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ELECTRICAL RESISTANCE STUDIES OF ANODIC AND CORROSION OXIDE FILMS FORMED ON ZIRCONIUM

by

R. D. Misch

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R. D. Misch

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ELECTRICAL RESISTANCE STUDIES OF ANODIC AND CORROSION OXIDE FILMS FORMED ON ZIRCONIUM

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ABSTRACT

Oxide films were produced on zirconium and zirconium-titanium alloys by anodizing and by exposure to oxygen and to water at elevated temperatures. The films were then examined by using evaporated aluminum and the zirconium substrate as electrical contacts. Resistances were measured in air at room temperature and in vacuum at temperatures up to 290°C.

At room temperature in air, anodic films had higher resistivities than the corrosion films, but both were essentially insulators. Upon heating corrosion films in vacuum to 185 and 290°C, the resistances dropped, and the films became semiconducting. Above 300°C, the resistances began to show a slight drift which may be attributed to irreversible diffusion changes.

The resistances of the oxide films on zirconium alloys containing 0.05 w/o to 0.50 w/o Ti did not drop significantly with titanium content, although the corrosion rate increased rapidly in this range. Such films showed potential differences in both air and vacuum. The zirconium was positive with reference to the evaporated aluminum film. The potential differences remained during heating to 290°C in vacuum and were used to determine the resistance.

The potential differences were relatively independent of titanium content up to 0.5 w/o Ti. In a series of alloys containing 10 to 95 w/o Ti the film resistances were much lower and dropped as a function of titanium content. The potential differences were absent in most films on the high titanium alloys.

The results suggested very strongly that measurements isolated from the corrosion conditions did not reflect differences which had been present during corrosion. The resistances, potential differences, and even an induced charge effect were sufficiently sensitive to atmosphere and thermal history that the drastic change from heating in water or steam to heating in vacuum would account for a lack of correlation with corrosion resistance. It was concluded that measurements of the electrical properties of the corrosion films should be made during corrosion.

By anodizing zirconium, the corrosion rate could be lowered, but the effect was temporary. Evidently, anodic films on zirconium influenced the corrosion process only until the film had equilibrated with high temperature water.

INTRODUCTION

A. General

This report contains a description of various studies of the electrical resistance of oxide films on zirconium and zirconium-titanium alloys, and of the attempt to relate these measurements to corrosion resistance. The results did not fulfill original expectations, but are described here to serve as a basis for future investigation.

Conductivity is an important property because it can control the corrosion rate directly or indirectly. The oxide film on zirconium is known to be a poor conductor at room temperature. In compounds such as ZrO_2 the conductivity is often determined by traces of impurities.⁽¹⁾ It is reasonable to assume that various additives could influence zirconium corrosion by changing the conducting characteristics of the oxide.

Direct control of corrosion follows from the well-known picture of metal tarnishing in which ionic and electronic migration take place simultaneously. Ideally, oxidation will be controlled by whichever process is slower. If electronic conductivity controls the reaction, the influence of additives on this process will produce changes in corrosion rate.

Indirect control is possible according to the hydrogen mechanism of film damage.⁽²⁾ The effect of water in accelerating the scaling of many metals is attributed to the penetration of hydrogen into the oxide. A poorly conducting oxide will force hydrogen to be discharged at the metal-oxide interface, where the evolving gas can damage the film. A conducting oxide should reduce hydrogen penetration and damage.

B. Course Pursued in Study

The original objective was a comparison of film resistivity and corrosion rates, but certain properties of the film did not permit a simple measurement. Because the procedure was modified in the course of the work, the best presentation appears to be approximately chronological. The investigation followed the course presented below.

Anodic films were considered for investigation first because they can be produced under carefully controlled conditions. The results were unsatisfactory, and corrosion films were used subsequently. Of various contacts, aluminum applied by evaporation proved to be the most satisfactory.

After a brief examination of anodic films using a mercury contact, the room-temperature resistance of specimens with aluminum films was found to vary with voltage. Various zirconium specimens were then heated

in air, and the resistance was found to drop appreciably. The temperature was then raised further, and resistances were measured at temperatures comparable with the temperature of formation of the oxide films. At this time, a vacuum system was introduced to avoid possible reaction of the zirconium when heated. A series of titanium-zirconium alloys with corrosion films produced in water and in steam were then examined in air and vacuum at room temperature and in vacuum at higher temperatures.

Experimental considerations bearing on all the work are given in the next section. Further details are presented in each section where they seemed appropriate to maintain continuity.

Additional studies dealing with anodizing are included for lack of a more suitable outlet. Some mention should also be made here of earlier attempts to measure film resistance on aluminum in high-purity water by means of a bridge circuit employing two auxiliary electrodes. This method was not successful because the high impedance of the water overshadowed the resistance contribution of the film.

GENERAL EXPERIMENTAL CONSIDERATIONS

A. Materials

Three sets of specimens were prepared. The first set was arc-melted Grade I iodide zirconium which had been rolled and cut into 100 squares of convenient size (total area of 9.5 cm²). The second set of specimens consisted of zirconium alloys containing titanium. These alloys were prepared by arc-melting crystal bar zirconium and crystal bar titanium. The resulting buttons were then machined into discs and etched. The alloys are listed in Table I. Other elements were present in the amounts usually associated with crystal bar zirconium. The third set of specimens consisted of small plates of Zircaloy-2.* These were studied only briefly for comparison with zirconium.

Table I

TITANIUM ZIRCONIUM ALLOYS WHICH WERE INVESTIGATED

Specimen Nos	Weight Per Cent Titanium	Atomic Per Cent Titanium	Specimen Nos	Weight Per Cent Titanium	Atomic Per Cent Titanium
1 2	0.05	0.095	16 17	50.0	65.6
3 4	0.10	0.19	18	65.0	78.0
5 6	0.25	0.48	19	75.0	85.2
7 8	0.50	0.95	20	85.0	91.6
9 10	10.0	17.5	21	90.0	94.5
11 12	20.0	32.3	22	95.0	97.3
13 14	30.0	45.0	23	100.0	100.0
15	40.0	56.0			

* 1.5 w/o Sn, 0.12 w/o Fe, 0.10 w/o Cr, 0.05 w/o Ni (60 ppm N max)

B. Surface Preparation

The surfaces were always prepared by wet-grinding to 400 grit silicon carbide and etching in a solution of 5 ml concentrated HF (47%), 45 ml concentrated nitric acid (70%), and 50 ml water. This was followed immediately by rinsing in running water. Specimens were never touched by hand between etching and corrosion exposure. If specimens were handled after the corrosion film had formed, they were degreased with methanol.

The zirconium and Zircaloy-2 specimens were exposed to degassed, distilled water for two weeks at 315°C. The weight gains resulting from corrosion varied from specimen to specimen, indicating variations in film thickness. Samples having low, medium and high weight gains were selected for examination. Film thickness could not be judged from appearance, because all these specimens were smooth, dark and iridescent.

