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***CORROSION OF ZIRCONIUM
/
SURFACE AREA DETERMINATION
AND SAMPLE PREPARATION STUDY***

by

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CORROSION OF ZIRCONIUM I

SURFACE AREA DETERMINATION
AND SAMPLE PREPARATION STUDY

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FOR DETERMINING THE
CORROSION RATE OF ZIRCONIUM

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-1- PART A
CHEMICAL PROPERTIES OF ZIRCONIUM

INTRODUCTION

A study of the initial corrosion of zirconium presents two main problems concerning the chemistry of the metal. The first of these is to find a solution which will rapidly remove films from the surface of the metal, and leave a surface free from other films which inhibit corrosion. The second problem is to discover a solution which will corrode the samples over a long period of time without producing reaction-inhibiting film growth. Another necessary requisite of the solution is that the concentration of the reactive species can be varied.

Previous observers^{1,2} have found that zirconium is resistant to corrosion in basic and most acidic solutions. Corrosion rates in various organic acid and saline solutions have been found negligible. The metal shows appreciable attack in concentrated sulfuric, hot concentrated phosphoric acids and in aqua regia, the corrosion susceptibility being altered somewhat by the presence of impurities such as hafnium, carbon, nitrogen and oxygen in small amounts.³ The high dissolution rate of zirconium in hydrofluoric acid is also well-known; however, the reaction produces a loose black deposit on the surface of the metal.⁴ Certain solutions containing both nitric and hydrofluoric acids have been found which appear to leave a clean surface on zirconium.^{5,6}

INVESTIGATIONS OF THE CORROSION BEHAVIOR OF ZIRCONIUM

The following observations were made on a qualitative basis in an attempt to find reagents with corrosion characteristics which would be suitable for the experiment. Where percentage values are given, it will be understood that they are on a volume basis.

Etchants.

5 HF, 10 HClO₄- The solution reacted violently with all types of zirconium which were tried, leaving a dull gray surface but no apparent build-up of a surface film.

10 HF, 30 HNO₃- Reacted violently with zirconium, with the evolution of brown nitrogen dioxide. When the sample was removed into the air, after a short delay period, a flash reaction occurred in which more NO₂ was evolved and a white film was formed on parts of the sample surface. The remainder of the surface had a mirror-like finish. If the sample was removed quickly from the etching solution and placed immediately into a beaker of water, the formation of the white film could be prevented, and the entire surface of the sample appeared shiny and free from any film.

6 parts glycerine, 2 parts HF, 1 part HNO_3^5 --- This solution produced a mirror surface, but occasionally it left a brown stain on the sample. The action of the glycerine seemed to be in preventing the formation of a white film as described in the above discussion. The solution, though quite suitable for cleaning the samples, was not used since there was a chance of contamination with H_2SO_4 and the subsequent danger of nitroglycerine formation.

8 parts glycerine, 1 part HF, 1/2 part HNO_3 , 2-4 parts H_2O^5 . The solution always produced a brown stain on the surface of the zirconium.

20 parts HF, 80 parts H_2O , 1 part HNO_3^5 --- This solution was not desirable because of the violent reaction and the formation of a black surface on the samples.

4 ml. HF in 100 ml. 1N $\text{NH}_4\text{F} \cdot \text{HF}$ --- Samples placed in the solution with a shiny surface usually turned dull gray after a short time.

25 ml. H_2O , 25 ml. HCl, 2 ml. HF--- This solution sometimes left a clean surface, sometimes formed a brown or dull gray film.

3% HF, 30% HNO_3 --- This solution seemed to be the most suitable, since it did not react as violently as the solutions with a higher HF concentration. It appeared to leave a shiny surface on the zirconium samples without the formation of a white film when the samples were removed to the air.

The above observations were made at room temperature (70-80°F.), using Foote Mineral commercial grade, and Bureau of Mines and Westinghouse hafnium-free zirconium samples.

Corrosion Solutions.

Surfural Acid-- The samples tested were first sanded to a smooth finish, then etched in a 5% HF, 10% HClO_4 solution before placing them in the corrosion solutions. Both types of zirconium samples were used in the observations. The percentage values given are in volume percent.

