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ANODIZING AS A MEANS OF EVALUATING
THE CORROSION RESISTANCE OF
ZIRCONIUM AND ZIRCONIUM ALLOYS

By
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December 1953

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December 1953

Metallurgy Division

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ANODIZING AS A MEANS OF EVALUATING THE CORROSION RESISTANCE OF ZIRCONIUM AND ZIRCONIUM ALLOYS

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ABSTRACT

Zirconium of varying quality was tested by anodizing at constant voltage and at constant current density. The pattern of film growth was found to be sensitive to metal composition and surface preparation. The relation of anodic film growth to corrosion must take into account certain characteristics peculiar to anodizing. These are chiefly concerned with the electrical field in the oxide and the effect of electrolytes.

Zirconium specimens were compared visually after anodizing at constant voltage for times below one hour. Initial work was conducted with a bath (dilute sulfuric and nitric acids) which gave rapid film breakdown on metal of low quality. Later work was conducted with baths giving very slow breakdown. Preliminary correlation with autoclave tests was promising but could not be improved by modification of anodizing conditions.

At constant current density (1 ma/cm^2), it was found on series of WAPD specimens that a high maximum voltage was an indication of failure on the 750°F steam test. Zirconium arc-melted at ANL did not confirm this relationship. At a lower current (0.1 ma/cm^2) the rise of the voltage time curve was found to correlate with metal quality. The electrical conductivity of the oxide layer may be a factor determining corrosion. Residual currents (at a constant voltage) correlated with the voltage-time curves.

A semi-conductor theory of anodizing is proposed to account for cell-voltage maxima and breakdown. A transition from p to n conductivity (at the inner layer) is believed to be responsible.

I. INTRODUCTION

A. General

Subtle differences in the corrosion resistance of zirconium are not easy to determine except by prolonged testing under service conditions. The development of useful alloys is hampered by the long time required in testing to differentiate slight changes in corrosion behavior. Present knowledge of the corrosion mechanism is not adequate to serve as a basis in formulating alloys. The performance of any particular piece of metal cannot safely be predicted.

The purpose of this investigation was to investigate anodic treatments as a means of determining corrosion resistance. Zirconium develops an oxide layer when made anodic in an aqueous non-corrosive electrolyte. Aluminum, tantalum, antimony, and other metals have the same property. A general review of anodic phenomena is given in Appendix I for reference purposes. In the case of aluminum the anodic coating is known to be sensitive to the composition of the metal or alloy.⁽¹⁾ The early data on zirconium⁽²⁾ are too meager to permit a similar conclusion. The more recent work of Charlesby was largely given to determining the physical constants associated with film growth;^(3,4) the effect of metal purity or composition was not investigated. From the standpoint of corrosion, even small changes in concentration of certain impurities are of paramount importance. It was desirable to detect such changes by forming the oxide layer anodically.

The effect of electrolyte on the anodizing of zirconium has been discussed in a recent review.⁽¹¹⁾ Both fluoride and chloride ions produce film breakdown on zirconium. Nitric acid has some specific effects which are highly dependent on concentration.⁽¹²⁾ Excepting those electrolytes and chromates,⁽³⁾ which bear some resemblance to nitric acid, the general pattern of oxide growth on zirconium is similar for most dilute aqueous electrolytes.

In the anodizing of zirconium the chief factor which governs film growth is the applied voltage.⁽²⁾ When a dc voltage is applied to the cell, Zr/non-corrosive electrolyte/inert metal, the formation of an oxide layer on the zirconium is observed when approximately 5 v is applied.⁽³⁾ From this point to a much higher voltage the film thickness increases in the ratio 21 Å/volt. The growth of oxide is attended by the appearance of interference colors and the structure is monoclinic ZrO_2 . At a fixed voltage the film grows very rapidly initially and then stops. It is concluded from this that a critical field of the order of 10^6 v/cm is necessary to initiate rapid ionic current through the oxide layer (and therefore produce film growth). Ionic current nearly ceases just below this value, although larger electronic currents still may flow. It is evident that some ionic current must still be flowing since the film continues to grow at the small e.m.f. of the corrosion reaction.

B. Comparison of Corrosion and Anodizing

The concept of the growing oxide layer as an electrolytic cell as developed by Wagner⁽⁷⁾ may be employed to demonstrate a close similarity in the factors governing film growth on zirconium, both in corrosion and by anodizing. A comparison of the basic mechanism is made in Figure 1. It is seen that film growth requires the conduction of both ions and electrons in the case of corrosion but not in anodizing. In anodizing zirconium, however, electronic current is not negligible and oxygen evolution accompanies film growth. The ratio of electronic to ionic current, i_E/i_I , is such that the efficiency of anodizing is close to zero in the region of 10 microamp/cm² and approaches 100% at approximately 2 ma/cm².⁽³⁾

Figure 1. Comparison of the Mechanism of Film Growth in Corrosion (lefthand figure) and Anodizing.

C. Scope of Investigation

The investigation may be divided into two parts. The first was a study of correlations based on surface appearance; the second was work on electrical measurements of anodic films. Initial efforts were devoted largely to a test of the first type while later work was given to the second aim. As a consequence, the results are given somewhat in chronological sequence.

Direct current was employed in all cases with platinum or zirconium as the cathode. The external variables subject to control by the investigator were the following: voltage, current, type and concentration of electrolyte, temperature, and variations of voltage and current with time. Data were obtained on various aspects of all of these variables.

II. EXPERIMENTAL PROCEDURE

A. Materials

The zirconium was obtained from different sources and had different histories of treatment. Nearly all specimens were crystal bar or arc-melted crystal bar. The specimens may be grouped as follows:

- 1) Early BuMines Plate of very poor quality.
- 2) Crystal bar, Grades I, II, and III.*
- 3) Arc-melted and rolled specimens from WAPD which had been subjected to the 750°F steam test. Duplicate specimens were undergoing long term testing in water at 550°, 600°, and 680°F.
- 4) Specimens arc-melted at ANL from Grades I and III crystal bar.
- 5) Miscellaneous alloys.

Further information was not available on groups 1 and 2. The available information on the remaining materials is closely allied to the data on anodizing and will be deferred to the section on results.

*These grades are defined according to the appearance of zirconium after exposure to water at 315°C for two weeks. Grade I indicates a surface with a uniform dark oxide film. The appearance tends toward a shiny black with some faint color. Grade II is the same surface but with white oxide on some areas. Grade III indicates an all-white surface. Zirconium alloying has developed to an extent where these terms are infrequently used.

B. Form of Specimens

Most of the crystal bar was used in the as-received form. The entire area was never anodized since the clamp making electrical contact was kept out of the solution. The WAPD specimens consisted of small samples cut from rolled plate. Each of these specimens was drilled to accommodate a tapered zirconium rod making contact by a press fit. All of the specimens were attached to threaded rods when measuring voltage-time curves. Various materials were used for masking off part of the surface.

The ANL specimens consisted of rectangular blocks machined from the top and bottom of four arc-melted ingots. They were also drilled and tapped.

C. Surface Preparation

The chief problem was one of removing oxide left as a residue from corrosion testing or previous anodizing. There was no chemical or electrochemical method for achieving this removal, so mechanical means had to be employed. Wet grinding was used for flat surfaces and vapor blasting for the irregular surfaces of crystal bar. The latter process consisted of blasting a slurry of fine silica gel in water against the surface with compressed air. It had the advantage over sand or shot blasting in that the surface was kept wet and cool.

Following mechanical treatment, the surface could be pickled or electropolished. The usual procedure in the former case was to employ solutions containing HF and HNO₃; the fluoride was sometimes added in the form of ammonium salts. The concentrations were not critical, but it was desirable to have the nitrate ion in excess. The use of HF alone left a black residue on the surface. The mixture found to be consistently satisfactory consisted of 8 ml con. HF (48%), 50 ml con. HNO₃ (70%) and 50 ml tap water. Some of the work on crystal bar was done after pickling with a solution of: 20 gm NH₄F, 500 ml con. nitric acid, 500 ml water. This mixture could be used at room temperature, but the action was improved by heating. After pickling, the specimens were rinsed in tap water, usually above room temperature. The surface was left bright and was generally suitable for anodizing if no crevices were present. The surface could not be allowed to dry before rinsing or premature film breakdown occurred. Evidently, fluoride salts were left on the surface.

The most effective method used thus far for surface preparation was electropolishing. A clean, bright surface was produced, just as in etching, without the danger of fluoride residue. The method was that devised by Jacquet for metallographic examination.^(8,9) The solution consisted of 1000 ml of glacial acetic acid and 50 ml of perchloric acid of density 1.59. The bath is safe under all conditions.⁽¹⁰⁾ According to Jacquet,⁽⁸⁾ "Operating conditions

are optimum at 60 volts and a high current density (80 to 100 amperes per square decimeter). During the electrolysis (30 to 60 seconds), the anode must be agitated rapidly through the solution." Insoluble constituents of the zirconium are said to be vigorously attacked and removed from the matrix. This is a disadvantage for metallographic examination but is not believed to affect anodic treatment. Electrical heating was appreciable during polishing and the electrolyte was cooled in a bath of running tap water (min temp $\sim 15^{\circ}\text{C}$). With small specimens, the surface was better if polishing was interrupted to permit the specimen to cool. Current was passed for 5-10 seconds, followed by up to one minute for cooling. Shorter polishing periods were necessary when the ratio of surface to volume was high. Overheating was more likely when a mount was used.

Degreasing was employed where necessary, prior to the above procedures. Wet polishing was always carried to 400 grit emery paper.

D. Procedures for Mounting and Making Electrical Contact

Contact with specimens other than crystal bar was made with zirconium wire or rod either press fitted or threaded into the sample. The latter was preferable. It was found desirable to mask the rod even when using zirconium.