C. Choice of Contact Material

Electrical measurements were always made through the oxide film by applying a metal contact to the outer surface and using the zirconium as the other electrode. Contacts were made using mercury or the following evaporated metals: aluminum, silver, and gold. An average resistance could then be measured which ideally was representative of the part of the oxide which controlled the corrosion reaction.

The evaporated contacts were prepared by placing oxidized specimens on a grating with regularly spaced circular holes, $\frac{1}{8}$ in. in diameter. The evaporation source was underneath and the shadowing effect of the grid left a number of conducting discs (0.079 cm^2) on the surface of each specimen. Different areas on the surface could be sampled by moving a wire probe from disc to disc.

Aluminum proved to be the most suitable contact material from the viewpoint of adherence. Silver and especially gold were much less satisfactory in this regard. It was found that a lightly touching probe would break through the gold spot and rest directly on the zirconium oxide. This led to highly erratic results, which were attributed to intermittent contact with the gold. This agreed with the conclusions of Holland⁽³⁾ who stated that less-noble metals adhered better to glass than to noble metals.

Aluminum had the disadvantage of forming an oxide film. This became apparent when a light wire probe on the aluminum surface occasionally encountered a high resistance similar to the bare ZrO_2 surface, and the probe had to be moved. The oxide film on the aluminum spots did not pose a problem if measurements were made soon after evaporation.

If several days or weeks were allowed to elapse, then specimens which initially gave quite reproducible results became extremely variable. Much more care was then required to ensure contact. There are obvious solutions to this problem, e.g., evaporating a second metal such as silver on top of the aluminum, but these were not investigated.

RESISTANCE MEASUREMENTS IN AIR AT ROOM TEMPERATURE

A. Measurements on Anodic Films Using Mercury

The resistances of thin anodic films were measured using mercury to reduce the possibility of mechanical damage. A number of specimens of zirconium were wet polished and coated with Unichrome 330 wax.* Spot-welded wires provided electrical contact. A circular area (0.28 cm^2) was then exposed by means of a cork borer and the bare metal was electro-polished in a solution of acetic and perchloric acids.** The specimen was then anodized at a potential of 2 volts, against platinum, in 1 w/o KOH at room temperature. The film was applied at the rate of 1 volt per min and held at two volts for one additional minute. The specimen was then rinsed, dried, and the anodized surface was submerged in mercury. A small direct current of $0.005 \mu\text{a}$ ($0.018 \mu\text{a}/\text{cm}^2$) was then passed through each of sixteen specimens, with the zirconium held at a negative potential. This polarity was chosen to avoid any rectification effect. The current of $0.005 \mu\text{a}$ was the minimum measurable on the galvanometer. The IR drop was then measured, and R was calculated. Each of six specimens had zero resistance, whereas the average resistance of the remaining ten specimens was $1.4 \times 10^7 \text{ ohms}/\text{cm}^2$. Because the film formed at two volts had a thickness of about $60 \text{ \AA}$, the specific resistance of the average film was of the order of $2.3 \times 10^{13} \text{ ohm-cm}$. In one case, the resistance was observed to drop suddenly after maintaining a high value for several hours.

The average voltage drop across the films was 0.250 v, which meant that the electric field in the film was $4.2 \times 10^5 \text{ v/cm}$. Dielectric breakdown occurs in the region of 10^6 v/cm .⁽⁴⁾ The anodic formation field at which ionic diffusion takes place is also of this order of magnitude. It is possible that the occasional low resistances were due to localized overstepping of the minimum field to produce electrical discharge.

*United Chromium, Inc., New York.

**100 ml 70% HClO_4 , 1000 ml glacial acetic acid.

B. Measurements Using Evaporated Films (Al, Ag, Au)

1. Experimental Technique

The type of arrangement used for subsequent work is shown schematically in Figure 1. The applied voltage was usually varied from 0 to 1 volt. In all cases the resistances were found to be independent of polarity.

Figure 1

Schematic of arrangement
for measuring the resist-
ance of corrosion films

Resistance was determined by applying a voltage across the film and electrometer in series. With the electrometer on direct measurement (10^{14} ohms internal impedance) all the voltage (E_1) appeared across the electrometer. The variable resistance was then added across the electrometer to convert the latter instrument to an ammeter. The variable resistance could be decreased in steps from 10^{12} , 10^{11} , 10^{10} , etc., down to 10^3 ohms. The applied voltage was divided between the unknown film resistance, R_x , and the known resistance, R_k . If the electrometer measured a voltage E_2 after switching in the known resistor, the voltage across the film was $E_1 - E_2$. Therefore,

$$R_x = \frac{E_1 - E_2}{E_2/R_k} = \frac{\Delta E}{I},$$

where I is the current through the system.

With resistances of the order of 10^{10} ohms at room temperature, it was necessary to shield the high-impedance lead on the electrometer to avoid ac pickup. Initial measurements were made in an air-conditioned room (24°C, 40% humidity) to avoid the possibility of surface conduction across films of moisture which could form in a more humid atmosphere. Shielding was provided by a grounded copper box.

Electrical contact to the specimen was made by clamping with a pointed screw. This method was abandoned when it was found that changes in the pressure of the screw caused abrupt changes in the film resistance. Usually, the spots of high resistance were affected most. The high resistance was lost and the film behaved as if it were short circuited. The factors responsible for this phenomenon were not identified.

The procedure was then modified to wet grinding one face of the specimen which then rested on a platinum sheet. In some cases a platinum wire was spot welded to the specimen with the same results as when one face of the specimen was cleaned.

2. Anodic Films

Oxide layers of well-defined thickness can be prepared by anodizing at constant voltage.⁽⁵⁾ The thickness of these layers depends upon time of anodizing, but the film thickness, as determined by weighing,⁽⁶⁾ is approximately $30 \text{ \AA}/\text{volt}$.

In order to determine the effect of increasing film thickness, a zirconium plate was anodized to successively higher voltages in different areas along the surface. After metallizing, the resistances of different film thicknesses could be measured.

It was found that the anodic films had very high resistances which were easily broken down by pressure on the probe. The applied potential difference was 10 mv. Most of the spots showed a low resistance, for no apparent reason. The 10-v films ($300 \text{ \AA}$) always had resistances below the range of the apparatus (approximately 1000Ω). At 20 and 30 v, the resistances were much higher. At 40 v (thickness of $1200 \text{ \AA}$), the resistance approached the upper limit of the equipment. A typical result is shown in Figure 2. In contrast with these data, the corrosion oxide layer (vide infra) had measurable resistances at a thickness of 1.40μ ($14,000 \text{ \AA}$).

Heating of the anodic films in air led to the development of a potential difference in which the zirconium had positive polarity. The potential difference appeared at about 300°C and slowly dropped with time. These data were not sufficiently reproducible to warrant discussion.

The potential difference (hereafter referred to as pd) was dependent on the presence of oxide, because the residual thermal emfs when the film broke through electrically were negligibly small. Consequently, the pd was an indication of an undamaged film. It was found later that the pd of corrosion films was sufficiently large and stable to be used for measuring resistance.