95% H_2SO_4 --- All of the samples tested reacted immediately at all temperatures, beginning at 0°C., with the evolution of a gas with an H_2S odor. A black film was formed on the samples, while the corrosion solution often turned milky. One of the commercial grade samples turned white over part of the surface and black over the other part, probably due to anodic and cathodic areas on the sample surface. The white portion of the sample gradually dissolved, leaving a white deposit in the bottom of the beaker. The X-ray diffraction pattern of the compound closely resembled that of zirconyl sulfate (ZrOSO_4).

80% H_2SO_4 -- The samples reacted immediately at all temperatures, beginning at 0°C . A black surface film was produced which always seemed to start at the bottom of the samples. The reaction could be detected by the vigorous evolution of a gas with an H_2S odor.

60% H_2SO_4 -- At temperatures up to 30°C , the samples reacted only slightly. At temperatures above this, some of the samples reacted vigorously, with the formation of a black or gray film, while others reacted only slightly at temperatures up to 140°C . The hafnium-free samples seemed to react for about 2 hours without the formation of a film at $20-90^\circ\text{C}$. After this time, a black deposit began to form along the bottom of the samples.

40% H_2SO_4 -- All of the samples appeared to react only slightly or not at all. Where a reaction could be seen, black film formed slowly on edges of the sample.

1-30% H_2SO_4 -- These concentrations did not appear to react with any of the zirconium samples.

OTHER SOLUTIONS

Concentrated H_3PO_4 -- A sample was etched in HF-HNO_3 and placed in the H_3PO_4 solution, together with a sample which was already covered with a black film from corrosion in H_2SO_4 . At room temperature neither of the samples appeared to react. When the solution was heated to boiling, a black film formed on the etched sample and the film on the other sample appeared to thicken.

0.005 N HF -- A hafnium-free sample was polished with sand paper, rinsed in distilled water, and washed in an alcohol-ether mixture. It was then dried, weighed, and placed in the HF solution. After two days the sample was removed, dried, and weighed. No weight loss could be detected.

0.02, 0.03, 0.04 N HF -- An intermittent gray film was formed on all of the samples tested. The slow formation of gas bubbles could be detected.

0.05-1 N HF -- The evolution of gas could be detected for all concentrations in this range. In all cases, a black film was formed on the samples.

0.025 N HF- 0.025 N HClO_4 -- A Hf-free sample was weighed and placed in the solution for 3 days. Upon removal from the solution, the sample appeared to be covered with an intermittent gray film. The sample had lost 10.2 mg.

1N Oxalic Acid -- A Hf-free sample, etched in HF-HNO_3 , was weighed and placed in the solution at room temperature. No reaction could be detected. After 24 hours, the solution was heated to 100°C . for about 3 hours. There was still no perceptible reaction. The sample lost 0.3 mg.

50% HCl -- A Hf-free sample was placed in the solution and left for 6 hours. It gained 0.5 mg, but appeared to remain clean.

10% HNO_3 - 0.001% HF-- No reaction could be detected.

10% HNO_3 - 0.005-0.1% HF-- In this concentration range, a reaction could be detected. At lower concentrations, the samples tested remained shiny for 1-2 hours, but gradually turned gray. At higher concentrations, the samples turned black in a shorter time.

DISCUSSION OF CORROSION OBSERVATIONS

Etchants.

Of the etchants tried in the experiment, a solution of 3-10% HF, 30% HNO_3 , and the remainder de-ionized water was found to be the most satisfactory. When zirconium is placed in a hydrofluoric acid solution, a loose, black deposit will form on the sample at higher concentrations and a black or gray film at lower HF concentrations. The formation of the black deposit is also reported by another observer.⁴ An x-ray analysis of the black film was made but it could not be identified. The action of hydrofluoric acid on zirconium is thought to produce stable soluble complexes of zirconium and fluorine, the ZrF_3^+ being predominant. However, it is probably that the film is an insoluble fluoride of zirconium. Further attempts will be made to identify the compound by x-ray diffraction.

