstroms["] in thickness. Indeed, as Cabrera and Mott⁵ point out, recent experimental work would indicate that at sufficiently low temperatures it is probable that the primary growth of oxide films formed on all readily

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oxidizable metals is governed by this same barrier mechanism. The oxidation of aluminum, zirconium, titanium, zinc, chromium, tungsten and many other metals follows this type of law at room temperature, while copper, iron, barium and other metals show the same behavior at liquid air temperatures. Oxidation is very rapid at first, but it then drops off to low or negligible values, with the formation of a stable oxide film 20 to 100 Å in thickness.

Films thicker than 200 Å can be studied accurately by capacitance measurements, but for the thin films produced in the narrow range of potentials along the branch AB of the potential time curve this method cannot be employed without some uncertainty, as Young⁶ has indicated. These very thin films can be studied easily by following the change in the potential of the electrode surface with time, and the aim of the present research was to study the growth of these thin films over a potential range in which they exist, i.e., in the lower branch of the potential-time curve. Interpretation of the results is greatly simplified by the fact that, for zirconium, the current efficiency of the film building process is unity below oxygen evolution potentials. The principal uncertainty in quantitative interpretation along the lines of the Mott theory lies in the assumption that the density of these very thin films is that of the oxide in bulk. However, this assumption seems no worse than that of a dielectric constant of very thin films identical to that of the thicker films showing interference colors; this assumption would be necessary if capacitance measurements were extended to the low potential range.

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In what follows, a method is worked out for obtaining the parameters A_+ and B_+ from potential-time measurements taken along the first branch of the curve. Two equations are derived from (1) and two sets of experiments were carried out to test the validity of these equations.

The Rate of Change of Potential at Constant Current

Introducing the apparent ionic current density, calculated from the projected area of the electrode, $I_+ = \sigma I_+^0$ (microamperes/cm², $\mu\text{A}/\text{cm}^2$) where σ is the roughness factor for the electrode surface, and identifying the ionic current with the total anodic current I (in the absence of electron current), (1) becomes:

$$I = \sigma A_+ \exp(B_+ F) \quad (2)$$

Let:

X_0 be the oxide film thickness on the electrode before anodization is begun;

r the volume of oxide formed per microampere minute (3.36×10^{-9} cm³/ μA min.), assuming, with Charlesby², that the oxide formed has a density of 5.7;

X the film thickness at time t built up by anodization, with

$$X = X_0 + r \int_0^t I/\sigma \, dt;$$

E the potential drop across the film at time t (millivolts, mv).

We then have

$$F = E/X = (1/B_+) \ln (I/\sigma A_+) \quad (3)$$

and

$$E = (r/B_+) \left[\int_0^t (I/\sigma) \, dt \right] \ln (I/\sigma A_+) + (X_0/B_+) \ln (I/\sigma A_+) \quad (4)$$

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For I and σ constant in time.

$$\left(\frac{\partial E}{\partial t}\right)_{I, \sigma} = (rI/\sigma B_+) \ln (I/\sigma A_+) \quad (5)$$

Designating by R_I and calling unitary rate at apparent current density I , the ratio

$$R_I = 1/I \left(\frac{\partial E}{\partial t}\right)_{I, \sigma}$$

we have

$$R_I = (r/\sigma B_+) \ln I + (r/\sigma B_+) \ln (1/\sigma A_+) \quad (6)$$

Potential-time measurements can be obtained for the film building process at constant polarizing current after the local anodic current has decayed to a negligible value (i.e. along the linear portion of branch AB, Figure 1). If $(\partial E/\partial t)_{I, \sigma}$ remains constant in time, it can be assumed that σ is also constant in time. If this is true, if equation (1) is valid for thin films, and if σ is independent of I , a plot of the unitary rate vs. $\ln I$ should give a straight line. From the slope S of this line (mV cm²/μA min.)^{and} its intercept H (mV cm²/μA min.) we obtain

$$B_+ = r/S\sigma \quad (7)$$

$$\ln (1/\sigma A_+) = H/S \quad (8)$$

Experiments at Constant Current

Equation (6) has been tested experimentally for zirconium in ammonium borate and sodium carbonate solutions and it was found that σ is constant with time and that R_I is linear with $\ln I$.