In handling smaller specimens, much consideration was given to the use of mounting and masking materials to expose a well-defined surface area. The following materials were tested under various conditions:

- 1) Lucite
- 2) Bakelite
- 3) VMCH resin
- 4) Kold-Mold
- 5) Unichrome 330

The first three require a mounting press and heating (VMCH resin can also be formulated as a paint). The Lucite was least and the VMCH was most satisfactory from the standpoint of resisting the attack of electrolytes such as glacial acetic acid (used in electropolishing) to 70% nitric acid (used occasionally in anodizing). However, all three suffered from the disadvantage of not maintaining a good bond with zirconium. As a consequence, electrolyte was found to penetrate into the area of contact, and rinsing could not be relied upon to remove etchant (of which F^- was the pre-eminent offender) from the area of contact. This fact was demonstrated by two observations: 1) The interface between metal and mounting material was a site for premature film

breakdown (as evidenced by the formation of bubbles of oxygen), and 2) interference colors developed on the covered areas. Other factors against these materials were the time required for mounting and the necessity for drilling and tapping after each mounting. Such mounts had the advantage of repeated specimen usage with a simple wet-grinding to clean the surface. Kold-Mold is a resin which polymerizes at room temperature when a suitable catalyst is added. It required the use of a mold to contain the liquid about the specimen. It was not satisfactory in nitric acid solutions.

The most successful mounting and stop-off compound was Unichrome 330 (a proprietary, high melting plasti-sol designed for electroplating). It was applied according to directions by dipping at 190°C, and layers of any desired thickness could be applied to a specimen. A convenient area was then exposed by scraping away the wax. This material was easy to apply and maintained a good bond to metal. It was satisfactory in both the electropolishing bath and in concentrated nitric acid.

III. RESULTS

A. General

In the present work, attention was focussed on differences in anodic behavior which might be correlated with corrosion resistance. Differences in the anodic characteristics of zirconium were very noticeable under certain conditions, e.g., in the rise of voltage with time at low current densities, and indistinguishable under others, e.g., in the relationship between interference colors and applied voltage.

Initially, it did not seem feasible to use low voltages since these would approach the prolonged testing conditions in water (where the e.m.f. is the driving force). As a consequence, the effect of electrolytes was studied in conjunction with higher voltages with the aim of accelerating film growth. Such an approach had inherent difficulties which became evident as the investigation proceeded. It was demonstrated, however, that anodizing could differentiate specimens which were not distinguishable by testing in water.

The surface changes produced by anodizing were found to resemble, at least superficially, the changes produced in high temperature water. Electrolyte and temperature were found to play an important role in determining the appearance of the surface. The present study was carried out with dilute sulfuric acid, mixed sulfuric and nitric acids, oxalic acid and 1 w/o potassium hydroxide. Several experiments were also conducted with solutions of sodium borate, boric acid and phosphoric acid. The effectiveness of equivalent concentrations of electrolytes in lowering the maximum voltage (cf. Appendix I) was, in order: $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4 > \text{oxalic acid} > \text{sodium borate} > \text{KOH}$. In the latter three electrolytes at room temperature, the maximum voltage at 1 ma/cm^2 was of the order of 250 v. Spark discharge occurred below this point. The maximum voltage was also lowered by an increase of temperature. Above about 100°C , the maximum was lower than the sparking voltage, and sparks were not observed. This observation is in agreement with that of Guntherschulze, who found that the sparking voltage is relatively temperature independent while the maximum voltage is lowered by a temperature increase.⁽²⁾

Despite the effects of electrolyte and temperature in breaking down the oxide film, the thickness/voltage ratio in the interference color range of thin films did not appear to be affected. As a consequence, visual inspection of anodic layers could lead to erroneous conclusions about the true accelerating nature of electrolyte and temperature.

B. Characteristics of the Oxide Layer

Accordingly, the pattern of film growth will be discussed in terms of film structure. There are two important points to be considered. The first is that oxide film growth on zirconium occurs with oxygen penetration inward.^(13,14) The second is that the character of the oxide layer changes with thickness. Three types of oxide were commonly observed in anodizing, and these are represented schematically in Figure 2. The thin layer which formed in the first stages of anodizing is indicated as layer I. This oxide was transparent and exhibited interference colors as it thickened. The layer became dark green or pink at high order colors and subsequently the surface appeared black. An inner layer of oxygen-deficient oxide is believed to form at this point (layer II). The absence of color indicates a wide absorption band which is often associated with nonstoichiometric oxides.

Anodizing accelerates film growth by imposing an electrical field across the interface. At low voltage a steady transition from I to II could be observed in the course of several days. On very poor quality zirconium the surface began to turn white after such treatment. It is believed that layer I was gradually breaking down into smaller oxide grains of random orientation. The white appearance can be explained as a result of crystal size and of the absence of an optically excitable electronic structure.

One might expect to accelerate this transition by using higher voltages. At some critical voltage, however, the film no longer grew uniformly but was broken down discontinuously to form a white layer III. At accelerated rates, the dark layer II was not observed. This occurrence was misleading from the standpoint of visual comparison of an anodized surface with the appearance of the same specimen after testing in high-temperature water. Breakdown in anodizing occurred as a result of electronic discharge or arcing across the thin oxide layer. Evidently, the field strength began to exceed the limit for orderly film growth, and dielectric breakdown set in. The discharge caused a disruption of the film with fragments being pushed away from the breakdown point. The film resistance was therefore lowered and the current concentrated on the areas of breakdown which steadily developed a layer of white oxide. Localized heating probably contributed to accelerating the process. Breakdown was accompanied by the evolution of oxygen (since electron transfer had now become appreciable), and this rate also accelerated with time at constant applied voltage. This process was observed on a large number of zirconium specimens and was sensitive to metal quality. The difference in dielectric breakdown among specimens was such that black and white surfaces resulted from identical treatment at constant voltage. In the initial stages, the points of breakdown were randomly scattered over the surface. The density of points per unit area increased steadily with time until the entire surface was covered. In intermediate stages the white oxide had a mesh appearance and the interference color of layer I could still be seen.

Figure 2. Schematic Representation of the Oxide Layers on Zirconium Obtainable by Anodizing.

An indication of these structural changes was found in the measurement of cell voltage with time at constant current density. Reference should be made to Figure 41, page 78. The first part of the curve, section "a," is a region of film thickness where V/δ is a constant, i.e., $1 \text{ v}/21\text{\AA}$ for zirconium. Layer I develops linearly with cell voltage up to the point of inflection where the slope becomes "b." The change of slope is believed to be associated with the formation of layer II. Slope "b" is usually not constant but changes gradually from a to c. This also means a change in V/δ and indicates that the ratio of electronic to ionic current is changing. When breakdown begins, the current becomes almost wholly electronic and the curve levels off to section "c." This slope is positive for tantalum, but became negative soon after the maximum in the case of zirconium. Evidently, layer III was not as effective a diffusion barrier as I and II although it might still be adherent. Layer III is usually adherent when first formed but becomes friable with time. This layer resembled the product denoting poor corrosion resistance in high temperature water. In this study, all anodic layers thick enough to be scraped have shown the structure of monoclinic ZrO_2 . A study by Schwartz, Vaughn and Cocks⁽¹⁵⁾ has indicated that the very thin oxide layers on zirconium are tetragonal. This structure disappears as the film thickens.

C. Dependence of Film Thickness upon Cell Voltage

Guntherschulze⁽²⁾ has shown that anodic film thickness increases linearly with cell voltage for Ta, Bi, Sb, Zr, W, and Al. The films did not exceed approximately $4,000 \text{\AA}$ in thickness and exhibited well-defined interference colors which are a measure of optical thickness. If light is reflected with a zero phase change, a film thickness, δ , will show an optical thickness, δn , where n is the refractive index. When a phase change is present, the intercept of the curve on the ordinate (thickness) will be positive or negative.

Charlesby⁽³⁾ extends this work for zirconium and obtained more precise values of the film constants. In the present work, the primary interest was centered on differences in film properties which could be related to corrosion behavior. Accordingly, a comparison was made of interference colors for different zirconium materials. The data are shown in Figure 3.

The first three materials were wet ground and etched in HF-HNO_3 . Specimens which were wet ground or wet ground and electropolished were not noticeably different. For each point (excepting the ANL arc-melt, *vide infra*) the specimen was brought to the indicated cell voltage and held for ten minutes. The electrolyte was $1\text{N H}_2\text{SO}_4$ at room temperature. Duplicate trials were reproducible within the limit of visual sensitivity. The colors are given in terms of a GE step-gauge consisting of layers of barium stearate. The indicated thickness may be converted to optical thickness by multiplying by 1.491, the index of refraction of barium stearate. The phase change is seen to be approximately 2 microinches. At higher voltages the

Figure 3. Change of Interference Color with Forming Voltage on Different Types of Zirconium.

tin alloy is seen to maintain a slightly greater thickness. The data for ANL arc-melt specimens 2T, 2B, etc. were obtained during measurements of voltage-time curves at 0.1 ma/cm^2 in 1% KOH. The changed conditions had substantially no effect on the curve.

Under these conditions, the field required to produce ionic movement (film growth) is apparently independent of impurity content. This field is approximately $5 \times 10^6 \text{ v/cm}$ according to Charlesby⁽²⁾ and represents a minimum energy for ionic diffusion. Such high field strengths do not occur in corrosion when temperatures above 250°C are necessary to show the effect of impurities. It may be concluded that the factors which control zirconium corrosion (at low e.m.f.) are not activated proportionally by high fields.

D. Visual Comparison after Anodic Treatment

This phase of the program was concerned with anodizing to produce a surface appearance indicative of zirconium quality. Oxide layers could be produced in various thicknesses and made to vary from black to white. Nearly all this work was done at constant voltage (except for an initial period of increasing voltage).

1. Investigations Using Crystal Bar

The first experiments were conducted with sections of crystal bar rejected by the 2-week corrosion test in water at 315°C . Upon anodizing in dilute sulfuric acid over a variety of voltages it was noted that the core of certain bars developed white oxide while the remainder of the bar showed a bright interference color. Breakdown also occurred at the water-line and was attributed to the presence of oxygen from the air. The accelerating effect of oxygen was thought to be verified when a small amount of nitric acid was added to the bath. This addition accelerated breakdown and produced a sharp contrast between good and bad areas.

