ANL-6149
Metallurgy and Ceramics
(TID-4500, 15th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois

CHARACTERISTICS OF ANODIC AND CORROSION FILMS ON ZIRCONIUM

by

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May 1960

Metallurgy Division

Program 10.2.1

Publication of this report supersedes parts of the following Metallurgy Division Quarterly Reports:

ANL-4712, p. 37
ANL-4825, pp. 75-77, item 3
ANL-4966, p. 54
ANL-5097, p. 72, item 4

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CHARACTERISTICS OF ANODIC AND CORROSION FILMS ON ZIRCONIUM

R. D. Misch

I. ABSTRACT

Zirconium anodizes similarly to tungsten in respect to the change of interference colors with applied voltage. However, the oxide layer on tungsten cannot reach as great a thickness. Hafnium does not anodize in the same way as zirconium but is similar to tantalum. By measuring the interference color and capacitative thicknesses on zirconium (Grades I and III) and a 2.5 w/o tin alloy, the film was found to grow less rapidly in terms of capacitance than in terms of interference colors. This was interpreted to mean that cracks develop in the oxide as it thickens. The effect was most pronounced on Grade III zirconium and least pronounced on the tin alloy. The reduction in capacitative thickness was especially noticeable when white oxide appeared. Comparative measurements on Grade I zirconium and 2.5 w/o tin alloy indicated that the thickness of the oxide film on the tin alloy (after 16 hours in water) increased more rapidly with temperature than the film on zirconium. Tin is believed to act in two distinct ways: 1) to counteract the tendency of the oxide to form cracks, and 2) to produce vacancies which promote ionic diffusion.

II. INTRODUCTION

The oxide film which forms on zirconium has many features in common with the films on other metals. The oxide will form as a result of heating in oxygen or water, or can be grown by anodizing. Various electrical measurements are possible on the corrosion film produced by anodizing or by corrosion. Such studies are useful in understanding the properties of the film which control the corrosion rate.

In recent years a number of investigators, notably A. Charlesby,(5) L. Young(8) and J. N. Wanklyn,(9) have made valuable contributions to the understanding of the oxide films produced on zirconium by anodizing and by corrosion. In particular, Wanklyn's capacitance work showed that the corrosion product forming on zirconium of low corrosion resistance was permeable to a large extent to the electrolyte used in capacitance measurements. A number of similar studies were made at Argonne several years ago and these data are presented here for what additional insight they offer into corrosion mechanisms. The minimum weight gain studied by Wanklyn was 47 mg/dm^2. The interference color films which are largely the topic of this report represent maximum weight gains of approximately 50 mg/dm^2. Because of the variety of subject matter, each section will be treated as a unit, with appropriate discussion.

Among the many techniques which can be applied to thin films are the use of interference colors or measurements of electrical capacitance. The first method has been reviewed by Kubaschewski.(1) The simplest technique is to compare the colors with a standard scale of reference. A more exact procedure is to determine reflectance minima by means of a spectrophotometer.(2) In the present case, a General Electric step gauge was used, supplemented by the table of colors prepared by Rollett(3) (cf. Appendix). The GE gauge consists of layers of barium stearate built in steps which are 2 to 16 microinches thick. By matching colors, the oxide thickness may be expressed in terms of thickness of barium stearate or converted to thickness of an air film where the refractive index is unity, by multiplying by the refractive index of barium stearate ($n = 1.491$). The thickness has been expressed in terms of an air film when it was desired to make a comparison with film thickness determined from a capacitance measurement. The barium stearate gauge is compensated for a slight phase shift of the light upon reflection from the glass support. This effect occurs at many interfaces, including that between Zr and ZrO_2. Therefore, while the optical thickness of the ZrO_2 film is obtained by color matching, the geometric film thickness is equal to the thickness of an optically equivalent air film divided by the refractive index of ZrO_2 plus the phase change. The phase change may be positive or negative.

The capacitance method is discussed in Section IV of this report.

III. ANODIC BEHAVIOR OF ZIRCONIUM IN RELATION TO OTHER FILM-FORMING METALS

Zirconium, as well as other transition metals, can be anodized in various electrolytes. With several exceptions the anodic film growth is characterized by a dependence on the cell voltage applied to the anode metal and the inert cathode. If anodizing is done at several volts, a reference cell is desirable because the potential of the auxiliary electrode is not fixed. However, above 10 volts and with low currents the contribution of polarization and IR drop become negligible. The anodizing results given here are reported in terms of cell voltage with platinum used as the cathode.

Oxide films were produced on zirconium as well as titanium, niobium, hafnium, tantalum and tungsten. When these metals were anodized at a constant voltage, the oxide grew to a thickness proportional to the potential of the anode. Above several volts, this potential was equivalent to the voltage applied to the cell. At constant voltage, the film-forming current was high initially, but dropped exponentially until a small residual current was reached. For practical purposes the film was completely formed after several minutes at voltage, but small additional growth was still observed after several hours and days.

Anodizing for ten minutes was sufficient to permit a comparison between zirconium and other film-forming metals. The specimens consisted of rods or sheet of commercial purity except for the zirconium and hafnium, which were crystal bar made by the iodide process. All metals were wet-ground and etched to produce a bright surface. The etchant consisted of 100 ml 70% nitric acid, 100 ml distilled water, and sufficient hydrofluoric acid to produce a vigorous etch.

By anodizing in 1N H_2SO_4 at room temperature, a range of interference colors could be produced by raising the cell voltage. The voltage was raised in steps, held constant for ten minutes, and the resulting color was matched with the barium stearate stepgauge. Three orders of colors were visible on the gauge.