Figure 2

The resistance of anodic films on a typical zirconium specimen as measured using evaporated aluminum spots (0.08 cm^2)

3. Corrosion Films Produced in Water

Corrosion films were much easier to measure and were not sensitive to probe pressure. It is believed that the reason for this lies in the greater thickness of these films (of the order of 1μ).

It was anticipated that thinner corrosion films might show resistances differing from those of thicker films, but this was not the case. The variation from one aluminized spot to another was as great as the variation from specimen to specimen. Many spots showed electrical breakthrough without apparent cause. Representative data have been selected to illustrate the general behavior of these films. Figures 3 and 4 show resistances in air at room temperature of various spots on a single specimen which had a weight gain of 8.1 mg/dm^2 . The calculated average film thickness was 0.50μ , if it be assumed that the geometric and true areas were equal. The same assumption, that the roughness factor equals 1, was made in all estimates of thickness.

In most cases the resistances at low applied voltages were either so low as to indicate breakthrough or were above the upper limit of measurement. By steadily raising the voltage, a point was reached at which a measurement could be made. As shown in Figure 3, this point was approximately 0.4 v. With a further increase to 1.0 v, the resistance showed a large decrease. Figure 4 shows the results of two spots which had lower resistances. Measurements at these two spots could be made at lower applied voltages, and the drop in resistance with increasing voltage was smaller.

Attention was directed primarily to the high-resistance spots because these were considered to be free of damage or inclusions which could lower the film resistance.

Figure 3

Curves of resistance vs. applied voltage for different aluminized spots (0.08 cm^2) on the oxide film of a Grade I zirconium specimen corroded two weeks in water at 315°C .

Figure 4

Curves of resistance vs. applied voltage for different aluminized spots (0.08 cm^2) on the oxide film of a Grade I zirconium specimen corroded two weeks in water at 315°C . Same specimen as in Figure 3.

RESISTANCE MEASUREMENTS IN AIR ABOVE ROOM TEMPERATURE (CORROSION FILMS)

A. Zirconium

1. Aluminum Contacts

The specimen for which results are shown in Figures 3 and 4 was heated to 115°C, cooled to room temperature, and heated again to 110°C. The resistance of one spot was determined at several intermediate temperatures and voltages. The data are plotted in Figures 5, 6, and 7. The data are presented twice at 70 and 100°C for ease of comparison. It is evident that the strong dependence of resistance on voltage became progressively smaller as the temperature increased. The film was essentially ohmic at 100°C, at which the applied voltage was less than 0.6 v. On the second heating cycle, the resistance was measured at an applied voltage of 0.5 v. The results are summarized in Table II. These data are plotted in Figure 8 for comparison with data at higher temperatures.

Figure 5. Curves of resistance vs. applied voltage for a single aluminized spot (0.08 cm^2) on the oxide film of a Grade I zirconium specimen corroded two weeks in water at 315°C.

Figure 6

Curves of resistance vs. voltage for the same spot (0.08 cm^2) as in Figure 5.

Figure 7

Curves of resistance vs. voltage for the same spot (0.08 cm^2) as in Figure 5, but at higher temperatures.

Table II

RESISTANCES MEASURED ON AN ALUMINIZED SPOT
AT DIFFERENT TEMPERATURES (0.5 v)

Temperature, °C	1000/T (°K ⁻¹)	Resistance (ohms)
75	2.87	6.8×10^9
85	2.79	4.9×10^9
99	2.69	1.7×10^9
110	2.61	1.0×10^9

Figure 8

Resistance as a function of temperature for several silver spots (0.08 cm^2) on the ZrO_2 corrosion film on Grade I zirconium. Data are shown for five spots plus the data from Table II.

2. Silver Contacts

Very similar results were obtained with silver contacts. Silver was applied by using a silver-containing paint which was baked on at 290°C , or by using silver deposited by chemical reduction. The two methods gave equivalent results. The paint was preferred because of ease of application. The silver paint became conducting after heating in air for 20 min. at 290°C . This procedure did not tarnish clean zirconium and was applied to the film

produced on a zirconium specimen after two weeks of exposure to water at 315°C. The film was 1.4 μ in thickness (22.7 mg/dm²). After applying silver paint, the resistances were measured at room temperature and then while the specimen was slowly heated in air. The results are shown in Figure 8. The slopes indicated a conduction energy gap of 1.0 ev. Above 300°C the resistance slowly drifted downward. The data from Table II are plotted at the top of Figure 8. The differences in the two sets of data illustrate the variation from one specimen to another.

B. Zircaloy-2 with Aluminum Contacts

When Zircaloy-2 was examined, the resistances were found to be much more variable than in the case of zirconium. This was attributed to the presence of inclusions (probably intermetallic compounds) in Zircaloy-2. Such inclusions could form conducting paths through the oxide.

As already mentioned, the resistances of films on zirconium and Zircaloy-2 were very similar when measured at room temperature. However, the time to reach a stable voltage was significant for zirconium, requiring ten to twenty minutes, while there was no appreciable time lag in the case of Zircaloy-2. There seemed to be a large capacitance associated with the oxide on zirconium and a small capacitance associated with the oxide on Zircaloy-2.

RESISTANCE MEASUREMENTS IN VACUUM ABOVE ROOM TEMPERATURE (ALUMINUM CONTACTS)

A. Experimental Technique

In subsequent work an evacuable bell jar was used. The metal cage around the bell jar served as a shield. The specimen was placed on a stand between two platinum sheets which served as the heaters. A specimen could be brought to 350°C in 5.5 min and cooled to 100°C in 16 min.

B. Zirconium with Anodic and Water Corrosion Films

Anodic films showed the same results under vacuum as they did in air, showing that the previous measurements were independent of the atmosphere.

The conductivity characteristics upon heating and cooling were studied for two zirconium specimens corroded in water at 350°C (instead of 315°C) for two weeks. The resulting oxide layer had a good, iridescent, black appearance. The corrosion weight gain for both specimens was 14.5 mg/dm² (0.89 μ). The specimens were made both positive and negative with respect to the aluminum spot, and the resistance was determined at voltages up to approximately 1 volt.

The data are plotted in Figure 9, where resistance is on a log scale and voltage on a linear scale. For simplicity, straight lines were chosen to represent the relationship between points and were drawn so that R was a maximum at $E = 0$. The lines represent a dependence of resistance on voltage of the type

$$R = Ae^{-BE}$$

where R is resistance, E is field strength (volts/cm) in the oxide, and A and B are constants.

As temperature increased, the resistance became less dependent on field strength. It is presumed that above 250°C the oxide film would become completely ohmic and the curve would then be flat. However, another effect was revealed by heating, which prevented obtaining reversible measurements above 250°C.