Ten crystal bars were then used to determine the mixture of nitric and sulfuric acids which produced the maximum contrast. Approximately 50 points were evaluated on a ternary diagram with the results shown in Figure 4. The diagram was obtained with a bath temperature of 90°C . Steadily increasing voltages were applied up to 100 v maximum over a period of several minutes. The test period on the average did not exceed 5 minutes. It will be noted that most of the points lie along a line corresponding to a volumetric ratio of acids: $\text{Con. HNO}_3 : \text{con. H}_2\text{SO}_4 = 2 : 3$. This was a border region between the area of stable film formation and film breakdown. All initial comparative work was done in this area.

From these results, a solution of 18 w/o H_2SO_4 and 5 w/o HNO_3 was chosen to evaluate zirconium. This composition is shown by the semishaded circle. The conditions of anodizing were as follows: bath at

Figure 4. Variation of anodizing characteristics with composition of solutions containing distilled water, 70% HNO_3 and 95% H_2SO_4 . The compositions are expressed as volume percent of the unmixed components.

90°C, 2 minutes test time with 100 v dc (first minute, 0 to 100 v; second minute, held at 100 v), platinum rod used as cathode. Grade I zirconium with a dry ground surface developed white oxide under these conditions while wet ground zirconium did not. Breakdown was also observed along streaks produced by scratching with a steel needle in air. The effect persisted despite pickling. Surfaces which showed a slightly smudged appearance after pickling were also prone to failure.

This test was then applied to 20 crystal bars of unknown quality, subsequently tested in 315°C water. Each of the bars was prepared by turning down approximately 1/4 inch of one end to a smooth surface. The end of the bar was pickled and the smooth tip was anodized. In some cases the concentration of HNO_3 was lowered from 5 to 3.3 w/o.

The appearance of the bars after anodizing is shown in Figure 5. A white coating may be seen on bars S, O, Q, T, N and P. The unlabeled bars were used in determining the ternary diagram. All "good" bars had a blue or blue-green coat.

After photographing, the bars were all tested for two weeks in 315°C water without removal of the anodized coat.

The resulting appearances are shown in Figure 6, 7, and 8. In making a comparison the length of bar next to the machined tip was given chief consideration. On this basis the corrosion behavior was predicted in 18 cases. Bars M and N did not correlate. The results were considered sufficiently encouraging to continue in this direction.

A further selection of crystal bar was tested in the mixed nitric-sulfuric acid bath. These bars were received as corrosion tested and in many cases had a heavy layer of white oxide. Vapor blasting and pickling were employed for cleaning. Approximately 10% of these bars did not correlate with the corrosion test when anodized. All of these "anomalous" bars were good in 315°C water but broke down prematurely upon anodizing. Attempts to pass these specimens by altering the anodizing conditions were unsuccessful. In addition, satisfactory cleaning became more difficult as a result of the rough surface. Crevices in the surface became a site for film breakdown with oxygen evolution. In addition to changing the composition of the bath, the following variables were investigated with a view to improving the correlation: slower rate of application of voltage, lower temperature, and modification of the cleaning procedure. None of these appreciably changed the breakdown sequence observed under the original conditions. Some results were described previously.^(15a)

In conjunction with this work, a number of general observations were made and are summarized below. In evaluating the ternary diagram it was noted that breakdown occurred at different film thickness

Figure 5. Specimens O, H, K, R, N, and the three unlabeled were tested in 5% HNO_3 , 18% H_2SO_4 at 90C for two minutes at 100v. The remaining specimens were tested in the same manner except that 3-1/3% HNO_3

Figure 6. Appearance of crystal bar after testing in water at 315°C.

Figure 7. Appearance of crystal bar after testing in water at 315°C.

Figure 8. Appearance of crystal bar after testing in water at 315°C.

depending primarily upon the concentration of HNO_3 and secondarily upon temperature. This effect was most evident in anodizing with increasing voltage in a series of HNO_3 solutions. At low concentrations (5 w/o) the film showed a series of interference colors before breaking down. At higher concentrations few color changes were noted before breakdown occurred. Above 20 w/o the film changed in character and the breakdown product became black. Breakdown was also promoted by a rise of temperature. Films produced in solutions containing HNO_3 were more sensitive to a temperature rise than those produced in dilute H_2SO_4 .

In concentrations of acid corresponding approximately to the center of the ternary diagram, the coating changed from interference colors to a gray surface without discontinuous breakdown. Differences in anodic behavior tended to disappear.

2. WAPD Zirconium Test Pieces

More convenient test material was made available by co-operation with the Westinghouse Atomic Power Division. A set of 84 zirconium specimens was obtained with the following approximate dimensions: $5/8 \times 5/8 \times 1/8$ inch. The metal was prepared from various base zirconium by various methods. Each piece was one of a quadruplicate set, each member of which was corrosion tested under different conditions. The corrosion history of each set is summarized in Tables I and II. All three sets tested in high temperature water have survived up to 61 days without evidence of failure (appearance of white oxide). The fourth set was steam tested for 18 and 36 hours at 400°C (750°F). Approximately a third of this set developed white oxide. These specimens were photographed on both sides and are shown in Figures 9, 10, 11, and 12.

All the steam test specimens were then machined lightly to remove the oxide and restamped. At ANL the specimens were pickled in HF-HNO_3 and anodized. The same specimens were used for several tests and recleaned each time by wet polishing and pickling.

A number of the WAPD specimens were first evaluated by anodizing in a mixed $\text{H}_2\text{SO}_4\text{-HNO}_3$ bath of the composition (parts by vol.): 72, distilled water; 8, con. HNO_3 ; 20, con. H_2SO_4 . Conditions were 90°C and 50 v with the voltage increased from 0 to 50 in one minute. Under these conditions the WAPD specimens began to develop white oxide (breakdown) in 4 to 15 minutes. These lifetimes were quite short as compared to poor quality crystal bar given the same test. The latter specimens would last from 30 to 90 minutes. In effect, the anodizing produced a reversal of breakdown sequence as compared to corrosion tests.

Figure 9. Appearance of WAPD specimens after 400°C steam test.

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Figure 10. Appearance of WAPD specimens after 400°C steam test.

Figure 11. Appearance of WAPD specimens after 400°C steam test.

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Figure 12. Appearance of WAPD specimens after 400°C steam test.

Table I

AVERAGE WEIGHT GAIN (mg/cm^2) FOR WAPD
SPECIMENS IN WATER

Total Time in Days	Test Temperature ($^{\circ}\text{C}$)		
	288 (550°F)	315 (600°F)	360 (680°F)
7	0.07 (± 0.028)	0.09 (± 0.022)	0.12 (± 0.024)
21	0.09 (± 0.024)	0.10 (± 0.025)	0.21 (± 0.028)
35	0.11 (± 0.028)	0.14 (± 0.027)	0.20 (± 0.025)
49	0.11 (± 0.024)	0.14 (± 0.024)	--
61	0.11 (± 0.025)	0.14 (± 0.027)	No failures

Table II

AVERAGE WEIGHT GAIN FOR
WAPD SPECIMENS IN STEAM
AT 400°C (750°F) AND 1500 psi

Total Time in Hours	mg/cm^2
18	0.12 ± 0.027
36	0.15 ± 0.017

Subsequent work was devoted to examining more detailed aspects of anodic phenomena on the WAPD specimens. It was felt that a better understanding of the factors underlying film breakdown was essential to further progress. The addition of HNO_3 was discontinued with the purpose of devoting attention to less-active electrolytes.

A solution of 36 w/o H_2SO_4 was next employed. The bath was used at the boiling point (approx. 110°C), and a large number of the WAPD specimens were anodized for 1 hour at 100 v. The resulting surface appearance ranged from black (very dark interference colors) to white (breakdown product). The results are summarized in Table III. The sensitivity of the treatment was evident from the sandwich-type structure which appeared on certain specimens with a sharp demarcation line from black to white. The stamped areas exhibited a much slower rate of breakdown.

The specimens were photographed in this condition and the results are shown in Figures 13, 14, 15, and 16, showing both faces. The arrangement conforms with the previous figures taken after steam testing at Westinghouse. A detailed comparison indicated that in many cases a reversal of appearance had resulted. White oxide had developed on areas which were black in steam and vice-versa. This was attributed to premature breakdown of the type already mentioned (layer I undergoing dielectric breakdown to give layer III). In view of these results, it seemed inadvisable to continue testing at constant voltage. One might resort to lower voltages, but the rate of film growth (after reaching a thickness proportional to voltage) was too low to be of practical value.

The effect of a change in voltage is demonstrated by the data of Figure 17. Here, the anodizing current was measured as a function of time for WAPD specimen 185. This specimen broke down very readily as may be seen from Table III. The same bath: 36% H_2SO_4 at 90°C , was used. The exposed area was 11.0 cm^2 . At 110 v the specimen was starting to turn gray after 50 minutes with noticeable oxygen evolution. At 60 and 90 v the appearance was still good at 60 minutes. The steady rise of current at these voltages indicated that breakdown was occurring. The time at which the current was a minimum was approximately the same in each case. It is evident that the breakdown voltage was below 60 for specimen 185 under these conditions.

The voltage at which sparking began on WAPD specimens was relatively independent of specimen and temperature, but was significantly affected by electrolyte. In 36% H_2SO_4 at 30 and 90°C , the occurrence of sparking was noted at 115 - 120 v.

The beginning of breakdown could be detected on both current-time and voltage-time curves. The latter effect became evident in a comparison of WAPD specimens 251 and 305. From the data of Table III it is seen that 251 was similar to 185, while 305 developed a resistant black film. Both specimens were also anodized at 50 v (36% H_2SO_4 , 110°C) for 2 hours. Under these conditions, 251 began to show breakdown after 1 hour and after removal was light gray with a thin, white, friable layer. X-ray diffraction of the white breakdown product showed monoclinic ZrO_2 . No. 305 with no breakdown in the same period was black with a purple tint. Both specimens were then wet

Figure 13. Appearance of WAPD specimens after anodizing.