The results of color matching are shown in Figure 1 for titanium, niobium and tungsten, and in Figure 2 for zirconium, hafnium, tantalum and tungsten. Zirconium and tungsten had similar curves, and hafnium and tantalum were identical as far as could be judged. The lengths of the curves were determined by the maximum voltage which could be applied

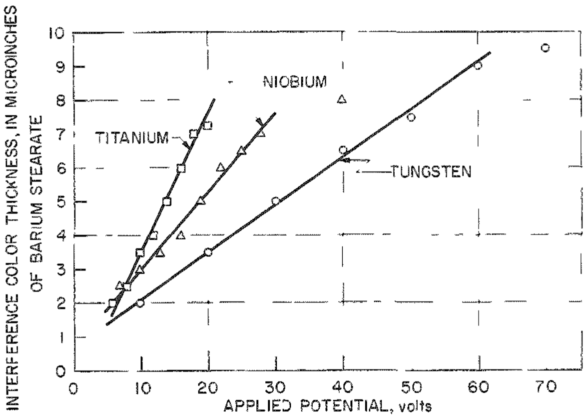

Figure 1

Film thickness vs. anodizing voltage for titanium, niobium and tungsten, held 10 minutes at each voltage in 1N H_2SO_4 at room temperature.

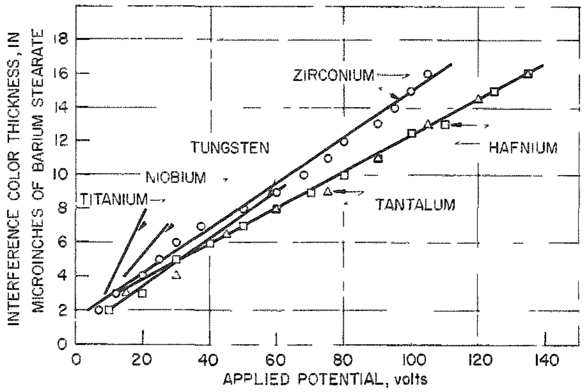

Figure 2

Film thickness vs. anodizing voltage for zirconium, hafnium and tantalum, held 10 minutes at each voltage in 1N H_2SO_4 at room temperature without breaking down the film. In this respect, titanium was least stable, and hafnium and tantalum were the most stable. It was interesting to note that zirconium differed from hafnium despite the close chemical similarity of these elements.

In addition, two grades* of zirconium (designated I and III) were compared with a 2.5 w/o tin alloy. The zirconium was differentiated by corrosion testing in water at 315°C for two weeks. The first grade formed a thin black oxide layer; the second formed a flaky white layer. The tin alloy formed a dark protective oxide similar to that formed by the more resistant sample of zirconium. The anodic films on these three materials were identical in respect to the curve of interference colors vs. applied voltage (cf. Figure 3). Consequently, the anodic film thicknesses appear to be relatively insensitive to compositional differences that are important in corrosion.

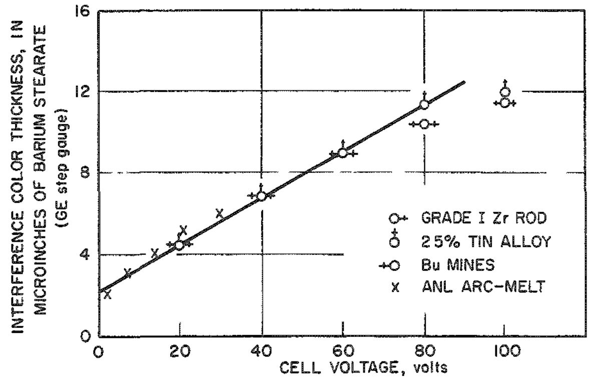

Figure 3

Variations of film thickness for zirconium from different sources

A comparison of the data for zirconium from this work and that of other investigators is given in Figure 4. Except for the Argonne data, the film thicknesses were estimated from tables of interference colors as a function of the width of an air space between glass plates.(4,5) The top curve is incorrect because it is based on Newton's colors as compiled by Quincke(6) for light reflected from an air wedge. Light reflected from an air film produces the so-called "bright" interference series, whereas an oxide film produces the "dark" series.(7) The "bright" series results from phase reversal at both boundaries or at neither boundary. Minima occur at thicknesses $\lambda/4n$, $3\lambda/4n$, $5\lambda/4n$.... The dark series results from

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*Zirconium crystal bar was classified at one time upon the basis of appearance after corrosion testing in water at 315°C for two weeks. Crystal bar with a uniform black or iridescent oxide film was called Grade I. Crystal bar with a white film (sometimes powdery or flaking) was called Grade III. Grade II crystal bar had a black film but was cut from bars which were partially covered with white oxide. In this study Grade III refers to arc-melted sponge zirconium instead of arc-melted crystal bar.

phase reversal at one boundary with minima at thicknesses 0, $\lambda/2n$, λ/n ... The color scale of the barium stearate gauge is complementary to Quincke's scale used by Guntherschulze and Charlesby. The complementary colors (which are transmitted) give the correct order for thin films on metals, and these were plotted by Charlesby using Rollett's table.(5) The difference between Charlesby's data and the Argonne data is not serious. Charlesby did not state the time used in anodizing. If his times had been shorter than the ten minutes used at Argonne, his films would have been thinner. There is no agreement on what constitutes a "standard" film thickness-voltage curve.

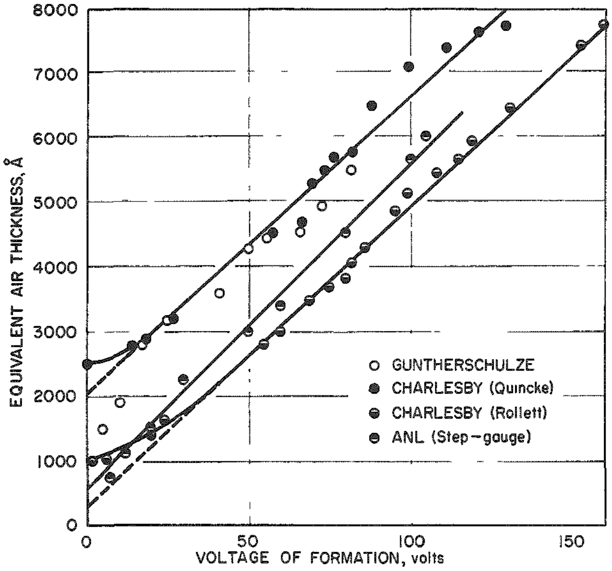


Figure 4

Argonne data on interference color thickness compared with those of other investigators

Independent correlations of optical thickness with the absolute thickness of the oxide on zirconium are complicated by the lack of knowledge of the true area of the surface and the density of the oxide. Consequently, weight gains cannot be translated directly into film thickness. The film thicknesses for anodic ZrO_2 given in ANL-4966, pg. 54, were based on an unjustified assumption and were in error. The present report does not treat the problem of absolute film thicknesses.