Figure 9 Resistance vs applied voltage for the corrosion films on two zirconium specimens. The films were formed in water at 350°C (2 weeks)

This was a drift downward in resistance, with a rate which increased with temperature. A study of this phenomenon was made at 400°C on a variety of films, and the results have been published.⁽⁷⁾

Two other phenomena should be mentioned at this point. First, a potential difference across the oxide was observed for corroded zirconium specimens heated above 100°C. A pd of this type was noted earlier for anodic films. Above 250°C, the pd decreased as the resistance of the film decreased. This phenomenon was not surprising, because the film was produced under conditions which would leave a concentration gradient. Because of the nonequilibrium conditions under which these pd's appeared, no significance was attributed to their magnitude. In some cases they were as large as 1 volt. The second phenomenon was an induced charge effect, which is discussed in detail in a later section.

When heating to the same temperature in vacuum as the original corrosion temperature, the specimen changed resistance, which was attributed to diffusion in the film, at a slow rate. At moderately high tem-

peratures, it was not possible to measure a resistance equivalent to that which was present under corrosion conditions. An example of this is shown in Figure 10. A zirconium specimen which had been corroded two weeks at 350°C in water was heated to 360°C in vacuum. The resistance dropped rapidly while heating to 360°C, then rose and again began to drop. The temporary rise was attributed to uneven heating of the specimen with the consequence that the spot-welded thermocouple did not show the true temperature of the film. The dotted line represents the change which might have occurred under more ideal conditions. It was obvious that a resistance representative of the film under corrosion conditions was unobtainable in vacuum.

Figure 10 Change of resistance of the oxide film on zirconium as a function of time of heating at 360°C. The film was formed in water at 350°C (2 weeks).

C. Films Produced on Zr-Ti Alloys in Dry Oxygen at 500°C

Titanium, zirconium, and a 50 w/o Ti-Zr alloy were oxidized in dry commercial oxygen at 500°C. The specimens were then aluminized

with the usual $\frac{1}{8}$ -in.-diameter spots, and the film resistance was measured at room temperature. The data are presented in Table III. Because the calculation of resistivity required information on the density of the film, the data of Ksendzov⁽⁸⁾ for solid solutions of TiO_2 and ZrO_2 were used. It is evident that the oxide on titanium had a much higher conductivity than the oxide on zirconium.

Table III

CORROSION AND RESISTIVITY DATA FOR SPECIMENS
OXIDIZED IN DRY O_2 (1 atm at 500°C)

Material	Time of Exposure (hr)	Weight Gain, mg/dm ²	Film Resistivity (ohm-cm)
Zr	15	29.4	1.0×10^{14}
50% Ti, 50% Zr	1	17.0	3.2×10^9
Ti	15	8.0	3.3×10^5

D. Films Produced on Zr-Ti Alloys in Water

1. The Resistance of Oxide Films Produced on Zirconium Alloys (10 w/o to 95 w/o Ti) in Water at 350°C and Steam at 400°C

Because adequate film thicknesses could not be produced in 350°C water on all these alloys, four of the higher titanium alloys were corroded in steam at 400°C. The film thicknesses for these specimens were barely adequate to obtain a meaningful resistance measurement, and the reproducibility was poor. The data are presented in Table IV.

The corrosion exposures were not uniform in view of the need to obtain suitable film thicknesses. The most reproducible data were those in the range from 10 to 50 w/o Ti. Here, the resistivity was highest for 10% Ti, reached a minimum for the 20 and 30% specimens, and then increased in the 40 and 50% Ti specimens. The 10% specimens exhibited slight p'd's which were confirmation of a high-resistance film. For the compositions from 65 to 100% Ti the resistivity did not show a consistent variation. These films were very thin (approximately 0.1μ) as compared to thicknesses of 0.30 to 2.8μ for the specimens with less titanium. The oxide on titanium did not have the very high-resistance characteristic of that on zirconium.

Table IV

CORROSION WEIGHT GAINS AND THE RESISTANCE OF OXIDE FILMS ON
Ti-Zr ALLOYS CORRODED IN WATER AT 350°C (SPECS 9-19) AND IN
STEAM AT 400°C (SPECS 20-23)

Specimen No	Composition (Wt % Ti)	Time of Exposure (hr)	Weight Gain (mg/dm ²)	Film Resistivity at Room Temp (ohm-cm)	Comments (Appearance, etc)
(Corroded in water at 350°C)					
9	10	16	71.6	1.2×10^{11}	Black with luster +0.008-v pd*
10	10	16	66.4	0.79×10^{11}	Black with luster +0.004-v pd
11	20	96	143.0	8.3×10^6	Dull black, Zero pd
12	20	96	147.0	3.2×10^7	Dull black, Zero pd
13	30	96	92.5	1.64×10^7	Dull black, Zero pd
14	30	96	92.1	5.8×10^6	Bluish black, Zero pd
15	40	96	46.2	1.46×10^9	Dull black, Zero pd
16	50	96	15.7	3.9×10^9	Lustrous bluish black, small pd
17	50	96	21.0	1.1×10^9	Lustrous bluish black, +0.003 v pd
18	65	48	5.1	6.8×10^8	Dull black, some iridescence
19	75	64	4.1	9.4×10^8	Violet-black
(Corroded in steam at 400°C)					
20	85	369	6.0	2.1×10^8	Dull violet and green
21	90	369	5.6	1.7×10^9	Green and blue interference colors
22	95	369	5.1	4.1×10^9	Green and yellow interference colors
23	100	369	4.7	3.4×10^8	Various clear interference colors

*These pd's were measured by the electrometer at room temperature

Specimen No. 11 (20 w/o Ti) was heated and cooled twice to determine the temperature coefficient. The resulting curve is plotted in Figure 11.

Figure 11

Log of resistance vs. reciprocal temperature for the oxide film on specimen 11 (20 w/o Ti). Measurements were taken from a single aluminized spot (0.08 cm²). The film was produced in water (350°C, 96 hr).

The activation energy for conduction was 0.61 ev, which was lower than the activation energies observed for the oxide on zirconium, which was also a poorer conductor. This result is in accordance with the Meyer-Neldel rule,⁽⁹⁾ which states that the temperature coefficient decreases as the conductivity of an oxide increases.

The corrosion weight gains did not agree with the data of Carver and Hayes,⁽¹⁰⁾ who found that the 85% Ti alloy had a much higher corrosion rate than the 65% Ti alloy. The data of the present study should be closer to the true corrosion picture because the alloys were made from crystal bar.

2. The Resistance of Oxide Films Produced on Zirconium Alloys (0.05 to 0.50 w/o Ti) in Water at 290°C.

a. Experimental considerations: The measurement of film resistance was extended next to the low titanium-zirconium alloys. Because the corrosion rate increased with titanium content, the 0.5 w/o Ti alloy, which had the highest scaling rate, was exposed to water for the shortest time. The purpose was to develop a film thick enough to avoid electrical breakthrough, but sufficiently thin to be as uniform as possible. Experience indicated that approximately 5,000 Å was a desirable thickness.