Figure 14. Appearance of WAPD specimens after anodizing.

Set 2

219

237

269

293

299

315

312

323

325

327

331

337

335

Figure 15. Appearance of WAPD specimens after anodizing.

Set RA

279

287

289

293

299

315

315

319

323

325

327

331

337

339

341

345

349

353

355

Figure 16. Appearance of WAPD specimens after anodizing.

Figure 17. Current vs. time for anodizing WAPD 185 at three different voltages in 36% H_2SO_4 at 90°C . The currents at one-half minute exceeded 100 ma in each case. Exposed area was 11.0 cm^2 .

Table III
 APPEARANCE OF WAPD SPECIMENS AFTER ANODIZING
 IN 36% H₂SO₄ AT 100 v (TEMP. 110°C)

General Description	Specimen Numbers	Specific Comments	General Description	Specimen Numbers	Specific Comments
Black	291	Trace of white oxide in one crevice on a corner.	Light gray	193, 195, 203, 205, 247, 255, 283, 289, 303, 351	
	211, 249	Localized white oxide on one edge, approx. 1/8" long.		345	80% of the stamped surface was lighter in appearance (nearly white)
	275, 327	A black bond line corresponds to a white line on the steam test.		277	The stamped surface was much darker than the opposite face except for an edge across from the stamp.
	261, 305	Localized white oxide, approx. 1/4" long.		325	White edge on face opposite the number.
Dark with incipient breakdown	187, 215, 223, 253, 267, 329, 349, 353		Very light gray to white	393	Uniform surface, lighter than others in this group
	221	Localized lighter coat on the stamped surface, 1/4" max. dimension.		335	Slightly darker inner layer, sandwich effect.
	217 [200V]	Center layer gray on two parallel edges, giving a sandwich appearance.		201	Three short black streaks on opposite edges.
Dark gray appearance; Breakdown more advanced	199	Localized white oxide on one edge, 1/8" max. dimension.	White	319	Three short black streaks on opposite edges.
	227, 229, [200V], 235, 261, 269, 281, 311, 315, 321, 355			207	80% of one face somewhat lighter.
Dark to light gray	297	Slightly lighter on half of one side.		341	Darker inner layer, 40% of the stamped side is slightly gray.
	197	Several light streaks on an edge close close to the stamping.	251 [110V]		Thin black streak on the edge of the stamped corner
	313, 339	Light gray.		209	Inner layer slightly darker.
	225 [193V]	Thin white streak on one edge.		185 [115V]	All white.
	331	Whiter on face opposite the stamp.			
	287	Medium gray - thin black crevice line on edge across from the stamp.			

ground, etched and anodized (36% H_2SO_4 , 90°C) at 5 ma/cm^2 . The change of cell voltage with time is shown in Figure 18. The trial was stopped in each case after reaching 60 v, leaving the specimens with a light violet color. The difference in slope indicates more rapid film growth on 305. It is evident that breakdown, at least under these conditions, is associated with a slow growth rate.

One further constant voltage test was made on No. 185 (passing the steam test) and 331 (failing) by anodizing at 50 v for 28 hours in a solution of 19 w/o oxalic acid at 101°C . Neither specimen showed any breakdown in this period, although 331 became somewhat darker than 185.

3. Detection of Bond Lines

The selective nature of breakdown suggested its use for detecting non-homogeneous areas such as bonds on rolled plate. The technique was applied to a series of specimens at WAPD using the bath: 20% by vol. con. H_2SO_4 , 8% by vol. con. HNO_3 .⁽¹⁶⁾ The test consisted of anodizing the entire specimen to breakdown and observing any non-uniformity at the bond. The good metal comprising the bulk of the plate was broken down preferentially and became gray or white in appearance. The bond area appeared as a thin black line; breakdown never occurred preferentially at the bond line.

Sixteen plates which had been water tested (10 good, 6 bad) were anodized after cleaning. Of these, all but 4 good plates were rejected by appearance of a black line. It was concluded that too many plates would be rejected by this method. In addition, the surface was left with a thin layer of white oxide which would be undesirable in subsequent corrosion testing.

The above work indicated the necessity of a more careful examination of the pattern of film growth. Subsequent efforts were devoted to measuring electrical changes during film growth.

E. Electrical Measurements of Film Characteristics

1. Voltage-time Curves using 19 w/o Oxalic Acid

A less active electrolyte was used in these measurements to lessen the incidence of breakdown. Preliminary trials indicated that oxalic acid had a sparking limit above 200 v and this electrolyte was selected for further work. It was also found, in contrast to H_2SO_4 solutions, that breakdown was not preferential at the waterline. Solutions of 19 and 25 w/o oxalic acid gave essentially the same results. The data described below were all obtained with 19 w/o oxalic acid solution at the boiling point (approx. 101°C).

Figure 18. Cell voltage vs. time for anodizing WAPD specimens 251 and 305 at 5 ma/cm^2 in $36\% \text{ H}_2\text{SO}_4$ at 90°C .

a. WAPD Specimens at 0.4 to 1.0 ma/cm²

Using this bath, cell voltages were measured as a function of time for currents of the order of 1 ma/cm². Several WAPD specimens showing extremes of appearance (Table III) were cleaned by wet grinding or were wet ground and pickled. Each piece was anodized for periods ranging from one to five hours. In every case, a maximum voltage was reached within one hour and then remained constant or dropped slightly. These maxima are listed in Table IV.

Table IV

MAXIMUM VOLTAGES UPON ANODIZING WAPD SPECIMENS IN 19 w/o
OXALIC ACID AT 101°C, WET GROUND EXCEPT AS NOTED

Specimen No.	Current Density, ma/cm ²	Maximum Voltage Attained	Rating on Steam Test*	Appearance after Anodizing (100 v, 1 hr)**
185	1	115	good	white
185(etched)	0.8	90	good	white
251	1	110	good	white
251(etched)	0.4	80	good	white
217	1	200	bad	dark black
225***	15	193	bad	dark black
229	1	200	bad	dark black
233	1	195	bad	not done
269	0.5	145	bad	dark gray
299	0.5	142	bad	not done

* 18 hrs, 400°C, 1500 psi. The appearance of the bad specimens is shown in Figures 9, 10, 11, 12.

** Cf. Table III.

*** Plateau attained in two minutes; curve not shown.

The maximum voltage is higher for specimens which failed the steam test and passed (using breakdown as the criterion) a constant voltage anodizing test. These data suggest that some common factor in the film growth process is operative in the following phenomena: 1) a good steam test, 2) a low maximum voltage, 3) an early breakdown in anodizing at constant voltage.

The complete voltage-time curves for Nos. 185 and 251 are given in Figure 19. These and others following were traced from a Micromax chart record. It is evident that the change in maximum voltage was not proportional to the change in current density.

The curves for specimens 217, 229, 233, 269, and 299 are shown in Figure 20. The first three specimens were anodized at 1 ma/cm^2 , the latter two at 0.5 ma/cm^2 . The initial slope was slightly greater than for 185 and 251. Raising the current had the effect of reducing the time to reach the maximum. None of these 7 specimens could be anodized indefinitely at 1 ma/cm^2 without getting breakdown. This was indicated by a drop in the curve which was accompanied by the appearance of white oxide. This voltage drop is the same phenomenon as the rise in current after reaching a minimum (cf. Figure 17). At 0.4 ma/cm^2 the maximum of 80 volts was maintained, and a noticeable break did not occur within 5 hours.

b. ANL Specimens at 1 ma/cm^2

The same procedure was next applied to 8 specimens of zirconium arc-melted at Argonne National Laboratory. Each sample was obtained from the top and bottom of four 3-inch diameter castings. Adjacent samples were used for obtaining the analyses, hardness and corrosion data presented in Tables V and VI. Ingot 3 was prepared from Grade I crystal bar and the others were prepared from Grade III. The corrosion behavior of the metal was not reflected in the weight gains as shown in Table VI. In particular, the weight gains of 3T and 3B were unduly high, and all of the white powder on the surface probably came from 5B.

This set was next given a steam test, anodized under various conditions as reported subsequently, then retested in water at 300°C . The surface preparation for the steam test was wet polishing and etching with results presented in Table VII. It is evident that Nos. 3, 4, and 5 specimens were not differentiated. These tests were conducted on the entire specimen. During the latter part of the anodizing study, the blocks were cut in half and one piece subjected to further water testing. The surfaces in this instance were wet ground and electropolished, and each pair (T and B) was placed in a separate autoclave. The weight gains are given in Table VIII, and a photograph after testing is shown as Figure 21.

Figure 19. Voltage-time curves for WAPD specimens having low maximum voltages, etched surface. 1 ma/cm², 19 w/o oxalic acid, 101°C.

Figure 20. Voltage-time curves for WAPD specimens having high maximum voltages, etched surface. 1 mA/cm^2 , 19 w/o oxalic acid, 101°C .