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In Figure 2 a sample run is shown, where a plot of R_I vs. time and vs. potential indicates the constancy of the unitary rate after the local anodic current has become negligible. In Figure 3 the linearity of the plots of the unitary rate vs. $\ln I$ is evident. Each point is the mean value of five determinations, and the vertical bars mark off the probable errors. The lines were drawn on the basis of the method of least squares. The mean values of the constant rates for a given current density for borate and carbonate solutions are reported in Table I, together with the values of A_+ , B_+ , and F/σ derived therefrom.

Comparison with Previous Work

The results obtained in borate solution at 200° C may be compared directly with those of Charlesby², which were obtained from measurements taken on much thicker films over a potential range of 10 to 100 volts and higher. His work was one at 18° C.

Line (a) of Figure 1 has a slope S of 1.69 and an intercept H of 7.68.

From (3), (7) and (8):

$$B_+ = 4.6 \times 10^{-9} \text{ cm/mV} \quad A_+ = 2.9 \times 10^{-5} \mu\text{A/cm}^2 \quad F/\sigma = 3.29 \times 10^{-9} \text{ mV/cm}$$

at $100 \mu\text{A/cm}^2$

Charlesby reports a B_+ value of 3.4×10^{-9} , and A_+ value of 1.6×10^{-5} , and an average value for F of 4.5×10^9 at $100 \mu\text{A/cm}^2$. These values include a roughness factor, which Charlesby takes as essentially unity.

If this evaluation is correct, we have, designating Charlesby's values by the subscript Ch:

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$$\frac{\sigma_{B_+}}{(B_+)_{Ch}} = 4.6/3.4 = 1.35; \frac{\sigma_{A_+}}{(A_+)_{Ch}} = 2.9/1.6 = 1.8$$

$$\frac{F_{Ch}}{F/\sigma} = 4.5/3.3 = 1.35,$$

and, for agreement we are led to assuming a roughness factor of about 1.4 for the surface of our abraded specimens after the unitary rate has decreased to its limiting value. The third ratio is independent of the other two because F_{Ch} was determined from capacitance measurements, which were not directly related to A_+ and B_+ . The second check does not carry the same weight as the others because of the large uncertainty involved in evaluating A_+ , due to its exponential relationship with the field.

The value of 1.4 thus deduced for the roughness factor of the surfaces of our abraded specimens after anodization to negligible local current has been substantiated further. The roughness factor for the freshly abraded specimens, prior to immersion, was found to be 2.1 ± 0.2 , using a small-volume gas adsorption apparatus with krypton gas as adsorbate⁺. The actual roughness, however, should decrease as the oxide film builds up on the abraded surface. This has been shown by comparing the unitary rates for highly polished electrode surfaces with those for abraded surfaces. The average unitary rate for a highly polished zirconium electrode surface is just forty percent higher than the unitary rate for an abraded surface, which again would indicate that, if the roughness factor for the polished

⁺ Determinations of roughness factors were made for us by Mr. Ralph J. Brodd through the courtesy of Professor Norman Hackerman, University of Texas, Austin, Texas.

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electrode surfaces was very nearly unity, as Young⁶ claims for Ta, the roughness factor for the abraded surfaces after preanodization to a constant rate would then be about 1.4.

A final check with Charlesby's results can be made independently of an assumed roughness factor. The product $B_r F$ is dimensionless. For a current density of $100 \mu\text{A}/\text{cm}^2$ this product is $4.6/\sigma \times 3.3\sigma = 15$, from our measurements. If F is extrapolated to $1000 \mu\text{A}/\text{cm}^2$, using (2), this product becomes 17.6. Charlesby gives a value of 17 for this product, but does not state the corresponding current density. Much of his work, however, was done at current densities in the range 500 - $1000 \mu\text{A}/\text{cm}^2$. The agreement seems satisfactory, in as much as the comparison was made between zirconium specimens which differed somewhat in chemical composition.