Two sets of measurements on the corrosion films formed in water at 290°C were made. The first set was taken after exposing the specimens for periods varying from 16 to 448 hours. After evaporating aluminum and measuring resistance, the specimens were wet ground, etched, and exposed again to 290°C water. The exposure times in the second experiment were varied from 16 to 272 hours. In each case it was desired to subject the specimens to 290°C water for the minimum time necessary to obtain a uniform dark film and avoid the white oxide which is typical of the post-transition period in oxidation. Because white oxide does not contribute to corrosion resistance, its resistance would not be expected to reflect the type of defects that control volume diffusion through the oxide. In the first series, the specimens were all dark grey to black, except for one of the 0.05 w/o Ti specimens, which had some patches of white oxide. The aluminum was applied only to the uniform dark coating. In the second experiment, the films were light grey in the case of the 0.5 w/o Ti alloy but there were no white areas. In the first experiment, one specimen had a surface deposit of magnetite particles, which apparently came from the walls of the stainless steel autoclave. It was not possible to recheck this specimen after discovering the deposit, because one side had been cleaned to provide electrical contact. After the second exposure, the films were carefully examined to ensure that adventitious matter did not remain on the surface.

The characteristics of the films on these alloys were noted at every stage of measurement. An oxidized specimen was placed in the apparatus after aluminizing and the probe was placed on an undamaged spot. The pd and resistance were then measured in air and recorded. The bell jar was then closed, and the pd was followed as the system was evacuated. The resistance was checked again after the pd had stabilized at the new value in vacuum. The system was then brought to temperature within a few minutes, and the pd and resistance were checked over a period of one hour. The system was then cooled to room temperature in vacuum, and the electrical properties were again checked before and after admitting air. In this way the reversibility or lack of reversibility of each step could be verified.

b. Results: The first set of measurements was carried out by heating each specimen to 185°C in vacuum. These data are indicated as the first series in Table V. When all eight specimens had been examined in this way, they were all cleaned by the usual polishing and etching, and were oxidized again in water at 290°C. The same sequence of measurements was repeated, except that now the specimens were brought to 290°C in vacuum instead of to 185°C. They were also held at 290°C for 100 min instead of for 60 min. The data from this sequence of measurements are called the second series, and are presented in Tables VI, VII and VIII. Table VI shows the corrosion data for the second series.

Because of higher corrosion rates in the second exposure, it was necessary to use shorter times to ensure that the films did not become too thick. A comparison in terms of $\text{mg}/\text{dm}^2\text{-hr}$ is given in Table IX. The corrosion rates were slightly higher for the 0.05 w/o Ti alloys and ten times as high for the 0.5 w/o Ti alloys. The higher alloys showed the greater change. It is possible that dissolved hydrogen from the first corrosion exposure influenced the second exposure.

Despite these differences, the important comparison within each set of specimens could still be made. Certain general remarks apply to both sets of data, but the second series was more detailed and, therefore, will be examined more closely.

c. Remarks

(1) General observations

In all cases the undamaged oxide at room temperature had a resistance of approximately 10^{10} ohms. The resistivities of these films at room temperature varied from 10^{13} to 10^{14} ohm-cm, indicative of an insulator. The resistance was independent of polarity, and was lowered by an increase in field strength. The effect of field strength was assumed to be similar to the effect shown in Figure 9.

Table V

CORROSION WEIGHT GAINS AND THE RESISTANCE IN VACUUM OF
OXIDE FILMS ON Ti-Zr ALLOYS CORRODED IN WATER AT
290°C (FIRST SERIES)

Specimen No.	Composition (w/o Ti)	Time in Water at 290°C (hr)	Weight Gain (mg/dm ²)	Calculated Film Thickness (μ)	Resistance of 0.08-cm ² Spot (ohms)			Resistivity Calculated from Column B (ohm-cm)
					A At Room Temp (25-27°C)	B Initially at 185°C	C After 1 hr at 185°C	
1	0.05	448	17.9	1.10*	1.2×10^{10}	1.3×10^8	0.7×10^8	8.5×10^{10}
2	0.05	448	10.7	0.66	4.0×10^{10}	3.0×10^8	1.5×10^8	33×10^{10}
3	0.10	168	18.8	1.16**	3.8×10^{10}	approx. 10^9 at 170°	-	-
4	0.10	48	12.9	0.79	2.0×10^{10}	0.75×10^8	1.3×10^8	6.8×10^{10}
5	0.25	168	21.0	1.29	3.0×10^{10}	4.2×10^8	7.1×10^8	23×10^{10}
6	0.25	168	21.3	1.31	0.2×10^{10}	1.0×10^8	2.3×10^8	5.5×10^{10}
7	0.50	16	7.0	0.43	1.4×10^{10}	0.40×10^8	0.47×10^8	6.7×10^{10}
8	0.50	16	8.3	0.51	3.0×10^{10}	0.83×10^8	0.63×10^8	11.7×10^{10}

*This specimen had some patches of thin white oxide. Consequently, the calculated thickness of the coherent film is too high.

**This specimen had a thin surface deposit attributed to autoclave corrosion products. The calculated film thickness is therefore too high.

Table VI

CORROSION DATA ON Ti-Zr ALLOYS EXPOSED TO WATER AT 290°C (SECOND SERIES)

Specimen No.	Composition (w/o Ti)	Time in Water at 290°C (hr)	Weight Gain (mg/dm ²)	Calculated Film Thickness (microns)	Appearance
1	0.05	272	7.05	0.43	Dark, shiny, pink and green iridescence.
2	0.05	272	8.06	0.50	Dark, shiny, pink and green iridescence.
3	0.10	80	17.4	1.07	Darker than above, turning grey, slight iridescence.
4	0.10	64	31.2	1.9	Same as above but lighter grey.
5	0.25	48	46.4	2.8	Grey and graphite, no iridescence.
6	0.25	48	38.5	2.4	Grey and graphite, no iridescence.
7	0.50	16	70.6	4.3	Light grey, turning white, still compact and adherent.
8	0.50	16	91.0	5.6	Light grey, turning white, still compact and adherent.

Table VII

POTENTIAL DIFFERENCE (IN VOLTS) ACROSS THE OXIDE FILM IN THE COURSE OF RESISTANCE MEASUREMENTS ON Ti-Zr ALLOYS (SECOND SERIES)

Specimen No.	Before Heating		At 290°C			After Heating	
	Air	Vacuum	Initially	After 60 Min	After 100 Min	Vacuum	Air
1	+0.04*	-0.080	-0.330	-0.210	-0.178	-0.097	-0.088
2	+0.053	-0.076	-0.260	-0.300	-0.200	-0.100	-0.078
3	+0.085	-0.080	-0.500	-0.335	-0.225	-0.345	-0.115
4	+0.185	-0.093	-0.250	-0.0065	-0.0041	-0.021	-0.042
5	+0.350	-0.098	-0.070	+0.0094	+0.0107	-0.092	+0.180
6	+0.43	-0.097	-0.065	+0.087	+0.079	-0.102	-0.067
7	-0.205	-0.101	+0.300	+0.062	+0.054	-0.104	-0.103
8	-0.083 with fluctuations, then +0.29	-0.101	+0.22	+0.25	+0.22	-0.102	-0.038

*The sign refers to the polarity of the zirconium.