Table V

ANALYSES⁽¹⁾ AND HARDNESS FOR ANL BILLETS 2, 3, 4, AND 5

Reference No. and Grade of Crystal Bar (6)	Casting No. (2)	N	C	Al	Cr	Cu	Fe	Mo	Ni	Pb	Sb	Si	Sn	W (3)	R _B (4)	V(5)
A-1869 A-1870 Grade III	2T	140	390	30	2	20	1000	<10	50	70	10	50	10	<1000	92	195
	2B	88	305	30	2	20	1000	<10	50	70	10	<50	<5	<1000	102	260
A-1871 A-1872 Grade I	3T	57	435	20	2	5	200	10	15	1	<5	<50	<5	<1000	53	90
	3B	54	155	20	2	5	300	30	20	1	<5	<50	<5	<1000	42	85
A-1873 A-1874 Grade III	4T	60	175	50	10	10	700	20	70	1	<5	<50	<5	<1000	72	126
	4B	95	140	50	10	10	700	10	70	1	<5	<50	<5	<1000	65	109
A-1875 A-1876 Grade III	5T	168	350	50	10	10	500	<10	70	1	<5	<50	<5	<1000	73	128
	5B	110	385	100	5	10	500	<10	70	1	<5	<50	<5	<1000	66	112

- (1) Ag, As, B, Be, Bi, Ca, Co, K, Li, Mg, Mn, Na, P, Ti, V, Zn below limits of spectrographic detection. All values in ppm.
- (2) 2T = top of billet No. 2; 2B = bottom of No. 2.
- (3) Spectrographic analysis for tungsten is not too exact. Some differences seemed to exist in the various billets, but a gravimetric analysis must be made for differentiation. All billets were less than 1000 ppm, however, and this figure is reported.
- (4) Rockwell B hardness, observed values.
- (5) Vicker's hardness numbers converted from Rockwell B.
- (6) Grade 1 metal - tested in water (2 weeks 315°C) and corrosion resistant. Grade 3 metal not corrosion resistant.

Table VI

CORROSION DATA* ON ZIRCONIUM ARC-MELTED AT ANL

Degassed, Distilled Water at 315°C for 380 Hours
(Specimens cleaned in 2% HF)

Autoclave No.	pH		Resistivity of Water (ohm-cm)		Specimen No.	Wt. Change, mg/cm ² /mo	Notes on Appearance
	Before	After	Before	After			
1	7.1	9.7	180,000	72,000	2T	+ 1.37	(loose) powdery white coating
					2B	+69.6	
					5T	+ 0.66	Small area had powdery adherent white coating. Most of area had dull black tarnish.
2	7.1	8.9	185,000	48,000	4T	+ 0.68	Slight adherent white coating Rest of area dull black tarnish.
					4B	+ 0.55	Half of area adherent white coating. Balance dull black tarnish.
3	7.2	9.0	165,000	32,000	3T	+ 2.7	Slightly lustrous black tarnish - very slight adherent white powder.
					3B	+ 4.1	
					5B	+15.3	Total surface adherent white powder.

*Data from tests by A. H. Roebuck, Reactor Engineering Division, ANL.

Table VII

**CORROSION DATA ON ZIRCONIUM ARC-MELTED AT ANL
STEAM TEST, 1500 psi, 400°C, 18 Hrs.***

Specimen No.		
2	T	Very good except for small spot
	B	90% white, one shiny spot
3	T	Very good (uniform black)
	B	Very good (uniform black)
4	T	Very good (uniform black)
	B	Very good (uniform black)
5	T	Very good (uniform black)
	B	Very good (uniform black)

* Test conducted by A. H. Roebuck, Reactor Engineering
Division, ANL.

Table VIII

**WEIGHT GAIN OF ANL ARC-MELTED ZIRCONIUM
EXPOSED TO WATER AT 300°C**

Specimen No.		Total Test Time	Weight Gain, mg/cm ²
2	T	2 weeks	1.19
	B	2 weeks	20.4
3	T	4 weeks	0.08
	B	4 weeks	0.07
4	T	4 weeks	0.09
	B	4 weeks	0.08
5	T	4 weeks	0.37
	B	4 weeks	0.12

Macro No. 15,441

1/2 X

Figure 21. Arc-melted zirconium specimens after exposure to water at 300°C. Specimens 2T and 2B were tested for 2 weeks; the others for 4 weeks.

It is quite apparent that 2B had a much higher corrosion rate than the remaining specimens. The differences between the No. 3 and 4 specimens were evident in appearance but did not show up in the weight gains. The No. 3 specimens still retained some interference colors after 4 weeks, with grain patterns readily visible. The No. 4 specimens were dull black with thin patches of white appearing on parts of the surface. This is most evident on 4B in Figure 21. Considering both appearance and weight gain, the corrosion evaluation in order of increasing corrosion rate is: 3B, 3T, 4T, 4B, 5B, 5T, 2T, 2B.

After wet-grinding and etching, the above set of 8 specimens was anodized at 1 ma/cm^2 in 19 w/o oxalic acid. The data are thus directly comparable with Figures 19 and 20. The curves are shown in Figures 22 and 23. The two Grade I specimens, 3T and 3B, had higher maxima than the others, excepting 5B. The curve for 2B was not noticeably different from the others. It is thus evident that the inverse relation between maximum voltage and corrosion resistance on steam test is not applicable to these specimens.

However, the curves indicate that a constant voltage test would develop breakdown on all specimens except 3B, in conformity with the original correlation (where breakdown indicated poor corrosion resistance). Comparison of these data with that for the WAPD specimens suggests that breakdown occurs least readily on metal of a quality intermediate between very pure and impure. As zirconium decreases in purity, the voltage maximum is believed to rise to a peak and then drop.

Curves for anodizing in oxalic acid were measured on other specimens as well. Figure 24 shows two voltage-time curves for arc-melted sponge of very low quality. The film developed slowly as anodizing proceeded and white oxide was appearing toward the end. The maximum was not well-defined and the irregular nature of the curve suggested the presence of localized breakdown. Curves for two other materials are shown in Figure 25. The specimens were 5% tin alloy* and a section of Grade III crystal bar. The latter showed a very low maximum.

2. Studies of ANL Specimens using 1% KOH

In reviewing the above data it was decided to investigate lower current densities, closer in magnitude to corrosion currents. This was not done previously since the time required to develop films of reasonable thickness (0.5 mg/cm^2) appeared prohibitively long. Attempts to duplicate

* Supplied by R. S. Peoples, Battelle Memorial Institute. Composition: 4.98 w/o tin, 0.03 w/o C, 0.005 w/o N. Prepared from arc-melted Grade I crystal bar and forged and rolled into sheet at 800°C . Corrosion tested in (400°C) steam (1500 psi) for 342 hours with formation of a good black film.

Figure 22. Voltage-time curves for etched zirconium from the top of four arc-melted ingots. 1 ma/cm^2 , 19 w/o oxalic acid, 101°C .

Figure 23. Voltage-time curves for etched zirconium from the bottom of four arc-melted ingots. 1 ma/cm², 19 w/o oxalic acid, 101°C.

Figure 24. Voltage-time curves for BuMinex plate of low corrosion resistance, etched surfaces. 1 ma/cm², 19 w/o oxalic acid, 101°C.

Figure 25. Voltage-time curves for a section of Grade I crystal bar and a 5% tin alloy (BMI), both etched. 1 ma/cm², 19 w/o oxalic acid, 101°C.

corrosion films by an accelerated technique cannot, therefore, be considered successful. However, significant variations in the properties of the anodic films were demonstrated, and experience was gained in surface preparation, temperature, choice of electrolyte and other variables.

a. Voltage-time curves at 0.1 ma/cm²

The remainder of the investigation was devoted primarily to the 8 ANL arc-melt specimens. It was decided to restrict further work to room temperature and examine the pattern of film growth at low currents. The investigation was made using two methods: 1) measurement of voltage-time curves at 0.1 ma/cm² and lower; 2) measurement of "leakage currents" through anodic films of known thickness. The data are interrelated and will be discussed in the most convenient order for presentation.

Careful consideration was given to the choice of an electrolyte for work at room temperature. A solution of 1 w/o KOH was selected for the following reasons: 1) Previous work had indicated a high sparking voltage; 2) the species donating oxygen for film growth would be similar to that for high temperature water, i.e., H₂O or OH⁻; 3) the solution has a high conductivity.

The initial results are shown in Figures 26 and 27. Each curve is for a single trial and shows the growth of film thickness with time. The No. 3 specimens (Grade I) were seen to develop an oxide much more rapidly and efficiently than the remaining (Grade III) specimens. Upon removal, each specimen had an interference color dependent upon its final voltage, e.g., in Figure 27, 3B and 2B (30V) were light blue while 4B and 5B were faint brown. Five distinct color changes were noted from 0 to 30 volts and were subsequently plotted on Figure 3. The color change was independent of specimen.

Previous experience indicated that these curves would have good reproducibility, so attention was turned to other surface treatments. Figures 28 and 29 show the effect of wet polishing. The voltage-time curves had altered appreciably, but the sequence of specimens (after the first hour) was the same as when the surface was electropolished. Another factor to be noted is the transient nature of the plateau as evidenced particularly by 5B. It was later found (cf. Figure 38) that the method of wet polishing would produce either a rising curve or a plateau on tin alloy. The plateau resulted when the polishing was done on a bench top with wet emery paper. Frequent rinsing served to keep the specimen and paper wet. In contrast, polishing with the specimen and paper under the surface of a water bath produced a rising curve on the tin alloys. It is possible that a similar procedure when polishing the T and B specimens would tend to eliminate the observed voltage plateau.

Figure 26. Voltage-time curves for electropolished zirconium from the top of four arc-melted ingots. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

Figure 27. Voltage-time curves for electropolished zirconium from the bottom of four arc-melted ingots. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

Figure 28. Voltage-time curves for wet ground zirconium from the top of four arc-melted ingots. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

Figure 29. Voltage-time curves for wet ground zirconium from the bottom of four arc-melted ingots. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

The investigation was repeated for surfaces etched in HF-HNO₃ (8 ml con. HF, 50 ml con. HNO₃, 50 ml dist. water). The surfaces were first wet ground (a prelude to any surface cleaning) and then etched for 15 to 30 seconds. All traces of oxide were carefully removed prior to etching. The resulting curves are shown in Figures 30 and 31. Here again the pattern was altered but the general sequence remained the same. Particularly noteworthy were the greater thicknesses attained by the 4 and 5 specimens and the absence of a well-defined plateau. It seems evident that wet polishing has more in common with electropolishing than with etching. Also, if a relatively flat curve can be considered as indicative of poor corrosion resistance, then etching may be said to be the most beneficial surface treatment.