Current Efficiency of Oxide Formation in the Low Potential Range.

The agreement with Charlesby's work is of course entirely based on the assumption of unit current efficiency for oxide formation below the potentials for oxygen evolution. The fact that agreement with his work was obtained is a point in favor of this assumption; another is the fact that the only reaction thermodynamically possible below the reversible potential for oxygen evolution is the oxidation of zirconium. Another point, is that when the potential-time measurements are being taken, the constant rate drops abruptly soon after the reversible potential for oxygen evolution is reached, showing that a second reaction is then starting (Figure 2). Further evidence for unit efficiency in the low potential range accrues from unitary rate

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measurements which have been obtained for the steep branch of the potential-time curve above 2 volts, where oxide film formation and oxygen evolution occur simultaneously. It has been found that the concentration of oxygen in the solution affects the unitary rate very noticeably. Thus, in borate solution at 20.0° C, increasing the oxygen concentration from its value in a nitrogen saturated solution to that in an oxygen saturated solution causes an increase in the unitary rate of some 20 percent. This is in the direction to be expected for an oxygen electrode. However, when the same experiment was repeated in the low potential range, no difference in rate was observed between a nitrogen saturated and an oxygen saturated solution. This result would be expected if the current efficiency for oxide formation was, in fact, unity in the low potential range.

An important consequence of these results is that, for zirconium at least, one must specify the actual oxygen concentration of the solution in which efficiency measurements are carried out, since otherwise the results have little meaning.

Correlation with our Previous Work

As we have shown recently¹, the experimental results from potential-time measurements on zirconium at constant current carried out along the low-potential branch of the potential-time curve can be formulated as

$$\left(\frac{\partial E}{\partial t}\right)_I = AI^B \quad (9)$$

where $(\partial E/\partial t)_I$ is the limiting value of the rate corresponding to the apparent current density, I . Here, A and B are empirical constants.

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In Figure 4, the same data used in constructing Figure 3 are shown as a log-log plot of the variables in (9). The straight lines were drawn on the basis of the method of least squares. Table II contains the mean rate values and ~~their probable errors, as well as~~ the values of the constants A and B of equation (9).

Equation (9) can then be considered as a good approximation to the theoretical relationship (6), in the current density range 1 to $100 \mu\text{A}/\text{cm}^2$.

It can easily be shown that the empirical constant A can be written as

$$A \approx H = (r/\sigma B_+) \ln (1/\sigma A_+)$$

and that

$$B \approx 1 + \ln (S/H+1) = 1 + \ln \frac{\ln 1/\sigma A_+ + 1}{\ln 1/\sigma A_+}$$

These two conditions are fulfilled to within one percent of accuracy.

For extrapolation to current densities other than those for which rates are measurable, equation (6) must be used. This is shown in Table III which gives a comparison between (6) and (9) for the borate data.

However, (9) is of a form which lends itself more readily to the estimation of local currents from potential-time measurements in the manner outlined previously¹.

It may be pointed out that a comparison of A values obtained for different electrolytes cannot properly be made except for identical values of B, since these parameters are not independent.

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Change in Potential with Change in Current at Constant Film Thickness

The validity of the relationship expressed in (1) can be tested by another approach. Equation (3) may be written:

$$E = X/B_+ \ln I + (X/B_+) \ln (1/\sigma A_+) \quad (11)$$

When an external anodic current flows in the polarizing circuit between the zirconium anode and an auxiliary cathode, the potential measured in the tensiometric cell, zirconium - S. C. E., will be

$$E' = E + K$$

where K is the constant sum of all potential differences in the chain other than that across the oxide film.

Hence

$$E = (X/B_+) \ln I + (X/B_+) \ln (1/\sigma A_+) + K \quad (12)$$

Now, for an experiment carried out at constant film thickness, a plot of the measured potential vs. $\ln I$ should give a straight line.