It has been found that if certain concentrations of nitric acid are used together with hydrofluoric acid, the formation of the black compound described above is prevented and the surface of the zirconium becomes very shiny. However, when the sample is removed from the solution into the air, a violent reaction takes place on the surface of the sample when higher concentrations of HF are used. In the reaction, NO_2 is evolved and a white deposit is formed on parts of the sample surface. The nature of the reaction has not yet been investigated, but it appears that the zirconium is oxidized, probably to ZrO_2 through the combined reaction of the HF, HNO_3 , and the oxygen in the air. Since this effect has not been observed with nitric acid and zirconium alone, the HF plays an important part in the reaction.

The concentration of HNO_3 necessary to prevent the black film formation seems to be independent of the HF concentration and must be at least 30% for HF concentrations up to 10% by volume, though in some cases, 20% HNO_3 has prevented film formation in solutions higher than 1% in HF. When the hydrofluoric acid concentration was more than 10%, the solution reacted too vigorously with the zirconium. Solutions with only 2-3% HF soon became depleted in fluoride ion and lost their etching power. The HF concentration was therefore varied between 3-10% depending on how long the solution was to be

used before discarding. If it was not necessary to use fresh solutions for each corrosion cycle, more HF could be added to a depleted solution to prolong its usefulness.

Corrosion Solutions:

None of the corrosion solutions tested would consistently corrode zirconium without the formation of a film. Concentrations of sulfuric acid from 60-70% often reacted for 1-2 hours before a film appeared, but the reaction was usually slow. Any violent reaction almost invariably produced either a black or a white film, the black being predominant. The HF-HNO₃ solutions tested would usually not form a visible film for sometime after the sample had been placed in the solution and the film did not seem to inhibit the reaction for the first 30-40 minutes. After this time the film seemed to affect the reaction since the rates began to decrease. However, this may also have been due to depletion of HF. It was not always possible to use a concentration of nitric acid which would prevent the film formation since the concentration had to be varied during part of the experiment.

CONCLUSIONS

1. The most satisfactory etchant found in the experiment, for the removal of films from the surface of zirconium is a solution of 3-10% (by volume) HF, 30% HNO₃, and the remainder water.

2. Solutions which react with zirconium, such as sulfuric, hydrofluoric and phosphoric acids, usually form a black film on the surface of the sample. The only consistent exception was found to be a HF solution to which the proper amount of HNO₃ had been added. /2

PART B
DETERMINATION OF SURFACE AREA
CHANGES ON ZIRCONIUM SAMPLES

INTRODUCTION

In order that corrosion rate data can be correctly interpreted, variations in the true area of the metal surface should be considered. The surface roughness factor is defined as the ratio of the true surface area to the apparent surface area and has been found to vary considerably depending on the treatment of the surface. Bowden and Rideal⁷ found that the accessible area of a metal sponge such as platinum black is about 2,000 times its apparent area, while that of a sand-papered metal is only 10 times the apparent area.

While measuring the surface area of copper by the electrolytic method, Weeks⁸ found that the roughness factor decreased from an initial value of 80 to a value which remained essentially constant at from 5 to 10. It is the purpose of this experiment to determine the behavior of the roughness factor for zirconium.

METHOD OF SURFACE AREA DETERMINATION

The electrolytic method has been found effective and accurate for measuring the surface area of small metal samples. While working with thin metallic films, Bowden and Rideal⁷ found that a mercury electrode in a solution of H_2SO_4 would give a linear relationship between the voltage of the electrical double layer at the $Hg-H_2SO_4$ interface and the amount of charge deposited at the interface, provided the hydrogen overvoltage was not exceeded. This may be expressed mathematically as follows:

$$\Delta Q = C \Delta V \quad (1)$$

where ΔQ is the charge built up at the double layer, ΔV is the change in voltage of the double layer, and C represents the capacitance. It was found that $C = K A_t$, where K is another constant and A_t is the true surface area. Therefore,

$$C = \frac{\Delta Q}{\Delta V} = K A_t \quad (2)$$

and the true surface areas of different surfaces can be compared by measuring their relative capacitances.