Color matching of oxide films can be very accurate if done with similar materials. This is illustrated by Figure 5, where colors were matched on titanium and zirconium without reference to the barium stearate standard. The zirconium was anodized first, and the titanium was then anodized to match the colors on the zirconium. This procedure probably eliminated certain distracting factors in comparing an oxide with a barium stearate film.

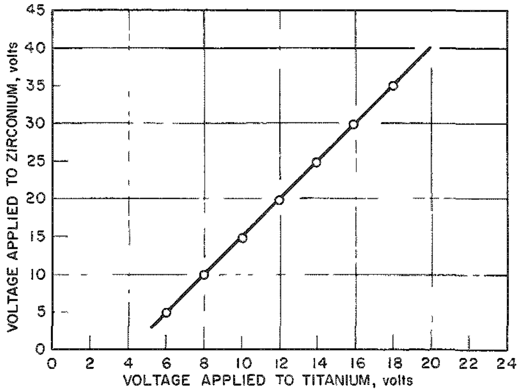


Figure 5

Comparison of anodizing voltages required to give identical colors on zirconium and titanium

IV. MEASUREMENTS OF FILM THICKNESS ON ZIRCONIUM DURING CORROSION

The corrosion films which form on zirconium in the initial stages of film growth in high-temperature water exhibit interference colors identical in appearance to those of the anodic films. Changes in thickness of the thin films can be followed by comparison with the GE stepgauge.

A. Capacitance as a Measure of Film Thickness

Preliminary tests also indicated that capacitance measurements could be readily made with zirconium. The capacitance method is applicable when the oxide is a good dielectric, as it is in this case. When an oxidized specimen is immersed in an electrolyte, the metal and electrolyte serve as the plates of a condenser. The auxiliary electrode such as platinum is chosen to have a larger capacitance which has a negligibly small impedance.

If C is the capacitance of 1 cm^2 of the surface and ϵ is the dielectric constant of the layer having a thickness δ, then

$$C = \epsilon/4\pi\delta \qquad (1)$$

or

$$\delta/\epsilon = 1/4\pi C \text{ cm (electrostatic units)} \quad . \qquad (2)$$

The relation of capacitance to film thickness can be demonstrated by using anodic films whose thickness is proportional to the anodizing voltage.

Some results are given in Figure 6 for various conditions. Young(8) anodized at 10 ma/cm^2 in 0.2 N H_2SO_4 and stopped when he reached the desired voltage. Charlesby(5) stated that the specimens were brought to the desired voltage, but times or current densities were not given. He used an ammonium borate solution. The two upper curves were obtained at Argonne by bringing the specimen to voltage in 5 to 10 minutes and holding constant for one-half hour. The anodizing electrolyte was a saturated boric acid solution which was carefully purified by repeatedly anodizing aluminum strip to 600 v. Impurities were presumably trapped in the porous anodic layer. Such treatment was necessary to reach 500 volts on the zirconium. In one case the capacitance was measured in dilute acetic acid and in the other case a dry measurement was made using mercury. The capacitance measurements were made with a General Radio Company impedance bridge type 650-A using a frequency of 1 kilocycle. The difference between the curves might be related to the existence of cracks which the acetic acid penetrated but the mercury did not. The lower curves of Young and Charlesby are believed to represent less complete stages of anodizing than were obtained at Argonne.

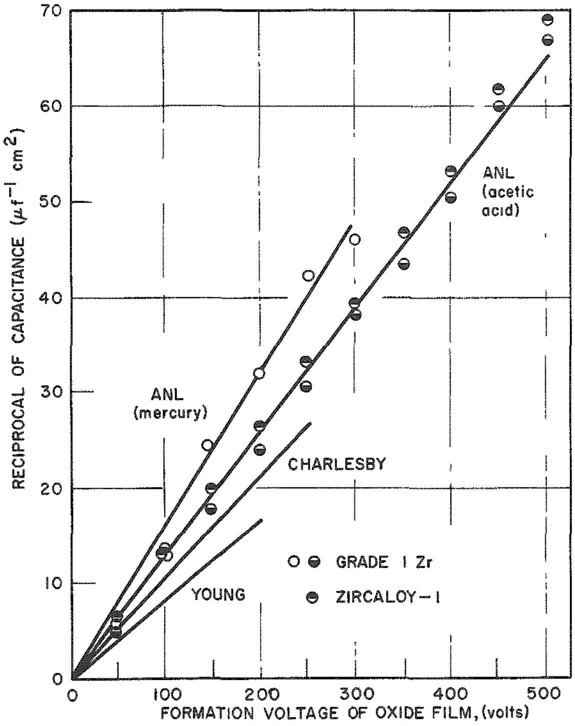


Figure 6

The reciprocal of capacitance of anodic films as a function of the voltage of anodizing of zirconium and Zircaloy-1, anodized in boric acid, measured in 1N acetic acid and mercury. The short lines represent the data of other authors.

B. Measurements of Film Thickness during Corrosion

The following materials were used in the corrosion study: zirconium melted from sponge in a graphite crucible (Grade III), zirconium arc-melted from crystal bar (Grade I), and a zirconium alloy (Zircaloy 1) containing 2.5 w/o tin. The available analyses are given in Table I.

TABLE I

COMPOSITION OF ZIRCONIUM ALLOYS USED IN CORROSION STUDY (wt. per cent)

Element	Grade III Zirconium	Grade I Zirconium	2.5 w/o Tin Alloy
C	0.17**	0.01*	0.01*
Sn	<0.01	<0.01	2.47**
Fe	0.02	0.04	<0.01
Ti	<0.1	<0.01	<0.01
Hf	0.7	<0.1	< 0.1
As, Ba, Ca, Mo, P, V, Zn	<0.1	<0.1	<0.1
All other	<0.01	<0.01	<0.01

*Typical analysis for arc-melted crystal bar.

**Gravimetric, remainder spectroscopic.

NOTE: In addition to carbon, other deleterious elements were undoubtedly higher in the Grade III metal, e.g., Al and N.