This has been done, and the linearity is indicated by the straight lines of Figure 5. ~~The points shown were obtained in the following way:~~ Points such as those shown are obtained as follows:

After the freshly abraded zirconium electrode has been polarized at constant current density I_1 to give a value of $(\partial E/\partial t)_I$ which is constant with time, the current density is increased abruptly to another value I_2 by short circuiting a resistor in the polarizing circuit. The potential rises rapidly, passes through a maximum, and then a minimum value, before settling down to another fixed rate of change with time. This behavior is shown in Figure 6, where E'_1 is the value of the potential at time t_0 when the current density I_1 is suddenly increased to a value I_2 . E'_2 is the value of the potential

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as it passes through its minimum before attaining a new steady rate.

If I_2 is large enough, the maximum and minimum merge together to give only a momentary stop before the rate reaches its new value.

Now E'_1 corresponds to the potential drop across the film of thickness X_1 at current I_1 , and E'_2 corresponds to the potential drop across the same film of thickness X_1 at current I_2 (neglecting the small increase in film thickness occurring between the change in current and the new potential readings). Now another run is begun with a freshly abraded electrode surface at a constant polarizing current density of value I_2 , and the potential is followed until it reaches the value E'_2 . At this time the film will have again reached the thickness X_1 ; the current density is now increased abruptly, as before, to a new value I_3 with a potential value E'_3 corresponding to the potential drop across the film necessary to pass current I_3 through the thickness X_1 . Again, starting with current density I_3 and E'_3 being reached, the current is increased to I_4 and a value of E'_4 is determined, and so on. The above values of $E'_1, E'_2 \dots$ are plotted against those of $\ln I_1, \ln I_2 \dots$ and a straight line should be obtained if (2) is correct.

This method has been tested experimentally in ammonium borate at 20.0°C and the results are shown in Figure 5. Tables IV contains the data from which lines (a), (b) and (c), respectively, were constructed. Duplicate runs were generally found to be sufficient because of the good reproducibility of the data.

The linearity indicated in (12) is thus experimentally established

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and this in itself is further evidence for the validity of (1). Since the linearity indicated in (1) has already been verified by experiment, the linearity of the curves in Figure 5 can be considered as a check on the experimental procedure just outlined, and we may conclude that this procedure does, in fact, give potential increments corresponding to current increments at constant film thickness.

The most important conclusion from (12) is that the oxide film thickness should be given by:

$$x = L (B_+) \quad (13)$$

where L is the slope of the line. From Figure (5(a)) we obtain an apparent film thickness x_a of 45.7 Å. Referring to Table IV, it is seen that this apparent oxide film thickness is that formed on a freshly abraded electrode anodized at $3.85 \mu\text{A}/\text{cm}^2$ to a potential of -358 mV vs. the saturated calomel electrode. Similarly, from the slope of line (b) an apparent oxide film thickness of 52.7 Å is obtained, and it is seen that this apparent thickness is attained by anodizing a freshly abraded electrode to a potential of -159 mV at $3.85 \mu\text{A}/\text{cm}^2$. The slope of line (c) gives an apparent thickness of 59.5 Å obtained by anodizing a freshly abraded electrode at $3.85 \mu\text{A}/\text{cm}^2$ to a potential of 41 mV.

Thus, increments in potential of 199 and 200 mV at $3.85 \mu\text{A}/\text{cm}^2$ represent increases of 7.0 and 6.8 Å, respectively, in apparent film thickness.

This increase in apparent thickness can be checked quantitatively. At $3.85 \mu\text{A}/\text{cm}^2$ the unitary rate is $8.63 \text{ mV cm}^2/\mu\text{A min.}$ (Table I);

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the time required for the potential to increase by 200 mV at this current density is $200/(3.85 \times 8.63) = 6.02$ minutes, or 23.2 micro-ampere minutes. This is equivalent to $23.2 \times 3.36 \times 10^{-9}$ cm or $7.7 \text{ \AA}$ in apparent thickness. This check is independent of the actual value of the roughness factor; the actual thickness is given by the ratio of the apparent thickness to the roughness factor.