In the experiment the capacitance was measured using the method suggested by Wagner⁹. The polarization capacity C_1 per unit was calculated from the expression..

$$C_1 = \frac{I}{A} \frac{\Delta t}{\Delta E} \quad (3)$$

B_1, B_2 STORAGE BATTERIES

P_1, P_2 POTENTIOMETERS

V_1, V_2 VOLTMMETERS

S SWITCH

G BALLISTIC GALVANOMETER

C ELECTROLYTIC CELL WITH MEASURING ELECTRODES AND REFERENCE ELECTRODE.

FIGURE 1. SURFACE AREA MEASURING CIRCUIT .

The current-time integral for a known change in potential was measured using a ballistic galvanometer. The potential range was chosen such that the steady-state current in the measuring cell practically disappeared.

If the absolute value of the roughness factor is to be calculated, then the measured capacitance must be compared with the capacitance of an ideal surface, which mercury closely approaches. Values of 6 and 20 microfarads per square centimeter⁹ have been reported for mercury. If, however, only the relative changes in the roughness factor are desired, the capacitance values for a series of measurements need only be compared together to determine whether or not the factor reaches a constant value after a number of corrosion runs.

APPARATUS

A schematic diagram of the measuring circuit is shown in Figure 1.

A. BALLISTIC GALVANOMETER.
B. CONTROL PANEL

FIGURE 2. SURFACE AREA MEASUREMENT EQUIPMENT.

In the beginning the switch S is open so that all of the voltage is supplied from B_1 through P_1 . The switch S is then closed and an additional known voltage is applied to the measuring cathode through P_2 . The current-time integral can then be evaluated from the maximum deflection of the galvanometer.

It is therefore possible to evaluate ΔQ in the foregoing expressions, and since ΔV is known, the capacitance can be calculated. The charge, ΔQ , is found by calibrating the galvanometer scale using a standard capacitor so that the charge per division on the galvanometer scale is known. Multiplying the charge per division by the number of divisions gives the total charge.

EXPERIMENTAL RESULTS

Calibration of Galvanometer.

The galvanometer scale was calibrated using a 2480 microfarad capacitor in place of the measuring cell. The galvanometer constant was found to be 1650 $\frac{\text{MF} \cdot \text{m.v.}}{\text{division}}$. The capacitance per unit area was calculated from the expression--

$$C = \frac{1650 \times d}{\Delta E \times A_a}$$

where d is the galvanometer deflection, ΔE is the applied voltage in millivolts and A_a is the apparent area in cm^2 . C is then given in microfarads per cm^2 .

Mercury-

A glass bulb was filled with mercury to 6.15 cm^2 cross section and placed in the measuring cell as the cathode, against a mercury anode in a 1 N H_2SO_4 solution. An average capacitance of 20.4 micro farads per square centimeter was obtained which agrees closely with the best value in the literature of 20 micro farads per square centimeter reported by Bowden and Grew⁹.

Zirconium

The zirconium surface area measurements are not yet completed and only the preliminary measurements will be included in this report.

The measurements were made using Westinghouse hafnium-free zirconium samples.

The general procedure was to etch the sample to be measured in an $\text{HF} + \text{HNO}_3$ solution, rinse twice in de-ionized water, place in the measuring cell as the cathode and allow the steady-state current to drop to a constant value before taking galvanometer readings. The electrolyte in the cell was .1 N KCl and the anode was platinum.

In the first experiment, an attempt was made to show that the galvanometer readings were an indication of the zirconium surface area exposed to the solution. Readings were taken on a sample fully immersed, then raised one-fourth, one-half and finally three-fourths of the way out of the solution. At first it was found that raising the sample even one-half of the way out of the solution did not reduce the galvanometer reading appreciably. This was found to be due to a conducting layer of solution which adhered to the portion of the sample which had been removed. When this film was allowed to dry, the results were reasonably close to the expected values as the following table will show.