The Grade I metal was in the form of extruded rod, while the other metals were rolled plate. The extruded rod was machined to a smooth surface and cut to 1-in. lengths. The plates were also cut to convenient size for insertion into autoclaves. Each piece was drilled and tapped for ease of handling. Several specimens of each type were available and all were used more than once.

The metal was either wet polished or vapor blasted and etched in HF-HNO_3 solution. The specimens were then placed in autoclaves containing distilled water at room temperature. The water was not boiled or gas-saturated prior to sealing. The autoclaves were placed in an oven at 315°C and removed at 15-minute or longer intervals. The reported time of exposure is based on a single uninterrupted test. Approximately one hour was required to arrive at temperature, as determined by a thermocouple taped on an autoclave in use.

The optical thickness of the oxide was estimated from the color of the specimens after removal, and the electrical capacitance was measured by inserting the specimen into an electrolytic cell with platinum gauze as the second electrode. Each piece was fully immersed except for the top, and all measurements were made at room temperature. The measured capacitances were independent of the nature of the electrolyte if the conductivity was high. Sulfuric, nitric or phosphoric acids could be used, but 1N sulfuric acid was preferred. The reported values were stable and reproducible. The General Radio Company impedance bridge type 650-A at one kilocycle was also used here.

There was no appearance of color on the specimens until the autoclave reached 315°C at approximately 1 hour. In this same interval the electrical capacitance dropped steadily from about 3 to 1.5 microfarads/cm^2. This drop was larger than those observed subsequently, but the reciprocal of capacitance (which is proportional to thickness) showed the most rapid increase after the autoclave had come to temperature.

1. Interference color changes

The data for change in optical film thickness are given in Figures 7, 8, and 9. The results are presented as the equivalent optical thickness of air (in millimicrons) vs. time in hours in the autoclave.

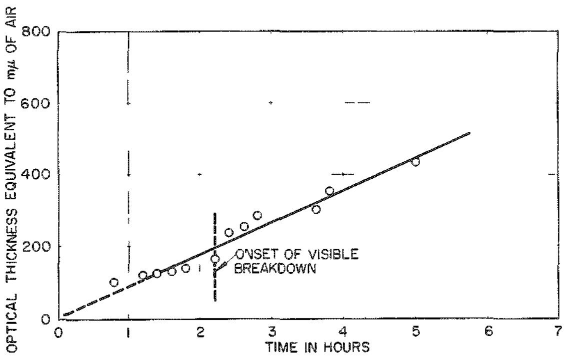


Figure 7

Optical thickness of the oxide layer on Grade III zirconium as a function of time of exposure to 315°C water. The specimens were at temperature from 1 hour on.

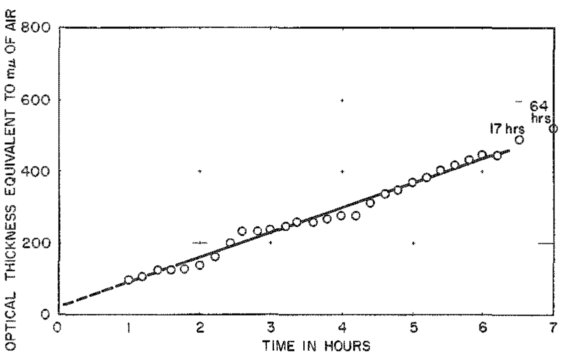


Figure 8

Optical thickness of the oxide layer on Grade I zirconium as a function of time of exposure to 315°C water. The specimens were at temperature from 1 hour on.

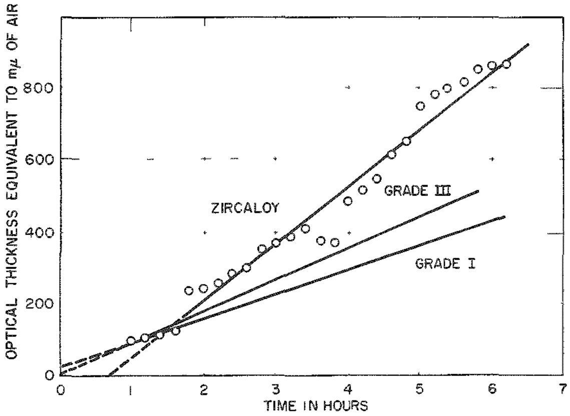


Figure 9

Optical thickness of the oxide layer on Zircaloy-1 as a function of time of exposure to 315°C water. The specimens were at temperature from 1 hour on.

The thickness was measured first by the step gauge to make an approximate color match. Rollett's data were then used to permit more exact identification. A ZrO_2 step gauge was also made by anodizing in increments of 5 v and was helpful in supplementing Rollett's descriptions. In general, the colors did not develop uniformly over the entire surface, and some judgment was necessary to select the one which was predominant. Accurate estimation was not possible beyond 6 hours, since the colors darkened as they reached the third and fourth orders. In the case of the Grade III zirconium, each point represents an average from two specimens. In the remaining figures, each point represents a single specimen. Some white oxide appeared on the surface of the Grade III zirconium at 2.2 hours and developed steadily until at 6 hours the surface was grey with only a slight underlying blue tint. In the period from 2 to 5 hours the color of the specimen continued to change, indicating increasing oxide thickness. At the same time, the fraction of the surface covered by white oxide also increased steadily until in 16 hours the surface was entirely white. The Grade I and tin alloy showed a steady color change without the appearance of white oxide. The rate of film growth was greatest for Zircaloy I, as seen from Figure 9, where the curves are compared.

2. Capacitance changes measured in 1N H_2SO_4

The data were obtained as specific capacitance in microfarads/cm^2 for each specimen. The capacitative thickness was then calculated using formula (2). Converting from practical to electrostatic units,

$$\delta/\epsilon = 1/113 \times 10^5 \; (1/C) \qquad (3)$$

where 1 microfarad = 9×10^5 electrostatic cgs units or statfarads.

The results were plotted as δ/ϵ, since ϵ, the dielectric constant was not known. The data are presented in Figures 10, 11, and 12. In contrast to the optical thickness, a definite maximum was observed in Figures 10 and 11 and possibly in 12. The three curves are compared in Figure 12.