Table VIII

RESISTANCE IN OHMS OF A 0.08-cm² SPOT ON THE OXIDE ON Ti-Zr ALLOYS PRODUCED IN 290°C WATER (SECOND SERIES)

Specimen No.	At Room Temperature Before Heating		At 290°C			At Room Temperature After Cooling	
	Air	Vacuum	Initially	After 60 Min	After 100 Min	Vacuum	Air
1	1.7×10^{10}	3.0×10^{10}	1.5×10^7	3.8×10^7	4.5×10^7	6.3×10^{10}	4.6×10^{10}
2	2.3×10^{10}	3.2×10^{10}	2.0×10^7	3.3×10^7	4.2×10^7	3.7×10^{10}	3.0×10^{10}
3	1.0×10^{10}	2.2×10^{10}	6.8×10^6	3.2×10^7	4.0×10^7	1.1×10^{10}	1.8×10^{10}
4	6.0×10^9	3.0×10^{10}	1.5×10^7	8.8×10^6	7.4×10^6	6.1×10^9	6.8×10^9
5	3.6×10^9	4.0×10^{10}	7.3×10^7	1.36×10^8	1.2×10^8	4.1×10^{10}	1.8×10^{10}
6	5.0×10^9	7.0×10^{10}	2.8×10^7	3.2×10^8	3.6×10^8	3.8×10^{10}	3.2×10^{10}
7	2.1×10^{10}	6.2×10^{10}	7.6×10^7	8.8×10^7	8.4×10^7	3.7×10^{10}	3.5×10^{10}
8	1.4×10^{10}	3.7×10^{10}	3.4×10^9	4.7×10^9	6.2×10^9	3.3×10^{10}	2.2×10^{10}

Table IX

COMPARISON OF THE AVERAGE RATE OF WEIGHT GAIN
(mg/dm²/hr) FOR THE FIRST AND SECOND EXPOSURE
OF LOW Ti-Zr ALLOYS IN WATER AT 290°C

Specimen No.	Composition w/o Ti	First Exposure		Second Exposure	
		Test Time (hr)	Total ΔW Total hr	Test Time (hr)	Total ΔW Total hr
1	0.05	448	0.040	272	0.026
2	0.05	448	0.024	272	0.030
3	0.10	168	0.11	80	0.22
4	0.10	48	0.27	64	0.49
5	0.25	168	0.125	48	0.97
6	0.25	168	0.13	48	0.80
7	0.50	16	0.44	16	4.4
8	0.50	16	0.52	16	5.7

The voltages used in measurement were the potential differences generated in the film and never exceeded 0.5 volt, as shown in Table VII. The usual potentials were closer to 0.1 volt, and the field dependence effect was assumed to be negligible.

(2) Potential Differences

In all these measurements, a potential difference was observed similarly to earlier mentioned observations on zirconium. If no pd was observed, the oxide was found to have a low resistance (of the order of several thousand ohms). Such spots were not studied further because the oxide had suffered electrical breakdown.

The following observations were made at room temperature. The pd did not arise from the Seebeck effect because it was dependent on the ambient temperature. In the first series of measurements, the characteristics of this pd were noted, but a detailed record was not kept. The polarity in air (the zirconium was positive relative to the aluminum) was observed to be reproducible. The maximum pd in air was 0.46 v in the first series and 0.43 v in the second. When pumping a vacuum, the pd diminished and the polarity usually reversed. A slow drift of pd with time in vacuum indicated that a reversal in polarity could always be expected. In the first series, a typical pd in vacuum was -0.070 v; the minus sign indicates that the zirconium was negative.

In the second series, the potentials were noted at each stage of the measurement, and the data are given in Table VII. The general behavior was the same as in the first series.

In nearly all cases the pd's showed a similar change after the specimen was cooled again to room temperature, i.e., the admission of air caused a positive change in pd. The polarity usually became positive immediately after the admission of air, but then slowly drifted to more negative values and again reversed. The final value in air was always more positive than the pd in vacuum.

The pd's were sufficiently large and stable to permit a determination of resistance independent of an external voltage source. However, the external source was used to determine the effect of polarity and changing applied voltage on the resistance.

(3) Change of Resistance with Temperature

As seen from Table V, the resistivity decreased with heating to the order of 10^{10} ohm-cm at 185°C , a value which is at the borderline between insulators and semiconductors. The resistances were fairly stable, as may be seen by a comparison of values in columns B and C. The dependence of resistance upon field strength diminished, but was still significant at 185°C .

As was expected, the second set of specimens showed lower resistances at 290°C than the first set at 185°C . As seen in Table VIII, the resistances were 10^7 to 10^8 ohms in value, except for specimen 8. Based on estimated film thicknesses, the average resistivity for specimens 1 and 2 was 2.7×10^{10} ohm-cm, and for 3 and 4 it was 5.1×10^9 ohm-cm. At 290°C , the oxide films showed a slight increase in resistance with time. The resistances at each temperature were all in the same range except at 290°C , for which specimen 8 had an anomalously high value. The presence of white oxide could account for this difference.

(4) Induced Charge Effect

An additional feature of these measurements was an effect which was called induced charge. This phenomenon was noted when an external voltage was applied to the corrosion films on the zirconium-titanium alloys. With a pure resistance film, the applied voltage appeared on the electrometer and was proportional to the setting on the potentiometer. With a film exhibiting induced charge, the voltage was not proportional to the potentiometer setting. A rise in voltage was observed when the applied voltage was first increased, but this voltage then began to drop and leveled at only a fraction of the applied voltage. In one case the effect was so large that after the system had come to equilibrium when applying ± 1.5 v, the original pd of the specimen (-0.067 v) remained unchanged. The film resistance in this case was 3.8×10^{10} ohms, as determined from the specimen pd.

The rate at which the induced charge developed depended on the specimen, but was slow enough so that the induced charge was readily observed upon removing the applied voltage. By applying and removing the applied voltage, the rates of buildup and decay of the induced charge were found to be comparable. The effect was independent of polarity and could be repeated several times without perceptible diminishment with time.

The induced charge was observed both in air and in vacuum at room temperature. However, the effect increased when the bell jar was evacuated. When specimens were then heated, the effect diminished rapidly. At 185°C in vacuum, the effect had generally disappeared, but a few exceptions having a greatly diminished induced charge were observed. Upon cooling to room temperature in vacuum, the induced charge was found to increase as compared to its previous value under the same conditions. Upon admitting air at room temperature, the effect diminished abruptly.

There was no evident relationship between the alloy composition and the magnitude of the induced charge. The effect obviously required a high-resistance film, as made evident by the fact that temperature lowered resistance.

EFFECT OF PERIODIC ANODIZING UPON THE CORROSION RATE OF ZIRCONIUM

In comparing the resistances of anodic and autoclave films at room temperature it was apparent that the latter films had lower resistivities. This difference was attributed to the retention of defects in the autoclave films upon cooling, whereas the anodic films formed at room temperature probably had very few defects. If the anodic film characteristics could be retained in corrosion films, a decrease in corrosion rate should result. In the light of this reasoning, an investigation was made of the effect of periodic anodizing upon the corrosion of low-quality zirconium having a high corrosion rate.