An important feature of the above data, independent of surface treatment, was the tendency of 3T and 3B to attain the highest voltage and film thickness at this current density. One may conclude that maximum voltage may be used as a measure of corrosion resistance at very low rates of anodizing. At 1 ma/cm² (Figures 22 and 23) this correlation was obviously not true. The properties of the oxide may be changing with current density or the voltage-time curve may not represent the same phenomena at low and high current densities.

b. Residual Currents at Constant Anodic Potential

A low efficiency of film formation indicates a high fraction of electronic current. One may expect, therefore, that direct measurements of current when the film is not growing should correlate with the efficiencies observed on anodizing. Another reason for this approach is the fact that electrolytic rectifiers such as tantalum exhibit a residual current when maintained at voltages below the forming voltage.⁽¹⁷⁾ The residual current is largest at the voltage of formation on a freshly formed surface. With this voltage held constant, the current drops steadily to an irreducible minimum. Figure 17 is an illustration of this effect for zirconium and indicates that the residual current may increase as a consequence of breakdown. In the case of zirconium, this minimum current could be a function of the same impurities that increase corrosion rate.

The technique employed was based on the following considerations: 1) comparison would be made at a fixed film thickness, produced by anodizing to some selected voltage below the breakdown limit; 2) residual currents would then be measured at a lower voltage where the film is stable and no further growth occurs.

The comparison was made on the ANL arc-melt specimens mounted in Unichrome 330 with approximately 80% of the surface exposed. Stainless steel support rods were completely masked. Each specimen was wet ground with flowing tap water and electropolished for 30 seconds in 5-second intervals to allow for cooling.

Figure 30. Voltage-time curves for etched zirconium from the top of four arc-melted ingots. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

Figure 31. Voltage-time curves for etched zirconium from the bottom of four arc-melted ingots. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

In a preliminary experiment, specimen 4T was anodized to 50 v dc vs. platinum in a saturated solution of boric acid made slightly alkaline with NH_4OH . After reaching 50 v, the current dropped rapidly at first and then more slowly following a logarithmic-type decay curve. Attainment of a steady value required approximately one hour. The current behaved similarly when holding at 50 v after anodizing to 100 v. The specimen was also brought to 200 v, but sparking occurred. A number of specimens were then compared in 1% KOH by anodizing at 20 ma total current until the cell voltage reached 50 v. The time to reach the maximum varied from specimen to specimen. The voltage was then reduced to 5 v and the current was measured. The values are presented in Table IX and were stable within about 10%. The currents were lowest for the No. 4 specimen and highest for the No. 5. There is no relation to corrosion resistance.

Table IX

LEAKAGE CURRENTS AT 5 v DC WITH AN
ANODIC FILM APPLIED AT 50 v

Ammonium borate solution at room temperature

Specimen	Current, ma/cm ²
2T	0.035
2B	0.036
3T	0.039
3B	0.041
4T	0.023
4B	0.024
5T	0.060
5B	0.043

The set of 8 specimens was next anodized simultaneously at 20 v (vs. platinum) in 1 w/o KOH at room temperature. The voltage was brought up in 5 minutes. The current flowing to each specimen was measured after 1, 2, and 38 hours had elapsed from the start of anodizing. The time required for current measurements is not included. For each reading, the anodizing voltage was reduced to zero and connections were made to individual specimens. 15 v was then applied and the current measured until a steady value was reached. Approximately 10 minutes were required to allow the current to level off. The data are listed in Table X. The results are

also plotted in Figure 32. There are two important features to be noted. First, the Grade I specimens (3T, 3B) have the lowest average currents; second, high residual currents drop more rapidly, and differences between specimens tend to decrease with time. The more rapid current drop from high currents suggests that polarization may be occurring within the film or at one of the interfaces. Therefore, the initial residual currents (below 10 hours) are believed to be the most significant. On this basis the corrosion rating of the specimens becomes: 3B, 3T, 2T, 2B, 5T, 4B, 4T, 5B. At 10 hours, the difference in residual current between 3T (Grade I) and 2T (Grade III) was 0.008 ma/cm^2 .

Table X

RESIDUAL CURRENTS AT 15 v AFTER ANODIZING AT
20 v FOR THE TIMES INDICATED. (ma/cm^2)

1 w/o KOH at room temperature

Specimen No.	1	Time in Hours 2	38
2T	0.027	0.030	0.021
2B	0.046	0.035	0.017
3T	0.030	0.021	0.017
3B	0.020	0.014	0.014
4T	0.051	0.073	0.032
4B	0.059	0.054	0.022
5T	0.048	0.044	0.017
5B	0.058	0.115	0.025

The data provided a good check on the voltage-time curves at 0.1 ma/cm^2 which showed essentially the same order for decreasing efficiency of film formation. No explanation is evident for the rise in residual current for some specimens (from 1 to 2 hours) and the drop for others.

c. Voltage-Time Curves with a Preformed Film

The values of residual currents at two hours were in good agreement with the voltage-time curves at 0.1 ma/cm^2 . Specimens with the lowest current had the highest efficiency on voltage-time curves

Figure 32. Residual currents at 15 V as a function of time of anodizing at 20 V. 1 w/o KOH, room temperature.

and vice versa. With further anodizing (over 2 hours) the currents tended to equalize with time and the original differences were eliminated. To determine whether the anodizing curves are influenced, the ANL series was given a pretreatment to develop a 20 v film and then anodized at 0.1 ma/cm^2 . All specimens were wet ground and electropolished. They were then anodized simultaneously at 20 v dc vs. platinum in 1% KOH at room temperature. The voltage was brought up to 20 v over a period of 30 minutes and held at 20 v for 35 hours. At the end of this period, the voltage was shut off and the specimens were removed individually to another bath for anodizing at 0.1 ma/cm^2 . The curves which resulted are shown in Figure 33. It is quite evident that the original order of the curves has been altered. In particular, 5T and 5B have steeper slopes while the 2 and 4 specimens have become more similar. The curves are tending toward the appearance shown at 1 ma/cm^2 in oxalic acid (Figures 22 and 23). By forcing film growth to 2 v in 30 minutes, the current densities exceeded 0.1 ma/cm^2 on all specimens with the possible exception of 3B (cf. Figures 26 and 27). This accelerated pre-treatment evidently produced changes which obscure the corrosion relationship. In order of decreasing slope, the curves in Figure 33 are: 3B, 5B, 5T, 3T, 2B, 4B, 2T, 4T. This is similar to the order of increasing residual currents (measured at 15 v) after anodizing at 20 v for 38 hours. The order as taken from Table X is: 3B, (2B, 5T, 3T), 2T, 4B, 5B, 4T. This relation is further evidence that the slope of the voltage-time curve is inversely proportional to the electronic or non-film-forming current.

3. Studies of WAPD and Tin Alloy Specimens using 1 w/o KOH

a. WAPD Specimens at 0.1 ma/cm^2

Anodizing at 0.1 ma/cm^2 was next applied to a series of WAPD specimens. As discussed previously, these all had good corrosion resistance but varied in resistance to the steam test.

Surface treatment was first compared for No. 251 with results given in Figure 34. The electropolished surface was better than the etched surface, in contrast to the T and B specimens. The result for the electropolished surface was close to the curves for 3T and 3B. The results for the wet ground surface was very similar to the curve for 2B and slightly better than 2T. The etched surface produced a curve below both the No. 2 and 3 specimens. Since WAPD 251 had good corrosion resistance, the correlation was only satisfactory for the electropolished surface. The next curve (Figure 35) illustrates the observation that short interruptions do not alter the pattern of the voltage-time curve. The recorder tracing is shown with a dotted line to extend the curve from the point of interruption. The combined curve is essentially continuous. The next figure, 36, shows curves for WAPD specimens 201 and 335. These specimens were similar in rate of breakdown at constant voltage (cf. Table III). The other specimens, 291 and 327, Figure 37, which showed a much smaller rate of breakdown (Table III) were examined for comparison. The four curves indicate metal of good quality and check well with the T and B data.

Figure 33. Voltage-time curves for electropolished zirconium after holding at 20 V for 36 hrs. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ \text{C}$.

Figure 34. Voltage-time curves for WAPD specimen 251 with different surface preparation as indicated. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ \text{C}$. This specimen has a low maximum voltage.

Figure 35. Voltage-time curve for WAFD specimen 249, wet ground surface. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$. The current was interrupted for an interval as shown.

Figure 36. Voltage-time curves for electropolished WAPD specimens 201 and 335. Both have high maximum voltages. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

Figure 37. Voltage-time curves for electropolished WAPD specimens 291 and 327. Both had low maximum voltages. 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

b. Tin Alloys at 0.1 ma/cm²

The remaining data were taken on two tin alloys, 2.5 and 5 w/o. It was decided to employ wet polishing for preparing the surface to avoid the possibility of selective etching. The data are shown in Figures 38 and 39. Wet grinding without special precautions to exclude air was found to produce a flat curve of the type labeled A in each figure. Up to this point, the wet grinding was done manually using wet emery paper on a bench top. The emery paper and specimen were rinsed under a faucet after each series of several polishing strokes. With the tin alloys, this procedure always yielded a flat curve, inconsistent with the corrosion behavior. The same specimens were then wet polished under the surface of a water bath. The curves labeled W were then obtained. The W curve for the 2.5% alloy was indicative of good corrosion resistance. The 5% W curve had a low maximum and was inferior to the 2.5%. Duplicate curves illustrate the reproducibility.

Figure 38. Voltage-time curves showing the effect of wet grinding 2.5% tin alloy under water (W) and in air (A). 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

Figure 39. Voltage-time curves showing the effect of wet grinding 5% tin alloy under water (W) and in air (A). 0.1 ma/cm^2 , 1 w/o KOH, $25 \pm 1^\circ\text{C}$.

