MASTER

Argonne National Laboratory

STUDIES IN ZIRCONIUM OXIDATION

by

J. Levitan, J. E. Draley,
and C. J. Van Drunen

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie Institute of Technology
Case Institute of Technology
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
Iowa State University

The University of Iowa
Kansas State University
The University of Kansas
Loyola University
Marquette University
Michigan State University
The University of Michigan
University of Minnesota
University of Missouri

Northwestern University
University of Notre Dame
The Ohio State University
Purdue University
Saint Louis University
Washington University
Wayne State University
The University of Wisconsin

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in the United States of America

Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

ANL-7252

Metals, Ceramics, and
Materials (TID-4500)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

STUDIES IN ZIRCONIUM OXIDATION

by

J. Levitan, J. E. Draley,
and C. J. Van Drunen

Metallurgy Division

Program 10.2.5

Portions of the material in this report have appeared in the
following Metallurgy Division Annual Report:

ANL-7155 pp. 282-284 1965

December 1966.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	4
I. INTRODUCTION.	4
II. RATE OF OXIDATION.	5
III. RATE-LIMITING PROCESS AND PHASE TRANSFORMATION.	8
IV. INFLUENCE OF OXYGEN PARTIAL PRESSURE ON THE POTENTIAL ACROSS THE OXIDE.	11
V. LOW-PRESSURE OXIDATION.	13
VI. OXIDATION OF ZIRCONIUM WITH A VAPOR-DEPOSITED GOLD FILM	18
VII. ELECTRICAL MEASUREMENTS IN ZIRCONIUM REACTIONS WITH NITROGEN, CARBON DIOXIDE, AND WATER VAPOR.	20
VIII. SUMMARY AND CONCLUSIONS	22
REFERENCES AND BIBLIOGRAPHY	24

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Zirconium Oxidation at 700°C and 100 mm Oxygen	6
2.	Zirconium Oxidation at 550°C and 100 mm Oxygen	6
3.	Zirconium Oxidation at 800°C and 10 mm Oxygen	7
4.	Oxidation of Zirconium at 700°C at Different Oxygen Partial Pressures.	7
5.	Ratio of R_e to R_i at 550 and 700°C	10
6.	Development of a Potential across the Growing Oxide at 550 and 700°C	11
7.	Potential Dependence upon Oxygen Partial Pressure at 700°C.	12
8.	Potential Dependence upon Oxygen Partial Pressure at 550°C.	12
9.	Potential Dependence upon Oxygen Partial Pressure at 800°C.	13
10.	Low-pressure Oxidation of Zirconium at 700°C	14
11.	Low-pressure Oxidation of Zirconium at 550°C	15
12.	Low-pressure Oxidation of Zirconium at 800°C	16
13.	Low-pressure Oxidation of Zirconium at 550°C (Volumetric Techniques).	17
14.	Early Stages of Zirconium Oxidation at 550°C (Volumetric Techniques).	17
15.	Early Stages of Zirconium Oxidation at 700°C (Volumetric Techniques).	18
16.	Oxidation of Zirconium with an Evaporated Gold Film (at 700°C)	19
17.	Zirconium Nitriding at 900°C and 100 mm p_{N_2}	20
18.	Oxidation of Zirconium in CO_2 at 750°C and 100 mm Pressure	21

STUDIES IN ZIRCONIUM OXIDATION

by

J. Levitan, J. E. Draley,
and C. J. Van Drunen

ABSTRACT

The oxidation of zirconium at 550, 700, and 800°C, and at moderate pressures, followed rate laws that were between parabolic and cubic. Resistance measurements generally indicated electronic control of oxidation, though control during initial stages was partly ionic.

The electric field across the growing scale exhibited a dependence on the partial pressure of oxygen in the low-pressure range. Gravimetric and volumetric measurements during the low-pressure oxidation indicated a different mechanism: initial oxidation was linear, suggesting surface-reaction control. Interpretation in terms of an "induction" period is also suggested.

Zirconium bearing a vapor-deposited gold film exhibited linear pressure dependence of oxidation for long times at moderate pressures.

Measurements of potential and resistance during interaction of zirconium with H₂O vapor, CO₂, and N₂ provided indications of the reaction mechanisms.

I. INTRODUCTION

Electrical measurements in experimental studies of zirconium oxidation have received only minor attention. Since Kirkbride and Thomas¹ measured the potential across growing scale on zirconium, electrical measurements have been employed at Argonne National Laboratory mainly by R. Misch² and more recently by Bradhurst, Draley, and Van Drunen.³ Their work, which showed that significant information can be obtained from these measurements, led to this study.