It should be pointed out that each of the lines (a), (b), (c) of Figure 5 is actually an anodic polarization curve at constant oxide film thickness. It is evident that the lines become steeper with increased film growth.

It is interesting to note that the ratio of the unitary rates at two different current densities, I_1 and I_2 is, from (6):

$$R_2/R_1 = \frac{r/\sigma B_+ \ln(I_1/\sigma A_+)}{r/\sigma B_+ \ln(I_2/\sigma A_+)} = \frac{\ln(I_1/\sigma A_+)}{\ln(I_2/\sigma A_+)}$$

The ratio of the ordinates of lines (b) and (a) in Figure 5 at the same current densities I_1 and I_2 is:

$$\frac{E_2^b - E_2^a}{E_1^b - E_1^a} = \frac{X_b - X_a}{X_b - X_a} \frac{1/B_+ \ln(I_2/\sigma A_+)}{1/B_+ \ln(I_1/\sigma A_+)} = \frac{\ln(I_2/\sigma A_+)}{\ln(I_1/\sigma A_+)} = R_2/R_1$$

Thus, an experimental verification of the equality of the first and last ratios should provide a check on the internal consistency of the two methods.

From line (a), Figure 5

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$$\frac{R_{\log I=0.5}}{R_{\log I=1.5}} = 0.834; \quad \frac{R_{\log I=1.0}}{R_{\log I=1.5}} = 0.916; \quad \frac{R_{\log I=2.0}}{R_{\log I=2.5}} = 1.083$$

and from the three lines in Figure 5, taking the average value of the vertical distance between lines, (since $X_b - X_a - X_c - X_d$)

$$\frac{(E')_{\log I=0.5}}{(E')_{\log I=1.5}} = 0.834; \quad \frac{(E')_{\log I=1.0}}{(E')_{\log I=1.5}} = 0.925; \quad \frac{(E')_{\log I=2.0}}{(E')_{\log I=1.5}} = 1.075$$

The difference is within the 1 - 2 percent error in the determination of the unitary rates.

This agreement serves as a check on the validity of the experimental procedure used in constructing Figure 5, especially in the selection of the minimal values of the increased potential resulting from abrupt increases in polarizing current (E'_2, E'_3 as sketched in Figure 6).

Discussion

From Figure 1 and Table I it is evident that the values of A_+ , B_+ and F for ammonium borate are significantly different from the corresponding values for sodium carbonate solution. The inequality is larger than can be accounted for by the five degree temperature difference between the two sets of measurements. This inequality must be due mainly to specific effects of the electrolytes themselves. Any such effect should manifest itself at the oxide-solution interphase.

A possible explanation for the observed difference is that preferential adsorption of either positive or negative ions on the oxide film surface occurs, and that this modifies the

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electrostatic field across the film. Preferential adsorption of a positive ion should decrease the field and preferential adsorption of a negative ion should increase it above its value for an adsorbed layer containing equal numbers of positive and negative ions. Young⁶ has suggested a similar mechanism to account for the increased film growth observed on tantalum irradiated with ultra violet light.

Alteration of the field by this preferential adsorption mechanism would then cause a change in the parameters A_+ and B_+ . Since A_+ is related exponentially to the field, a small change in F would be accompanied by an order of magnitude change in A_+ .

Another tentative explanation might lie in the ability of small pores through the thin oxide film to reduce the effective electrostatic field built up across the film; it might be expected that pores filled with a strong electrolyte such as sodium carbonate would reduce the field to a greater extent than when filled with a weak electrolyte such as the borate solution used in our work.

It is hoped that experiments to test the effects of surface-active anions and cations and of other strong and weak electrolytes on the unitary rate, and experiments on the variation of the unitary rate with electrolyte concentration, will elucidate this question.

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Experimental

Polarizing Circuit and Cell: This apparatus has been described previously¹.