The curve for Grade III zirconium began to level off at just the point (2.2 hours) where the white oxide first made its appearance. The drop in capacitative thickness paralleled the steady covering of the surface by white oxide. An indication of the relative capacitative thicknesses reached at 6 hours is given by the comparison in Figure 12.

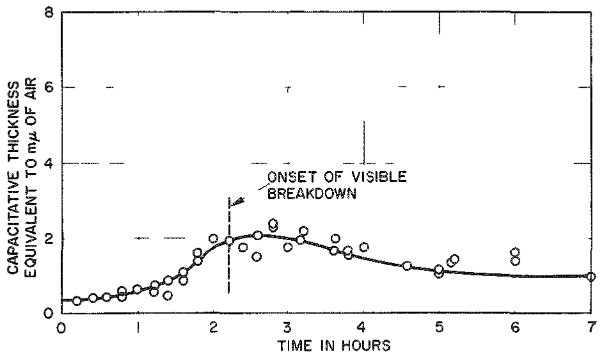


Figure 10

Capacitative thickness of the oxide layer on Grade III zirconium as a function of time of exposure to 315°C water

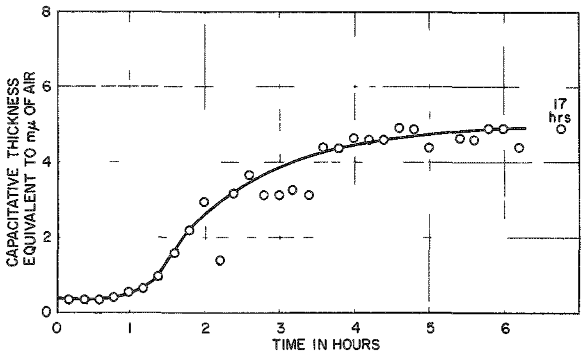


Figure 11

Capacitative thickness of the oxide layer on Grade I zirconium as a function of time of exposure to 315°C water

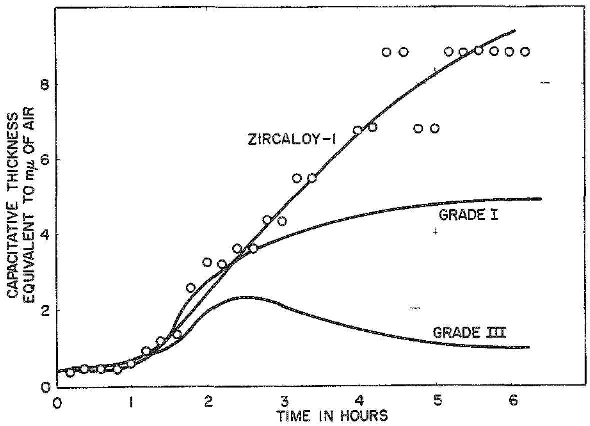


Figure 12

Capacitative thickness of the oxide layer on Zircaloy-1 as a function of time of exposure to 315°C water

The relationship between the preceding sets of data is shown in Figures 13, 14, and 15. Optical thickness is plotted vs capacitative thickness for each material, and all three curves are compared in Figure 15 Straight lines would result if both methods were measuring the thickness of films of uniform properties. The tendency upward is most likely due to a leveling off in capacitative thickness.

The slopes of the straight-line portions for Grade I zirconium and Zircaloy-1 should be equal to the corresponding values of the product of the dielectric constant and refractive index n. For the two materials, these products were about 48 and 64. It is interesting that the value for zirconium is close to that deduced by Charlesby,$^{(5)}$ who reported $n = 2.2$ and $\epsilon \simeq 20$ for anodic films, with the product equal to ~ 44. Apparently the oxide properties for the tin alloy are different.

The intercepts of these curves on the ordinate are a measure of the phase shift when light is reflected from the metal-film interface. This constant is of the order of 60 mμ and is smaller than the 205 mμ

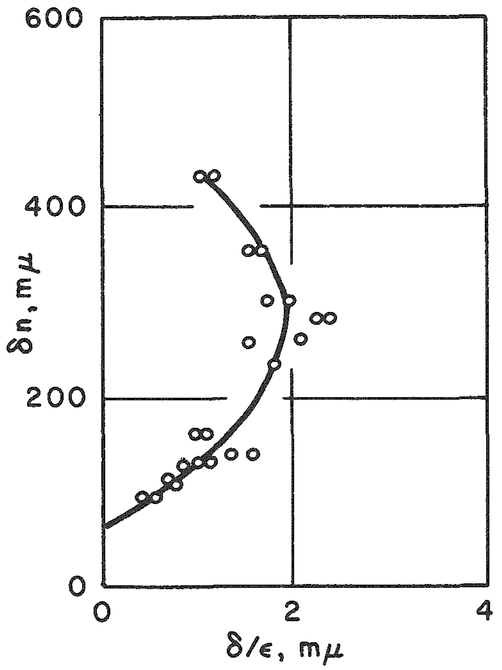
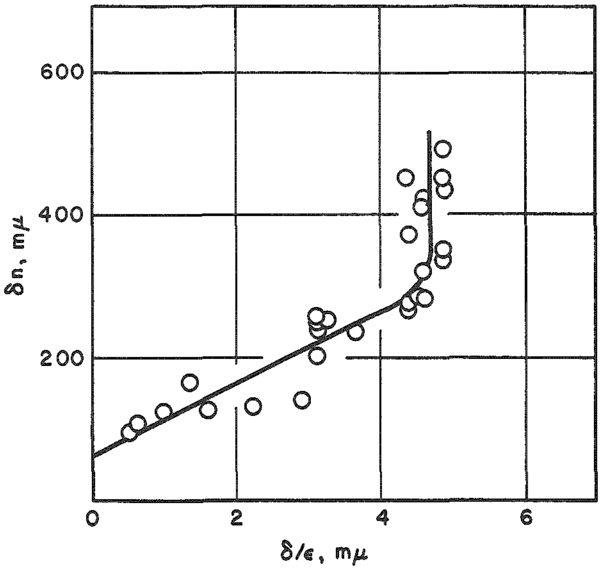


Figure 13

Optical vs. capacitative thickness for oxide layers produced on Grade III zirconium by exposure to 315°C water