A. Experimental

As a matter of convenience, a zirconium was chosen which exhibited white oxide soon after exposure to water at 340°C. Two specimens were anodized in the intervals between autoclave exposure after the specimens were weighed. Two other specimens served as controls.

The zirconium had been melted in graphite from sponge and contained 0.17 w/o carbon. Many inclusions, presumably carbides and nitrides, were visible. Four specimens were cut to the dimensions 0.35 x 1.5 x 2.3 cm, having a geometric surface area of 9.6 cm². The plates were wet ground and etched in HF-HNO₃ solution. After rinsing and drying, the four specimens were weighed and placed in degassed, distilled water in autoclaves. The autoclaves were placed in a circulating air oven at 340°C. The autoclaves were in the ovens two hours between weighings, but the autoclave temperature was not constant for most of this time. As measured by a thermocouple spot-welded to the autoclave, the temperature was 225°C at 30 min, 300°C at 60 min, 330°C at 90 min, and 340°C at 120 min. All four specimens were weighed periodically, and the two anodized specimens were weighed before and after anodizing. They were in the anodized condition when the test was started. The anodizing was done in 1 w/o KOH at room temperature with 50 v applied to the cell. Higher voltages could not be used in this electrolyte because of sparking on the surface. One-half the specimen was anodized first, holding at 50 v for 15 min, and the procedure was then repeated for the other half. The anodizing did not produce visible changes except on the etched surface which developed interference colors. After several autoclave exposures, some of the oxide began to flake off. A fiber brush was used on the surface to equalize the removal of oxide. The weighings were carried out to 0.1 mg.

B. Results

The weight changes during corrosion are shown in Figure 12. The change of weight during anodizing was negligible (changes of zero to several milligrams). The weight changes were positive initially but soon became negative, characteristic of breakaway. The corrosion was significantly greater for the unanodized specimens, as may be seen from the plot. The test was ended when the unanodized specimens lost 206 mg after 44 hours (not shown on graph). The surface was darker on the anodized specimens up to about the tenth exposure (20 hr). Subsequently, the specimens were all white and indistinguishable. It was apparent that the anodic film had an effect in retarding the corrosion rate even after the surface had become white. The anodizing may reinforce and retard the breakdown of an inner barrier layer. Apparently this layer could not be maintained indefinitely because the corrosion rate increased despite anodizing. Hydrogen accumulation in the surface layers, surface roughening, or other factors may have prevented effective reforming of the barrier layer.

Figure 12. Weight losses of four zirconium specimens, two of which were anodized to 50 v at each weighing interval.

EFFECT OF ANODIC FILMS UPON SUBSEQUENT OXIDE GROWTH ON ZIRCONIUM

Various zirconium specimens were anodized in dilute sulfuric and in dilute oxalic acid to determine whether any corrosion inhibition was effective upon later exposure to water. After 15 hr in 315°C water there was very little difference between anodized specimens and unanodized controls. Further exposure indicated that any initial differences in the films disappeared when the films darkened to the point where distinct interference colors were no longer visible. It was concluded that the effect of thin anodic films was probably very similar to their effect on dry oxidation as reported by Polling,⁽¹¹⁾ who observed that the anodic films became thicker at times when unanodized surfaces had reached the same thickness. He concluded that the anodic and dry oxidation films have the same structure. The results of the work in this report indicate that anodic and corrosion films differ in resistance at room temperature, but these differences probably become insignificant at higher temperatures and under corrosion conditions.

Another point of interest was whether or not an oxide film could be formed on zirconium that would put the specimen into the post-transition period without the necessity of reaching the transition point by exposure in the same environment. Oxide films which are considerably greater in thickness than the transition thickness can be formed readily in two ways. The first is to oxidize in dry oxygen at a considerably higher temperature than the water exposure. The second is to anodize in concentrated nitric acid at low voltage to produce a heavy, black, adherent oxide. The difference between this latter process and the usual anodizing (e.g., employing dilute sulfuric or oxalic acids) has been discussed before.⁽¹²⁾

One set of zirconium specimens was oxidized in dry oxygen at 800°C for 1 hour, and the second set was anodized in concentrated nitric acid. These specimens were then placed in water at 315°C for 15 hours. The dry oxide film was unchanged after water exposure, but the film formed in nitric acid had become white and was flaking. A thin interference film had formed underneath the white oxide. If post-transition conditions had been duplicated, the interference film would not have formed. The original layer was not an effective barrier and apparently was penetrated by water.

DISCUSSION

The many effects which were observed in this study showed a complicated dependence of the electrical properties of corrosion films on method of preparation, on temperature, and on atmosphere. These phenomena indicate that only direct measurements under corrosion conditions can be expected to correlate with corrosion rates. In no other way can

one be assured that changes in the film will not obscure a definitive result. At the present time, the emf of a growing ZrO_2 scale is being measured in dry oxygen, and a number of alloys are being compared. The emf gives an indication of the conductivity of the scale. This approach has proved to be very profitable, and the method is being extended to use steam as a medium.

Certain general features of the films on titanium-zirconium alloys were delineated in the work presented here, but the results were not definitive in the range of low titanium concentrations (0.05 to 0.50 w/o Ti). In Table X are presented the results of calculations of the film resistivities at 290°C in vacuum from the data in Table VIII. Film thicknesses were calculated from the weight gains. Whether or not the titanium was in solid solution in the ZrO_2 , the effect on resistivity was minor.

Table X

RESISTIVITIES OF THE CORROSION FILMS ON Zr-Ti
ALLOYS CALCULATED FROM THE INITIAL
RESISTANCES AT 290°C IN VACUUM
(SEE TABLE VIII)

Specimen Number	Alloy Composition, w/o Ti	Initial Resistivity at 290°C , ohm-cm
1	0.05	2.75×10^{10}
2	0.05	3.2×10^{10}
3	0.10	0.50×10^{10}
4	0.10	0.62×10^{10}
5	0.25	2.1×10^{10}
6	0.25	0.92×10^{10}
7	0.50	1.40×10^{10}
8	0.50	48.0×10^{10}

This result is in contradiction with the result from the viewpoint that titanium forms Ti^{3+} in the ZrO_2 lattice, with accompanying oxygen vacancies to compensate the lowered cation charge. The presence of Ti^{3+} would increase the electronic conductivity because this ion can be ionized readily to Ti^{4+} and one electron. This mechanism accounts for the conductivity of TiO_2 under reducing conditions.

At higher titanium concentrations, the resistivity dropped and was very low for pure TiO_2 . The films on the Zr-Ti alloys above 10 w/o Ti showed a steady decrease in resistivity while the corrosion resistance was increasing. Up to 50 a/o Ti, the film composition could be: ZrO_2 (TiO_2 in solid solution) plus $\text{TiO}_2 \cdot \text{ZrO}_2$. Above 50 a/o Ti, the composition might alter to $\text{TiO}_2 \cdot \text{ZrO}_2$ and TiO_2 (ZrO_2 in solid solution), and the TiO_2 would predominate in producing a low resistance. The decrease in corrosion rate would result from lower diffusion rates in $\text{TiO}_2 \cdot \text{ZrO}_2$ and TiO_2 than in ZrO_2 , particularly from ZrO_2 containing dissolved TiO_2 .