Preparation of Metal Electrodes: Coupons were cut from 0.070 inch zirconium sheet in the shape of square electrodes with extensions for electrical connections. These were completely covered with an impervious baked coating of enamel. The enamel was then ground away from one face of the electrode to leave a projected area of 2.6 cm². Prior to each run the exposed face of the electrode was abraded with 0, 2/0 and 3/0 emery cloth, using a standardized procedure.

Analysis of Electrode Specimens: The work reported here has been done on a sample of hafnium-free zirconium prepared by the Kroll process, designated by the code number WA-3983, and having the following analysis:⁺

Al	20	Cu	50	Ni	20	V	50
B	0.3	Fe	600*	O ₂	1650*	Zn	< 50
C	370*	Mg	10	Pb	30	Hf (estimated)	< 300
Cd	0.5	Mn	10	Si	100		
Co	10	Mo	10	Sn	500*		
Cr	< 5	N ₂	70*	Ti	50		

All figures are in parts per million. The values marked with an asterisk were determined chemically, the others were determined spectroscopically.

⁺ We appreciate the cooperation of Dr. Earl T. Hayes, Chief Physical Metallurgy Branch, Bureau of Mines, Albany, Oregon, in supplying us with this analysis.

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This metal is 10-20 percent cold worked with a hardness of Rockwell B 68 to 81.

Solutions: All solutions were made up from A. R. salts and distilled water. The ammonium borate solution was prepared by saturating distilled water with boric acid at 20.0° C. Ammonia gas was bubbled through the solution until the pH reached a value of 8.0.

All results reported here were obtained with air saturated solutions, unless otherwise stated.

Potential-time Measurements at Constant Current: Runs were always begun within three minutes of the completion of the abrasion operation. All potentials were measured against the saturated calomel electrode (S.C.E.). The polarizing current was maintained constant by manual control. Measurements of current, potential and time, as well as current control, were all carried out with an accuracy of one percent or better. The range of current densities employed was from 1 - 100 $\mu\text{A}/\text{cm}^2$ and the potential ranged from -1200 to +600 mV.

During anodization the potentials were recorded at given time intervals and the unitary rates calculated. The results for a single run are shown in Figure 2, where it is seen that, after a period of decreasing rate corresponding to the decreasing local current, there is a constant rate period which terminates when potentials are reached for which a second reaction, the oxidation of hydroxide ion, is possible. The rate then decreases because the current efficiency for the film building process is no longer unity. In order to avoid inclusions of portions of the first and last branch/ of this curve in the constant

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rate, the two values nearest -200 mV were averaged to give the unitary rate to be used in equation (6). The scatter in the five individual runs taken at each current density is higher than would be expected from the accuracy in the basic measurements. This scatter is probably due to differences which exist in the abraded electrode surfaces in one run compared to another⁺. However, with five individual runs taken per point the probable error is reduced to a value of 1 to 2 percent.

Potential Measurements at Constant Film Thickness.

The general procedure has been discussed above. It should be added, however, that large current increments at constant film thickness give potentials which fall low, compared to those obtained with smaller increments. Thus, it was found that, for a current range from 10 to 316 μA , steps of 10 to 31.6, 31.6 to 100 and 100 to 316 μA gave points which fell on the same straight line. When this current range was divided into four, five, or six increments, the resulting points all fell on the same straight line as that obtained with three increments. However, if this range was divided into one or only two steps, the resulting points fell low. A safe change of current density was found to be one for which $\Delta \log I \approx 0.5$.

Summary and Conclusion

Methods are described for making quantitative studies on the growth of very thin oxide films on zirconium, and for estimating the

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Recent experiments have been carried out which indicate that increased precision can be obtained by₂ pre-anodizing specimen electrodes at a current density of 0.1 $\mu\text{A}/\text{cm}^2$ for about 12 hours, until the same starting potential is reached before a run is begun. This improved technique, and the use of highly polished electrode surfaces should increase the overall precision of the method to one percent or better.

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film thickness as this growth progresses. These methods have been shown to be internally consistent and have been correlated with Mott's theory of metal oxidation. Experimental results so obtained have been found to be in agreement with previous work.