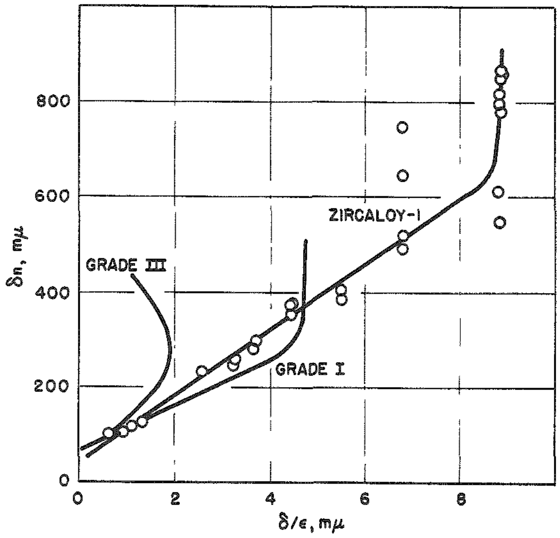


Figure 14

Optical vs. capacitative thickness for oxide layers produced on Grade I zirconium by exposure to 315°C water

Figure 15

Optical vs. capacitative thickness for oxide layers produced on Zircaloy-1 by exposure to 315°C water

which Charlesby found for anodic films.(5) The curve for Zircaloy-1 gave the longest linear relationship. One may assume that the leveling-off in capacitative thickness represents the maximum thickness of a diffusion barrier layer at the metal-oxide interface. On the basis that $\epsilon = 20$, as determined by Charlesby for anodic films,(5) the barrier layer thickness becomes: Grade III, 54 mμ; Grade I, 135 mμ, and Zircaloy-1, 238 mμ. Strictly speaking, the same dielectric constant should not be used for Zircaloy-1 as for zirconium because of the tin content of the alloy. The suggested barrier layer thickness is probably a reasonable approximation.

The same specimens were next exposed for 16 hours at 100, 150, 200, 250, and 300°C. The surfaces were freshly cleaned for each test. Autoclaves were used except for the lowest temperature, where beakers were employed. The total time was chosen sufficiently long that the time to arrive at temperature would not be a significant factor.

The data are presented in Figures 16, 17, and 18. Three specimens were exposed at each temperature, and each point represents a single specimen. The capacitative thickness is proportional to the reciprocal of these values. All three materials showed a linear relationship between capacitance and temperature in the range between 100 and 250°C.

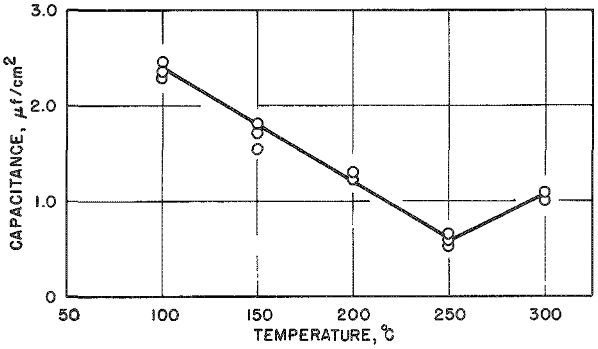


Figure 16

Electrical capacitance of the oxide layer on Grade III zirconium after 16-hour exposure to water at temperatures from 100 to 300°C

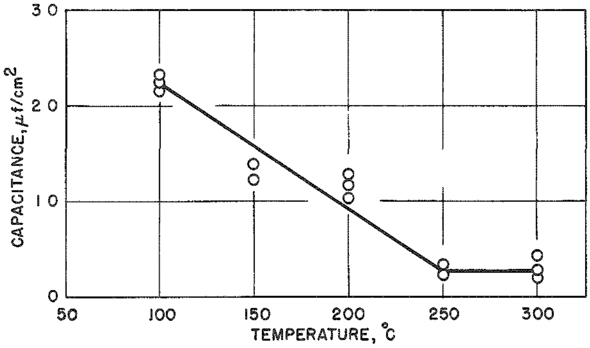


Figure 17

Electrical capacitance of the oxide layer on Grade I zirconium after 16-hour exposure to water at temperatures from 100 to 300°C

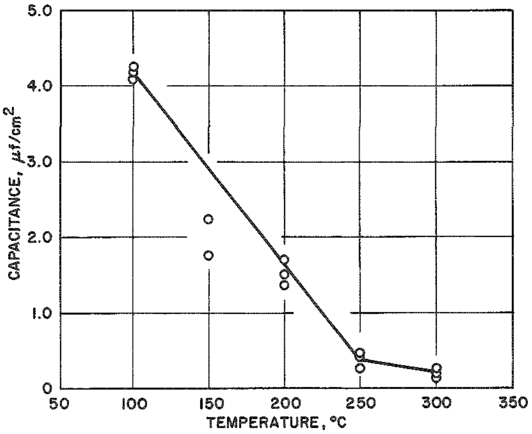


Figure 18

Electrical capacitance of the oxide layer on Zircaloy-1 after 16-hour exposure to water at temperatures from 100 to 300°C

The slope of the line for the tin alloy was greater than those for Grades I and III zirconium, which were similar. The capacitance then leveled off for the Grade I zirconium and tin alloy but increased for the Grade III zirconium. The latter was covered with white oxide.

These data may be considered in the light of a logarithmic-type growth law in which the oxide grows rapidly initially and then slows to a very low rate. The effect of such a growth law is that the oxide thickness reaches a plateau or "limiting thickness" which is temperature dependent. At 350°C the oxide on zirconium is approaching the plateau at 16 hours, but 50 hours are required before the weight gains level off. However, the change of capacitance at 16 hours is a good indication of the relative variation of the "limiting thickness" with temperature.

Apart from theoretical considerations, these data indicate that the corrosion of zirconium is measurable at temperatures as low as 150°C, where the oxide is still invisible, and that the presence of tin changes this corrosion rate. More precise measurements of this type may permit derivation of a useful temperature coefficient.

An interesting technique was employed by Charlesby,(5) who measured the capacitances of zirconium specimens which had been anodized at a constant voltage at 20 and 85°C in an electrolyte of ammonium borate. The films were formed for six hours, and the capacitance was measured at room temperature. Extrapolation from these two temperatures to zero capacitance (infinite film thickness) gave an intercept of 250°C. According to Charlesby, this temperature represented the upper limit of applicability of the Mott-Cabrera theory,(11) which states that corrosion films under certain conditions will grow only to a well-defined thickness.