IV. DISCUSSION

A. General

The highest efficiency of film growth at 0.1 ma/cm^2 was observed on zirconium of high corrosion resistance: specimens 3T and 3B. Less resistant zirconium, Nos. 2, 4, and 5, showed lower efficiencies, although not in the same order as decreasing corrosion resistance. These data suggest that variations occur in the electronic conductivity of the ZrO_2 film as a function of the composition of the parent zirconium. The pattern of these variations suggests that high corrosion rate may be associated with electronic conductivity. The high fields essential to anodic film growth at low temperatures are probably responsible for the complicated effects of electrolyte and current density. From the standpoint of evaluating corrosion resistance, the best criterion for corrosion resistance is probably maximum cell voltage after anodizing at low current density. Voltage-time curves at 0.1 ma/cm^2 were not taken beyond 30 v so the maximum for good metal is not known. It is probably above 200 v.

Surface preparation exerts a greater influence on the development of anodic films than it does on the nature of corrosion films. This can be attributed in part to the thinner films produced in anodizing. If a surface is polished with access to air, a thin outer layer can absorb nitrogen such that the oxide layer will have a low resistance until its thickness exceeds the depth of nitrogen penetration. A temporary plateau will then be produced on the voltage-time curve.

An important aspect of this work was the change in film properties with film thickness. As shown by pre-anodizing with 20 v, the voltage-time curves were changed in an unpredictable manner. The electrical resistance of the film was apparently increased by this treatment (as evidenced by the increase of slope), but the change was not proportional to the previous slope. These data suggest that conducting paths in the film are formed or destroyed as the film thickens. Such changes are believed to form the basis of the difficulties encountered in correlating corrosion resistance with anodic breakdown in the initial work. If the films had retained their relative electrical properties at high as well as low currents, the correlation should have proven successful.

The experiments on the WAPD specimens indicated that breakdown was a function of maximum voltage. The occurrence of breakdown is believed to result from a diminishing rate of film growth caused by increasing resistance to ionic diffusion. The field within the film then rises above the formation field ($5 \times 10^6 \text{ v/cm}$) until the electronic breakdown field is attained. Arcing then sets in, and destruction of the film results.

B. Theory of Anodizing

The nature of the anode process varies widely from one metal to another, since relatively few metals exhibit simple cation dissolution. The type of anode reaction is indicative of the corrosion process, and some generalizations are useful to characterize the film forming metals such as zirconium.

The major factors which determine the type of anodic process are believed to be the following:

1. The ionic potential (ionic charge/ionic radius) of the cation which determines the extent to which hydrolysis will occur with water. In water of pH 7 to 8, a cation will form complex hydrolysates or the hydroxides will be insoluble if the ionic potential is between 4 and 12.⁽¹⁸⁾ Among the metals which meet this condition are: Be, Sc, Al, Th, Ce, Zr, Ti, Si, Nb, and Mo
2. If the anode reaction product is an oxide, the electrical conductivity of the oxide (ionic plus electronic) will determine the subsequent course of the anode process. The two extreme cases are of particular interest:
 - a. Ionic transference numbers close to 1, and
 - b. electronic transference number close to 1.

If the ionic transference number is close to unity, then oxide will grow with high efficiency and the metal will anodize. If the electronic transference number is close to unity, the film will grow with very low efficiency and most of the current will go into oxygen evolution. Dielectric breakdown will probably not be observed.

Examples of a. and b. are tantalum and titanium, respectively.⁽¹²⁾ Zirconium is intermediate in anodic properties and varies in efficiency of film formation depending on current density. The present study suggests that the efficiency of film formation (proportional to ionic transference number) is also a function of electrolyte. This was brought out by extremes in behavior between dilute nitric acid and concentrated NaOH. In the former case, the cell voltage rose very rapidly and leveled off sharply, suggesting high anodic efficiency with dielectric breakdown of the thin high resistance layer. In the later case, the film grew very slowly, even with passage of 10 ma/cm², and showed no tendency to breakdown.

These variations in behavior suggest that the semiconductivity of ZrO₂ is a function of the mode of formation.

C. Theory of the Corrosion of Zirconium

From the results of this study, the corrosion of zirconium is believed to follow the pattern outlined by Mott.⁽¹⁹⁾ According to this viewpoint, a metal piece oxidizes through the following three stages when it has the tendency to make an excess type semiconductor, whereby its conduction band is considerably higher than the Fermi level in the parent metal.

1. Initial period: The oxide layer formed is not thick enough to prevent electron passage by the tunnel effect. The diffusion velocity of cations or anions is the limiting factor in this period.
2. Intermediate period: The thickness of the oxide layer is from 20 to 40 Å, and the oxidation is limited by the velocity of electrons supplied by means of the tunnel effect.
3. Final period: Electrons are supplied only through the conduction band of the oxide layer. As the work function into this conduction level is comparatively large (in the case of Al) the oxidation practically stops by this period. With an increase in temperature, this work function becomes smaller and the available conduction levels in the oxide then become important.

The presence of such levels in ZrO_2 is believed to be largely determined by the presence of impurities incorporated, usually from the metal. Thus, the corrosion of zirconium in high temperature water is considered to be chiefly a function of impurity semiconductor in the ZrO_2 film. The effect of different elements, some favorable to corrosion resistance, others unfavorable, is believed to be a result of p or n conduction⁽²⁰⁾ produced in the film. Oxides can exhibit either type of conductivity, dependent on the stoichiometric excess (p-conductivity) or deficit (n-conductivity) of oxygen.⁽²¹⁾ The electrical nature of an oxide is thus sensitive to its composition and environment (partial pressure of oxygen, temperature, etc.).

The effect of impurities is most important below the intrinsic conduction range where the number of p and n conductors are equal. This phenomenon is illustrated in Figure 40, taken from the work of Pearson and Bardeen.⁽²²⁾ The data were obtained from measurements of electrical conductivity and the Hall effect with silicon to which a small amount of phosphorus had been added. Below approximately 600°C, the conduction is nearly all electronic as a result of the donor action of the phosphorus. Above 600°C, the number of carriers produced thermally (p and n in equal number) outweighs those due to phosphorus, and the silicon is said to be in the intrinsic range. The theoretical curves (solid lines) were obtained on the basis of considerations of the energy level diagram for the semiconductor and the Fermi-Dirac statistics.

Figure 40. Concentrations of conduction electrons and holes in Si + 0.001 per cent P vs. inverse absolute temperature (Pearson and Bardeen).

Previous analyses of the zirconium corrosion process have proposed that deleterious impurities increase the number of anion vacancies.⁽²³⁾ This picture accounts for the effect of nitrogen, but is not satisfactory for Sn, Fe, Cr, Ni. These elements should increase the corrosion rate since they will also promote the formation of anion vacancies. The usual rule is that the oxidation rates of metals forming anion-defect oxide layers will be increased by the addition of cations of lower valency.⁽²⁴⁾ The ability of tin to compensate for deleterious impurities, chiefly nitrogen, is ascribed to a "trapping" or immobilization of anion vacancies.⁽¹³⁾ There is no independent evidence to support such a mechanism.

The role of alloying elements can be understood in terms of their effect on the electrical properties of the oxide. Alloying elements deleterious to the corrosion resistance of zirconium are considered to alter the oxide in such a way that it becomes an n-conductor. Favorable alloying elements will promote p-conductivity. Large p-conductivity may also be detrimental, but to a lesser extent than n-conductivity as may be inferred from the lower mobility of holes as compared to electrons. The ability of tin to counteract the effect of nitrogen is attributed to the phenomenon of compensation, where the effect of donor and acceptor elements is canceled.

Nitrogen in the ZrO_2 lattice is believed to produce the effect of oxygen deficit by creating one oxygen vacancy for each two nitrogens (two N^{-3} equivalent to three O^{-2}). Tin in the ZrO_2 lattice presumably creates the effect of oxygen excess by virtue of its lower valence (+2). If the elements are balanced with a very slight tin excess, the oxygen deficit and p-conductivity will be maintained.

Other favorable elements are believed to act in the same manner, forming cations of lower valence than +4 and stabilizing an oxygen excess lattice. These elements will also delay breakaway* by retarding transition to the oxygen defect lattice. Such a transition would represent a change from intrinsic to n-conductivity. It will depend on oxygen partial pressure (at the interior of the oxide layer) and probably on dissolved hydrogen. After breakaway, corrosion will continue at a high rate unless the oxide is removed by cleaning.

An interesting aspect of zirconium corrosion is the effect of titanium. In small amounts (0.1 w/o), this alloying element increases the corrosion rate, but larger amounts (>4 w/o) cause a decrease.⁽²³⁾ The conducting character of TiO_2 is well known⁽²⁵⁾ and would explain the effect

* "Breakaway" is an inflection point at which the corrosion rate of resistant zirconium begins to increase after a significant period of slow corrosion. Subsequent corrosion is believed to follow a linear law.

of small additions. In larger amounts, titanium begins to alter the lattice parameters of the metal,⁽²⁶⁾ and presumably of the oxide. Such changes could be expected to make ionic diffusion the rate-limiting factor.

Rogener⁽²⁷⁾ found that the resistance of ZrO_2 ceramic compacts varied markedly with the presence of impurities and pretreatment. For individual specimens in the temperature range $340^\circ\text{--}700^\circ\text{C}$ the conductivity followed the exponential law $\sigma = Ae^{-B/T}$ as shown by plots of the data.

V. CONCLUSIONS

The anodic film properties of zirconium have been demonstrated to bear a close relation to corrosion resistance. From the data obtained, it is believed that the chief factor common to these phenomena is the electronic conductivity of the oxide layer. From a testing standpoint, the easiest application of this technique would be measurement of maximum cell voltage after anodizing for a certain period at current densities of 0.1 ma/cm^2 or less. Sensitivity to surface treatment indicates that wet polishing or electropolishing would be preferable for cleaning.

Small defective areas of a specimen might be identified by using an electrolyte which would produce a deposit or color at points where oxygen was evolving. An iodide starch solution might be useful for this purpose.