These methods should be readily adaptable to studies on the effect of temperature, ultra violet radiation, adsorption at the double layer, electrolyte, and metal composition and physical properties, on the ionic current causing oxide film growth.⁺

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Table I

Variation of Unitary Rate with Apparent Current Density

Solution	$\frac{I}{\mu A/cm^2}$	Log I	$\frac{R_I}{\frac{mV \cdot cm^2}{\mu A \cdot min.}}$	$\frac{B \cdot \sigma}{cm/mV}$	$\frac{A \cdot \sigma}{\mu A/cm^2}$	$\frac{F \cdot \sigma}{mV/cm}$
Ammonium borate 20.0° C	1.22	0.085	7.84±0.09			
	3.85	0.585	8.63±0.03			
	12.2	1.085	9.52±0.04	4.6x10 ⁻⁹	2.9x10 ⁻⁵	3.3x10 ⁹
	38.5	1.585	10.4 ±0.10			
	122.	2.085	11.2 ±0.06			
Sodium carbonate 25.0° C	1.22	0.085	7.43±0.08			
	3.85	0.585	7.99±0.02			
	12.0	1.078	8.70±0.04	6.0x10 ⁻⁹	0.20x10 ⁻⁵	2.9x10 ⁹
	37.5	1.575	9.33±0.07			
	118.	2.074	9.94±0.10			

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Table II

Variation of Log Rate with Log Apparent Current Density.Ammonium Borate -20.0° C.

Solution	Log I	Log dE/dt	A	B
Ammonium borate 20.0° C	0.085	0.98		
	0.585	1.52		
	1.085	2.06	7.77	1.08
	1.585	2.60		
	2.085	3.13		
Sodium carbonate 25.0° C	0.085	0.96		
	0.585	1.49		
	1.078	2.02	7.37	1.06
	1.575	2.54		
	2.074	3.07		

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Table III

Comparison of Unitary Rates as Calculated from
Equation 6 or from Equation 9. Ammonium Borate -20.0°C.

$I \mu A/cm^2$	$1/I \left(\frac{dE}{dt} \right) \frac{mVcm^2}{\mu A \text{ min.}}$ Equation (6)	$1/I \left(\frac{dE}{dt} \right)_I$ Equation (9)	Percent Difference
0.1	5.99 ⁺	6.64 ⁺	10.8
1	7.68	7.76	1.04
10	9.37	9.30	0.74
50	10.6	10.5	0.94
100	11.1	11.1	0.00
1000	15.7 ⁺	13.3 ⁺	15.3

⁺ By Extrapolation

Table IV

Variation of Potential with Apparent Current Density at
Constant Film Thickness. Ammonium Borate -20.0°C.

Log I	(a) E'	Log I	(b) E'	Log I	(c) E'
0.585	-358	0.585	-159	0.585	41.
1.015	-265	1.002	- 52.5	1.002	164.
1.585	-135	1.585	- 99.	1.585	334.5
2.139	0	2.129	252	2.129	505.5

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Fig. 1--Potential time curves for zirconium in air saturated ammonium borate solution at 20.0°C.

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Fig. 2--Unitary rate vs. potential and time for a single run at $12 \mu\text{A}/\text{cm}^2$. $1.0 \text{ M Na}_2\text{CO}_3$, air saturated, at 25.0°C .

Fig. 3--Unitary rate vs. log apparent current density for air saturated solutions; (a) ammonium borate, 20.0°C ; (b) sodium carbonate, 25.0°C .

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Fig. 4--Log rate vs. log apparent current density for air saturated solutions: (a) ammonium borate, 20.0° C; (b) sodium carbonate, 25.0° C.

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Fig. 5--Potential vs. log apparent current density at constant film thickness. Air saturated ammonium borate solution, 20.0° C.

(a) $\sigma X_a = 46 \text{ } \Omega$ (b) $\sigma X_b = 53 \text{ } \Omega$ (c) $\sigma X_c = 59 \text{ } \Omega$

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Fig. 6--Change in potential with change in current at constant film thickness. Air saturated ammonium borate solution, 20.0° C.

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