This technique was extended to higher temperatures at ANL by using a pressure autoclave with insulated leads. Capacitance and color changes were both used to measure film thickness. Electrodes of Grade I zirconium crystal bar or 2.5 w/o tin alloy were inserted into the electrolyte consisting of 0.5 w/o sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$). The autoclave was quickly brought to the desired temperature. The zirconium was then made 10.2 volts anodic to a surrounding electrode of 347 stainless steel. The voltage was maintained for 30 minutes and then disconnected. After cooling the autoclave rapidly to room temperature, capacitance measurements were made with the bridge at 1 kc using a platinum gauze electrode and the same sodium borate solution. The color of the specimen was then compared with a color gauge prepared by anodizing a zirconium rod to different voltages at room temperature. These voltages are designated as arbitrary units on Figures 19 and 20.

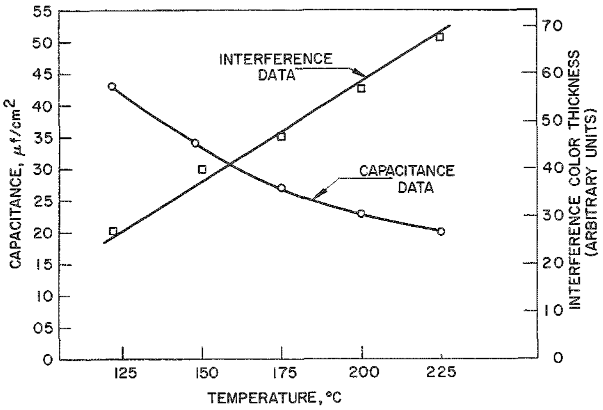


Figure 19

Capacitance and interference color thicknesses of the oxide on Grade I crystal bar zirconium after anodizing at 10.2 v vs. stainless steel in 0.5 w/o sodium borate solution for 30 minutes

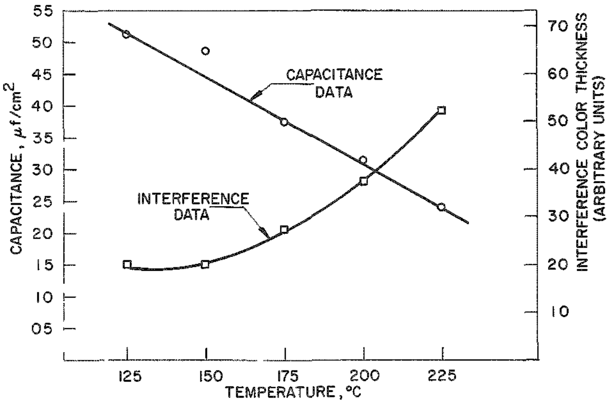


Figure 20

Capacitance and interference color thicknesses of the oxide on zirconium after anodizing at 10.2 v vs. stainless steel in 0.5 w/o sodium borate solution for 30 minutes

The capacitance-temperature curve for Grade I crystal bar cannot be extrapolated to zero capacitance because of the curvature. The curve for the tin alloy seems to extrapolate to zero capacitance at 315°C, but this curve probably changes as zero capacitance is approached. It is apparent from the interference colors that the film on the tin alloy grew more rapidly with temperature than did the film on the zirconium. Higher temperatures were desirable but not feasible because of the presence of Teflon seals.

C. Measurements on Thicker Corrosion Films

1. Spectrophotometric Examination

It is theoretically possible to carry the interference method beyond the point where the eye can distinguish distinct colors by using a spectrophotometer. Some measurements of this type were made by using the reflection attachment of a Beckman spectrophotometer and looking for absorption maxima. The method has been used for thin films on tantalum.(2) Three zirconium specimens which had been exposed to high temperature water (cf. Table II) were obtained. The first specimen was a lustrous black with a slight pink and green cast. The lower-grade zirconium had a graying coat with slight coloration and small white areas. The 2.5 w/o tin alloy was completely black. Each specimen was compared for intensity of reflection with a metallographically polished piece of Grade I zirconium which had been etched to a bright surface in HF-HNO_3. No absorption maxima could be distinguished over the range from 400 to 800 mμ. As seen from Table II, the second specimen reflected significantly more light (120 to 180%) than did the standard. This was attributed to the presence of white oxide, because the reflected intensity of the polished zirconium should have been a maximum as compared to the coated surfaces. However, polarization upon reflection from several mirror surfaces may have reduced the intensity as compared to a nonpolarizing matte surface.

TABLE II

REFLECTIVITY AND CAPACITANCE FOR ZIRCONIUM WITH THICK FILMS

Specimen	Per cent Reflectivity*	Capacitance, μf/cm^2	
		1N H_2SO_4	Evaporated Gold
Grade I Zr, 336 hr at 315°C	54 to 64	3.7	0.00065
Lower-grade arc-melted crystal bar, 112 hr at 260°C	120 to 180	0.00023	indefinite
2.5% Tin alloy, 324 hr at 315°C	56 to 69	0.048	0.0043

*Based on 100% reflection for polished and etched zirconium.

For comparison, two types of capacitance measurements were also made. The first method was similar to that already used except that a Lucite cell was used with an O-ring gasket which fitted against the metal surface. The exposed area was 0.71 cm^2. It was also found that a sharper null was obtained when the zirconium was made 1.0 volt positive to the platinum. This voltage was too low to have any perceptible effect on the coating. The second method used a film of evaporated gold, 10^{-5} cm thick and 1 cm^2 in area. Contact was made by a gold wire. The values in the table are averages for two spots. The higher capacity in 1N H_2SO_4 probably represents the penetration of cracks in the coating.

The failure of these techniques to give meaningful results is attributed to the thickness and nonhomogeneity of the corrosion film. Wanklyn's technique,(9) where capacitances (as measured in aqueous electrolytes) were correlated with corrosion resistance, is probably the best approach to evaluating thicker corrosion films It is obvious from Table II that the capacitances measured with gold had no relationship to the capacitances measured in 1N H_2SO_4.