Electrical measurements can profitably be combined with oxidation data to provide insight regarding the oxidation mechanism. This is the

course pursued in the present study. Since several independent topics are covered in this report, they are described in separate sections.

II. RATE OF OXIDATION

Knowledge of oxidation kinetics at different temperatures was needed for the electrochemical calculations to follow. Such data often differ from laboratory to laboratory, and depend upon material and testing conditions.

High-purity zirconium, obtained from Materials Research Inc., was used in the work. Impurity content of the batch, as found by spectrometric analysis was (in ppm by wt):

H ₂	3.3	Al	3.0	Cl	2.0	Ti	1.0
B	0.005	Si	1.5	K	0.004	V	0.05
C	6	P	0.1	Ca	0.04	Cr	0.5
N ₂	2.1	Ni	1.5	Hf	40.0	Fe	30.0
O ₂	25	Cu	0.01				

Sodium, sulfur, and scandium were not determined owing to spectral interference; other elements were below detectable limits.

Specimens were prepared from 1/16-in.-thick sheets by punching out discs or cutting rectangular pieces. Samples were wet-ground through 600 SiC paper, rinsed in hot water, etched to a depth of about one mil in a 45:5:50 (by volume) HNO₃ (70%): HF (49%): H₂O solution, rinsed in cold water, degreased in ethanol, and dried.

The weight gain of an oxidized specimen was measured with an Ainsworth RV-AV-2S vacuum microbalance, which makes possible continuous recording of the weight change with a sensitivity of $\pm 10 \mu\text{g}$. The balance and furnace assembly were connected to a vacuum system in which the pressure could be maintained at about 10^{-7} mm Hg. A platinum basket hanging on a platinum wire was used as a sample holder. The system containing the sample to be tested was evacuated, then heated to the necessary temperature and thermostatted there. Oxygen (or another gas) was admitted, and the system was evacuated at the end of the run.

The conditions used to anneal the specimen were found to influence oxidation kinetics. To obtain reproducible results or to compare runs at the same oxidation temperature, annealing and outgassing conditions were strictly reproduced. Sample geometry also was found to have a significant influence on oxidation kinetics, and for the same series of oxidation runs the sample geometry was maintained.

Good reproducibility of results was found for three temperatures in the range from 550 to 800°C. Figure 1 shows the reproducibility for 700°C and 100-mm O₂. Results for 800°C were fairly reproducible, but for 550°C they were not as reproducible as for 700 and 800°C.

Fig. 1. Zirconium Oxidation at 700°C and 100 mm Oxygen

Typical oxidation results for 550, 700, and 800°C are presented in Figs. 1, 2, and 3. Oxidation did not obey a simple kinetic expression. Typically, oxidation data fell between parabolic and cubic lines on a log-log plot, but a straight line was not formed.

Fig. 2. Zirconium Oxidation at 550°C and 100 mm Oxygen

Fig. 3. Zirconium Oxidation at 800°C and 10 mm Oxygen

Accurate analysis of the early stages of oxidation by examination of the weight-gain recordings was difficult. Better analysis was obtained by using volumetric techniques (reported in Sect. V).

The effect of oxygen partial pressure on oxidation was studied in the pressure range between 1 and 400 mm Hg. Little or no effect was found at various temperatures. Results for 700°C are presented in Fig. 4.

Fig. 4. Oxidation of Zirconium at 700°C at Different Oxygen Partial Pressures

III. RATE-LIMITING PROCESS AND PHASE TRANSFORMATION

The structure of zirconium oxide has been the subject of extensive investigation. Monoclinic zirconia transforms to the tetragonal modification at temperatures exceeding 1000°C .^{6,8} On cooling, monoclinic phase is formed from the tetragonal, though there is a significant hysteresis. The transformation has many characteristics typical of martensitic shear transformations.¹⁰ The positions of the atoms in both lattices are similar, the most significant difference being a change in coordination of zirconium atoms and of one of the two oxygen atoms that requires the severing of some bonds during the inversion.¹¹

Thermodynamic considerations indicate that tetragonal zirconia can also be stabilized at temperatures much lower than 1000°C by application of pressure.^{7,8} The back transformation upon the release of pressure is apparently sluggish.