The failure to obtain well-defined resistance changes with low titanium concentrations could be accounted for in various ways. One possibility is the presence of cracks in the film. Capacitance measurements have shown that even the interference color films seem to have cracks.⁽¹³⁾ The influence of cracks should be slight if they are perpendicular to the surface. On the other hand, horizontal cracks would diminish the effective cross section and would produce high resistances. In such a situation the bulk of the oxide does not control the corrosion rate. The number and nature of cracks in a specimen after removal from water at high temperature and pressure are probably not the same as under corrosion conditions. Water may be present in the film at high pressure and diffuse out at low pressure. Therefore, postcorrosion measurements could not reflect the true situation during corrosion.

Another possible disturbing factor is the formation of a high-resistance layer. Such surface layers are adduced to explain the resistance of oxide powders. According to Hauffe,⁽¹⁴⁾ a thin high-resistance layer forms on n-type oxide semiconductors as a result of the absorption of oxygen. An indication of this type of effect was found in changing from air to vacuum and back again. The resistance changes were not large, but the aluminum may have acted as a barrier to equilibration with the atmosphere.

Another possibility is that titanium is deleterious because of changes in the film unconnected with electrical properties. Thus, if titanium is present as Ti^{4+} and not as Ti^{3+} , the vacancy structure of the ZrO_2 would not be affected. In larger amounts, titanium lowered the film resistance, as shown by measurements on the corrosion scale at 500°C in 1 atm oxygen.⁽¹⁵⁾ A 2 w/o Ti alloy had a distinctly lower film resistance than pure zirconium. Whether or not 0.5 w/o Ti also has a low resistance at 500°C in oxygen was not investigated. Consequently, the lack of a correlation indicated in this report cannot be taken as final evidence against a relationship between film resistivity and the effect of titanium in increasing the corrosion rate. However, the evidence thus far indicates that more than one factor may be operative in determining corrosion rate. As an example, the high titanium alloys may be more resistant to water or steam

than low titanium alloys because the high film conductivity prevents hydrogen damage. The low titanium alloys may have sufficient conductivity to promote diffusion but not enough to prevent hydrogen damage.

As described in this report, these films exhibited a dependence on electric field as well as potential differences and an induced charge effect. These phenomena are worthy of consideration because they indicate the complexity of film behavior.

At room temperature, the dependence on field strength showed that current carriers must be generated by the field before conductivity becomes appreciable. As the temperature increased, the field effect diminished as current carriers (presumably electrons) were generated thermally. The films then became semiconductors upon heating, and the dependence of conductivity upon field strength disappeared.

The pd's which were observed were more difficult to understand. In the case of anodic films, a pd was not observed except upon heating. The anodic films were produced at room temperature under conditions such that a high field strength was necessary to pull ions through the film. According to Haring,⁽¹⁶⁾ the forming process leaves an ion gradient in the oxide which is compensated electrically by electrons in the cases of excess cations or anion vacancies. Heating such a system would not have an equivalent effect on the two types of charges, and a potential would develop as the electrons were thermally liberated. At a sufficiently high temperature the cations would also become mobile, and the potential would disappear as the system equilibrated. The observed phenomena corresponded to this pattern.

Autoclave films also exhibited pd's, but at room temperature as well as upon heating. These potentials were dependent on temperature and disappeared when the oxide became more conducting as a result of heating at temperatures of 350°C or above in vacuum. The existence of these potentials and their variability is another factor favoring measurements under corrosion conditions.

The ability of the corrosion oxide layers to acquire an induced charge was an interesting difference between the anodic and corrosion films. The phenomenon appeared only in corrosion films of high resistance and disappeared when these films were heated sufficiently to become moderately conducting. The absence of this effect in anodic films suggests that certain properties of the oxide are necessary to show this phenomenon. Interpretation of these differences can only be speculative.

The influence of anodic films on corrosion showed that corrosion could be decreased only when the anodizing procedure was periodically renewed. Evidently, the high-resistance characteristics of anodic ZrO_2

did not persist in high-temperature water. Impressing anodic current in situ might be of value in improving corrosion resistance.

The attempt to accelerate transition indicated that pre-oxidation by anodizing in nitric acid could not duplicate the formation conditions of the corrosion layer in water. Thomas has shown that accelerated formation in water or steam at higher temperatures can substitute for a longer pre-transition period at lower temperatures.⁽¹⁷⁾ The means by which ZrO_2 films are formed is obviously an important factor in their subsequent behavior.

The work of this report has directed attention to direct measurements during corrosion with the object of avoiding changes in temperature and atmosphere upon removal of a specimen from an autoclave. At present a number of zirconium alloys in addition to titanium are being studied during corrosion in oxygen. The changes in film conductivity (both increases and decreases) are being related to the oxidation rates.

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REFERENCES

1. A. B. Libiard, "Ionic Conductivity," pp. 246-349 in Encyclopedia of Physics, S. Flügge, ed., volume 20, Electrical Conductivity II, Springer-Verlag, Berlin (1957).
2. J. E. Draley and W. E. Ruther, J. Electrochem. Soc. 104, 329-333 (1957).
3. L. Holland, Vacuum Deposition of Thin Films, John Wiley and Sons, Inc., New York (1956).
4. F. W. Peek, Jr., Dielectric Phenomena in High-voltage Engineering, McGraw-Hill, New York (1929).
5. A. Charlesby, Acta Metallurgica, 1, 340-347 (1953).
6. R. D. Misch, ibid, 5, 179-180 (1957).
7. R. D. Misch and F. H. Gunzel, Jr., J. Electrochem. Soc. 106, 15-20 (1959).
8. Ya. M. Ksendzov and V. G. Prokhvatilov, Zhur. Fiz. Khimii, 31, 321-7 (1957).
9. W. Meyer and H. Neldel, Z. f. technische Physik, 18, 588 (1937).
10. M. D. Carver and E. T. Hayes, The Effect of Microstructure on the Corrosion Rate of Alloys of Zirconium, USBM-U-123 (June 1, 1956).
11. J. J. Polling and A. Charlesby, Acta Metallurgica 2, 667-674 (1954).
12. R. D. Misch and W. E. Ruther, J. Electrochem. Soc., 100, 531-537 (1953).
13. R. D. Misch, Characteristics of Anodic and Corrosion Films on Zirconium, ANL-6149 (March 1960).
14. K. Hauffe, Oxydation von Metallen und Metallegierungen, Springer-Verlag, Berlin (1956).
15. R. D. Misch, to be published.
16. H. E. Haring, J. Electrochem. Soc., 99, 30-37 (1952).
17. D. E. Thomas and S. Kass, J. Electrochem. Soc., 103, 478 (1956).