Other applications of this study to corrosion are suggested by the semiconductor theory proposed in this report. If the n p picture is correct as applied to the "breakaway" phenomenon, then it should be possible to restore the initial high corrosion resistance by forcing oxygen into the inner layers of oxide. A treatment of this type could be carried out by anodizing and should not be difficult of realization. It might be necessary to build up the anodic voltage slowly to effect uniform penetration without localized breakdown. One should also consider the possibility of spalling off the original oxide with formation of a new film underneath. The significance of these factors could only be determined by experiment. A vacuum anneal to remove dissolved hydrogen might be desirable if the resistance of oxide subsequently formed is lowered by its presence.

From a long-term viewpoint, the direction of alloy development is probably of chief importance. Anodizing can be used as a means of alloy testing, and the semiconductor theory can be applied to the role of impurities in the ZrO_2 lattice. A quantitative treatment of the problem of zirconium corrosion may be possible on the latter basis.

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APPENDIX I

Classification of Anodic Phenomena According to A. Guntherschulze

The anodic phenomena associated with electrolytic rectification have been classified by A. Guntherschulze⁽²⁾ as follows (translated):

1. Complete rectification and
2. Incomplete rectification.

Complete rectification is present if the solubility of the metal in the electrolyte is so slight that the phenomena are not influenced. Incomplete rectification occurs if the phenomenon is influenced by the solubility of the metal.

Serious difficulties are encountered in the forming of a rectifying metal if amounts as much as several tenths of a milligram per cm^2 of surface go into solution.

As an introduction to this extensive and difficult field, a review will be given of the most important single groups of phenomena, which fall under the conception of electrolytic rectification.

If an electrolytic cell, composed of a

3. Rectifying metal, e.g., Ta as anode, a suitable electrolyte, e.g., dilute H_2SO_4 , and an optional indifferent metal, e.g. lead, as cathode with a constant

4. Forming current density is charged, then the voltage initially rises in the cell in proportion to the duration of anodizing. The surface of the rectifying metal begins to glow in a uniform pale light. Initially, this is visible only to a well-rested eye; however, the brightness rapidly increases with voltage. At a well-defined voltage there suddenly arises extremely fine sparks on the surface of the rectifying metal.

From this point on, the voltage of the cell rises more slowly, but again continues proportional to time. The sparks gradually become brighter until at a second equally sharply defined voltage, a new type of spark is encountered. The voltage completely or almost completely ceases to climb. The forming of the cell is at an end. Figure 41.

During the forming, the surface several times goes through the entire series of interference colors, which on many rectifying metals are very magnificent.

The following groups of phenomena can then be distinguished during the forming:

Figure 41. Schematic representation of typical forming curves exhibited by tantalum. Cell voltage vs. time.

5. The rate of voltage increase from the beginning of forming up to the sparking voltage is designated "slope a."

6. The rate of voltage increase between the sparking voltage and the maximum voltage is designated "slope b."

7. The rate of voltage increase beyond the maximum voltage period (generally close to zero) is designated "slope c."

8. The sparks ("metal sparks").

9. The sparking voltage.

10. The maximum sparking voltage ("electrolyte sparks").

11. The maximum voltage.

12. The phosphorescent glow.

13. The interference colors.

Figure 41 gives a typical example for the voltage increase on a rectifying anode during forming.

During the forming a very hard, non-porous, extremely thin oxide layer occurs on the metal surface. It is the origin of the interference colors since it is transparent. If an alternating current is superimposed on the direct current of forming, one observes that a very large electrostatic capacity is present on the surface of the rectifying metal and is inversely proportional to the forming voltage. The oxide layer is the dielectric of this capacity; the rectifying metal is one plate and the electrolyte is the other.

Additional definitions, therefore, appear:

14. The oxide layer

15. The thickness of the oxide layer as a function
of the forming

16. The capacity of the oxide layer voltage.

17. The dielectric constant of the oxide layer.

During the forming, a part of the forming current serves to build up the oxide layer; the remainder serves to generate the escape of free oxygen. So there appears

18. The working voltage of forming.

If the rectifying cell is subjected to a constant voltage, which is beneath the maximum voltage, then the current passed by it finally takes on an extremely small value. It is called the

19. Residual current.

If one permits the voltage on the oxide layer to run through all values between zero and the forming voltage, and measures the attendant current density, then one observes that this current consists of two parts:

20. The electron current in the layer.

21. The ionic current in the layer.

Both follow different laws.

If a forming cell is treated with ac, there are produced next two groups of rectifying metals, namely,

22. Direct current rectifiers which pass dc in one direction but hinder the other; with ac, however, the rectifying action does not build up, and current passes in both directions.

23. ac rectification with dc effect.

A current first occurs in the permissible direction with an ac rectifier if a well-defined voltage, the

24. "Minimum voltage," is attained.

In the flow direction there are found on the rectifying metal peculiar forms of metal deposition, if the cations of the electrolyte are heavy metal ions. Therefore,

25. Metal deposition in the flow direction.

If the cell as a capacitor is treated with pulsating dc or with ac, then one encounters in it

26. Dielectric loss.

Here are also worthy of note:

27. The rectifying action in molten salts.

28. The rectifying action in non aqueous solutions.

29. The capacity measured by momentarily applying ac to Ta, W, and Nb is not reproducible.

30. Perforation through contact with metal and dry perforation.

Each of these 30 groups of phenomena of electrolytic rectification depends in an often complicated way on the different variables: temperature, type and concentration of electrolytes, current density, voltage, etc.

APPENDIX II

Observations on Black Oxide Produced Anodically on Zirconium in Nitric Acid

Zirconium anodized in nitric acid develops a black oxide of low resistance which begins to flake only after attaining thicknesses of the order of 0.02 mm.⁽¹²⁾ A number of observations made on this oxide are described below. The most favorable conditions found for this type of film growth were a low voltage (approx. 5 v) in a bath of con. HNO_3 (70%) at room temperature or below. Under these conditions, it is possible to prepare gram amounts of oxide by collecting the flakes spalled off while anodizing for one or more days. Various tests were conducted with the oxide flakes and with coated specimens prior to flaking.

Four materials were used: Early Bu Mines plate, Grade I crystal bar, and 2.5 or 5% tin alloy. Examination consisted of: X-ray diffraction, chemical analysis, petrographic examination, melting points, and conversion to white oxide upon heating in air, water, and vacuum.

1. Examination by X-ray diffraction. The flakes were monoclinic ZrO_2 in every case with some cube phase, particularly noticeable in the Bu Mines metal. This was considered to be most likely carbide or nitride. The patterns were somewhat diffuse and small differences, such as might have occurred with the tin alloy, would be obscured. The diffuseness may have resulted from strain in the lattice or from small crystal size. Charlesby reports a cubic phase in anodizing with dilute HNO_3 .⁽³⁾ It is possible that the formation of cubic oxide is favored by this acid.
2. Chemical analysis. The 5% tin alloy flakes were analyzed chemically to determine whether the tin remained in the oxide in the same proportion as in the metal. Volumetric analysis of two samples of nominal 5% tin alloy gave the following weight percentages: 4.95 and 5.05 w/o tin. Analysis of the oxide flakes for tin (volumetric) and zirconium (gravimetric) yielded the following results:

w/o Tin in the oxide	w/o Zr in the oxide	$\frac{\text{Wt. Tin}}{\text{Wt. Tin} + \text{Wt. Zr}} \times 100$
3.95	69.8	5.35
<u>4.06</u>	<u>69.6</u>	5.51
Av. 4.00	Av. 69.7	

From these data the mol ratio of oxygen to metal in the oxide was calculated as 2.06. More accurate work is needed to determine if this figure is significant.

3. Microscopic examination of the oxide flakes indicated the following:
 - a. Grade I zirconium. Estimated anisotropic or glassy phase 50%, isotropic 50% (with a small amount of opaque phase). The anisotropic has a small crystal size.
 - b. Bu Mines zirconium. Same as above except anisotropic crystals are relatively large and contain more opaque phase.
 - c. 2.5% tin alloy. Same, except the anisotropic crystals are better developed than in (b). There is more opaque phase in (c) than in (b).

The above estimates were based on observation and not statistical analysis of the powder slides.

4. The melting points of the three oxides were determined by the Ceramics Group of the Metallurgy Division. The samples were melted under helium atmosphere, and the results with an optical pyrometer are believed precise to $\pm 2^{\circ}\text{C}$. A single observation was made, melting not cooling. The data were as follows:

Material	M.P. ($^{\circ}\text{C}$)
Commercially available pure ZrO_2	2794
From Grade I Zr	2736
From Bu Mines	2761
From 2.5% tin alloy	2824

The presence of tin significantly raised the melting point.

5. The black oxides were found to convert to white oxide upon heating. The black flakes were not distinguishable macroscopically but exhibited differences upon heating. Approximately one gram of each oxide was placed on a copper sheet and heated slowly on a hot plate. Temperatures were not recorded. After 10 minutes the Grade I and Bu Mines oxide began to turn white; 5% tin alloy flakes were still black. After 45 minutes there was a gradation in appearance: Grade I, gray; Bu Mines, light gray and tin alloy, still black. After 64 hours, the Grade I oxide was pure white; the Bu Mines

was light gray and the tin alloy was light brown or tan. In the second case the shading was due to numerous dark inclusions distributed in a predominant mass of pure white oxide. In the third case, the coloring was uniform and the product was homogeneous.

6. Conversion to white oxide upon exposure to water at 300°C. The black oxide coating was not protective to zirconium exposed to water at 300°C. In the case of Bu Mines metal the layer turned completely white and was nonadherent. The black inclusions noted on flakes after heating in air were not present. If these particles were carbides or nitrides, they probably were hydrolyzed to oxide. The coating on Grade I zirconium turned out white but remained adherent except at the edges of the specimen. The coating on 5% tin alloy became light brown with flaking only at the edges. In the latter two cases, the coatings were translucent, and interference colors could be seen underlying the transformed black layer.
7. Heating in vacuum. One sample of black oxide from Grade I zirconium was heated in vacuum (10^{-5} mm. Hg) and another sample was heated simultaneously in air. As far as could be judged, the rate of transformation to white oxide was the same.

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