TABLE I

Fraction of the Sample Immersed*	1	3/4	1/2	1/4
Galvanometer reading (divisions)	10.5	6.6	5.0	2.4
Expected value	10.5	7.9	5.25	2.6
*approximate				

In further investigations of the surface area effect, a large hafnium-free sample (5 x 5 cm., 1/8 in. thick) was sanded to a medium rough finish and the following readings taken:

TABLE II

Treatment of Sample	Galvanometer reading
1. Sanded to medium rough finish	19.5
2. Etched in HF-HNO ₃ and rinsed	13.3
3. Etched in HF-HNO ₃ and rinsed	8.7
4. Etched in HF-HNO ₃ and rinsed (sample badly striated)	16.8
5. Sanded off striations and etched in HF-HNO ₃	11.7
6. Etched in HF-HNO ₃	9.6

It was found that when a sample had been placed in a solution containing HF, there was a considerable reduction in the galvanometer reading, even though there had been very little change in the nature of the sample surface. A possible explanation is that the negative fluoride ion is adsorbed on the sample surface and reduces the flow of electrons which normally could be transported to the interface, thus reducing the current flow and therefore the galvanometer reading.

The difference in the first two readings in Table II was probably due partially to this effect and partially to a reduction in the true surface area. The readings show that the surface area decreased until the sample

became striated, at which time it increased. When the striations were sanded off and the sand marks etched smooth, the surface area was again reduced.

Preliminary calculations of the capacitance for zirconium range from 5 to 57 microfarads per square centimeter depending on the condition of the zirconium surface. It is hoped that further measurements will compare more favorably with the value calculated for mercury.

Another effect has been observed which has not yet been explained. When a newly-etched sample is measured the galvanometer readings fall off with time and reach a constant value after about 24 hours. A sample which has not been etched will always give a constant deflection. In order that data from freshly-etched samples can be compared, it is necessary that the initial readings be taken at the same time after the samples have been removed from the etchant.

SUMMARY

1. ²/The electrolytic method has been used successfully to measure surface areas of ^{Pt}platinum, ^{Hg}mercury and several other metals. Preliminary measurements indicate that the method can be used for ~~zirconium~~ ^{zirconium} samples. >

2. The surface area is measured by comparing the capacitance of various surfaces. The capacitance is calculated by evaluating the current-time integral with a ballistic galvanometer when a known voltage is applied to the measuring cathode.

3. The value of 20.4 microfarads per square centimeter calculated for mercury compares very well with the values reported in the literature.

4. Capacitance ranging from 5 to 57 microfarads/^{cm²} per square centimeter have been measured for ^{zirconium}zirconium. Further work is necessary before final values can be reported. ² _{and}

PART C
INVESTIGATION OF ELECTRO-REDUCTION TECHNIQUE
FOR DETERMINING THE
CORROSION RATE OF ZIRCONIUM

This phase of the research was undertaken to determine whether the film of corrosion products on a zirconium surface could be electro-reduced in an aqueous system. This technique as applied to copper⁹ made it possible to investigate the initial slow process in the corrosion of that metal and it was hoped that the hydrogen overvoltage on zirconium would be sufficiently high that reduction of the metal ions might take place.

The following experimental observations were made:

1. Reduction of the zirconyl or fluo-zirconyl ion is not possible at current densities attainable with the equipment.
2. The initial reduction potential and the hydrogen production potential is are sensitive functions of:
 - a- Inert gas passing through the cell--Argon gave a higher initial reduction potential than nitrogen.
 - b- Ionic strength of the K Cl solutions.
 - c- Hydrogen ion concentration.
 - d- Partial pressure of oxygen in the solution.
 - e- Adsorbed SO₂ gives a significantly lower potential.
3. The hydrogen evolution potential was also a function of the type of corrosion film produced.
 - a- The potential increased in order for samples corroded for five hours at 70°F., 100°F., 120°F. and 198°F.
 - b- A sample oxidized in a tube furnace at 800°F. in oxygen at atmospheric pressure had a higher electro-reduction potential than any samples oxidized in aqueous solution. Furthermore, the film produced was protective; the sample proved to be inert toward the nitric hydrofluoric acid solution used for metal dissolution on all other samples.

It was decided to postpone further work on the surface phenomena on zirconium until after completion of the corrosion rate study utilizing the radio-active zirconium. This phase of the work was carried out by Mr. Gordon Price under the direction of Dr. George Richard Hill.

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