V. DISCUSSION

The present study was confined to the thin film region where the oxide layer exhibited interference colors. These thin films are generally assumed to be homogeneous with no significant changes until the breakaway thickness is reached. This assumption is incorrect because the capacitative thickness begins to deviate from the optical thickness after relatively short times. This deviation suggests that the oxide is becoming permeable to electrolyte, perhaps by means of cracks perpendicular to the surface. Such cracks would not change the light reflection until they became very numerous. The surface probably becomes white when the density of cracks is high. A residual barrier layer is assumed to remain at the metal-oxide interface. The rate of oxide growth is higher on 2.5 w/o tin alloy than on the Grade III zirconium, but more of the film degenerates to a permeable layer in the latter case.

For films having thicknesses beyond the interference color range, Wanklyn(9) showed that the corrosion resistance of zirconium could be expressed by combining weight gain and capacitance data. He proposed the factor 1/CW, where C is the capacitance in $\mu f/cm^2$ and W is the weight gain in mg/cm^2. A good alloy such as Zircaloy-2 was found to have low C and low W while a poor alloy had high C and high W. Tin alloy was found to be an exception, with low C but high W. The Argonne data given in this report show that these phenomena extend to the thin-film range where Wanklyn's technique has not been applied.

The changes reported here indicate an important difference between film growth during anodizing and during corrosion. A consideration of the method of formation of these films indicates why this is so. The growth of anodic films occurs because a high electric field in the oxide produces electrolytic migration of oxygen anions. In addition, the high field strength during anodizing (approximately 10^6 v/cm^2) will tend to compress the anodic film in its direction of growth. By contrast, the growth of the corrosion film occurs because of diffusion caused by thermal activation of diffusing oxygen and a concentration gradient in the film. The formation of cracks in the anodic and corrosion films will doubtless be different as a consequence of the different influences of these factors.

Another consideration is that the ZrO_2 film in water is subjected to hydrolysis which will cause the decomposition of ZrC, ZrN and other intermetallic compounds. The conversion of these compounds to ZrO_2 may cause cracks in the protective film, which lead to the formation of white oxide.

This is probably one reason why Grade III zirconium develops white oxide so rapidly in high-temperature water, while the anodic films at room temperature have the same thicknesses as Grade I zirconium. To be acceptable, this mechanism must also be able to explain the ability of tin to compensate for the presence of nitrogen. It is possible that these elements compensate in some other way to reduce stresses in the oxide arising from nitrogen alone. Tin by itself is not desirable, as evidenced by the higher corrosion rate of the binary alloys in high-temperature water as compared with pure zirconium.(10) A specific mechanism of compensation has been suggested by Thomas,(10) who proposed that tin and nitrogen ions associated in the ZrO_2 lattice to tie up anion vacancies.

At least two distinct types of deleterious additives can be envisaged. The first is an impurity which is in solid solution in both the zirconium and the corrosion oxide. This type of impurity is assumed to create defects in the film which promote ionic diffusion. The second is an impurity which is largely present in a second phase. Second-phase impurities may be deleterious because they promote mechanical breakdown of the film. It may be possible to distinguish these two cases by means of an anodizing technique.

Using homogeneous alloys it may be possible to measure anodic currents in such a way that the data are indicative of point defects in the oxide. Such measurements should be made at a number of temperatures to obtain the temperature coefficient of these currents. A useful evaluation of homogeneous alloys might be possible on the basis of such measurements.

The second type of impurity will depend on compatibility with the ZrO_2 lattice and stability to attack by high-temperature water. Anodizing techniques will not be applicable here. Further studies are desirable to delineate the specific role of various elements on the conductivity and structure of the oxide.

ACKNOWLEDGEMENT

The author is indebted to J. E. Draley for many valuable suggestions and to W. E. Ruther for advice in the course of the experimental work.

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APPENDIX 1

Thicknesses of Color-producing Air Films According to Rollett*

Color-order	Color in reflected light	Color in transmitted light	Thickness of air film, mm
I	black	white	0.000000
	dark lavender-gray	brownish white	0.000100
	brighter lavender-gray	bright brown	0.000107
	very bright lavender-gray	dark brown	0.000116
	bluish white	red-brown	0.000124
	greenish white	dark purple	0.000129
	yellowish white	dark violet	0.000135
	pale straw-yellow	dark blue	0.000140
	brown-yellow	brighter blue into greenish	0.000164
	orange	still brighter blue	0.000235
	red	pale blue-green	0.000245
II	purple	pale green	0.000257
	violet	bright yellow-green	0.000272
	indigo	bright yellow	0.000282
	sky-blue	golden-yellow	0.000300
	brighter sky blue	orange	0.000352
	very bright blue-green	red	0.000372
	bright green	deep purple	0.000387
	yellow-green	violet	0.000409
	yellow	blue	0.000435
	bright orange	brighter blue	0.000465
	red	bluish green	0.000490
III	purple	green	0.000520
	violet	bright yellow-green	0.000550
	blue	yellow	0.000570
	sea-green	flesh-red	0.000600
	green	purple	0.000650
	pale yellow-green	grey-blue	0.000680
	pale yellow	grey-blue	0.000726
	red	sea green	0.000750
IV	purple, then faint purple	green, then yellow-green	0.000780
	grey-blue	faint yellow	0.000852
	sea-green	flesh-red	0.000870
	green and grey-green	grey-red	0.000912
	grey red, red, faint red	grey green, then green and greenish white	0.000996
V	blue green, faint initially and finally	flesh-red	0.001168
	flesh-red, faint initially	sea-green	0.001264
VI	and finally blue green, faint initially	flesh-red	0.001450

*A. Rollett, Sitzber. Akad. Wiss. Wien. Math.-naturw. Kl., 77, Abt. III, pg. 229 (1878).

APPENDIX 2

Thicknesses of Air Films Corresponding to Microinches of Barium Stearate

(Index of refraction = 1.491)

Color-Order	Microinches of Barium Stearate	Millimeters of Air
I	2	0.000072
	3	0.000109
	4	0.000145
	5	0.000182
	6	0.000218
II	7	0.000255
	8	0.000291
	9	0.000328
	10	0.000364
	11	0.000400
	12	0.000437
	13	0.000472
III	14	0.000510
	15	0.000546
	16	0.000581