Studies of zirconia transformation have been extended to films formed during zirconium oxidation. Tetragonal zirconia was observed in these films by means of differential thermoanalysis, X-ray diffraction, and electron diffraction.^{5,7,10,13} Small mean crystallite size favors formation of the tetragonal phase.^{12,13} Pemsler's¹⁵ study of the kinetics of zirconium oxidation takes into account the presence of tetragonal phase. Conditions at the beginning of the oxidation that are favorable for formation of the tetragonal modification (even far below 1000°C) are: (1) rapid oxidation and small mean crystallite size, (2) compressive stress in the initially formed film, and (3) a high degree of nonstoichiometry of the zirconia formed. According to Krauth and Meyer,¹⁷ rapid formation of a large surface area provides sufficient energy for the transformation to a higher-energy tetragonal modification--exactly what we believe is occurring at the beginning of zirconium oxidation. With increasing duration of oxidation, the factors stabilizing the tetragonal phase are weakened: the occurrence of grain growth favors stability of the monoclinic modification; compressive stresses are reduced and so is the defect concentration.

The change in volume associated with tetragonal-monoclinic transformation may be one of the causes for formation of cracks in the oxide. Though the transformation is not believed to be the cause for breakaway,¹⁸ Pemsler interprets his kinetic data after extrapolating to lower temperatures the high-temperature (above 1000°C) data for tetragonal zirconia. He postulates the initial formation of tetragonal zirconia. A higher degree of nonstoichiometry contributes to the increased oxidation rate. Later, because of the unfavorable factors listed above, a hybrid monoclinic-tetragonal phase is formed, then the monoclinic modification is stabilized.

A better understanding of the factors controlling oxidation is necessary: (1) what are the contributions of ionic and electronic processes to rate control during the initial stages of oxidation, when tetragonal phase is present; (2) what are the changes in ionic and electronic retardances with oxidation time and in connection with the changing oxide crystalline structure?

The investigation was undertaken on the basis of the electrochemical model for zirconium oxidation developed by Bradhurst, Draley, and Van Drunen.³ From measured resistance R to the passage of small currents passed through the oxide film and oxidation rate i , values of R_e and R_i (electronic and ionic retardances) were calculated from the following:

$$R_e = \frac{E_0}{2} \left(1 + \sqrt{1 - \frac{4iR}{E_0}} \right) \quad (1)$$

and

$$\frac{1}{R_i} = \frac{1}{R} - \frac{1}{R_e}, \quad (2)$$

where E_0 is the thermodynamic potential for oxidation.

These equations are based on the assumption that the retardances controlling the applied current during the resistance measurement are the same as those controlling the rate of oxidation. This is known not to be true: for one thing, the resistance determination involves a differential measurement, and the retardances limiting oxidation are integral quantities.

During oxidation of zirconium, R_i is small compared to R_e , and R_e is nearly equal to E_0/i . It follows that there is little error in the determination of R_e (integral), although there can be substantial error in the determination of R_i .

When it is desired to examine the relative control of oxidation by electronic and by ionic processes, a convenient quantity is R_e/R_i . This is the quantity chosen in the present investigation. Although its actual value is admittedly questionable, variations in the calculated ratios are expected to be in the same direction as the actual (unknown) ratios. It is in this vein that they are interpreted.

Resistances have been measured by a number of investigators using different techniques. One of the recent methods was based on measuring the resistance of a specimen resting on platinum powder, and then measuring the resistance in a molten bath of alkali metal carbonates. This method

has the obvious advantage of allowing consecutive measurements on one specimen during oxidation; however, this is overshadowed by irreproducibility of contact area and its change during the run. To overcome this difficulty five identical zirconium samples were oxidized together in the same chamber; at each of five selected exposure times, one specimen was immersed in the salt bath for resistance measurement. Film-resistance measurements were made at 550 and 700°C and an oxygen pressure of 100 mm.

The ratio of R_e to R_i was lower at the beginning of oxidation, then increased and remained constant during the rest of the run (see Fig. 5).

Fig. 5. Ratio of R_e to R_i at 550 and 700°C

The low value of the R_e/R_i ratio at the beginning of oxidation suggests a controlling influence of the ionic process on the rate of oxidation at this stage. If extrapolation to zero is correct, the control is entirely ionic for very short times. The similarity between the curves at 550 and 700°C indicates a similar mechanism at the two temperatures. Perhaps the tetragonal phase present during the initial oxidation stages allows a higher oxidation rate largely because of its greater electron conductivity (higher defect concentration?). Appearance of the monoclinic phase during oxidation increases the electronic retardance and the R_e/R_i ratio. Finally, when monoclinic phase is stabilized, this ratio approaches an approximately constant value.

The R_e/R_i values and potentials recorded for a growing scale on zirconium at 700 and 550°C (100 mm O_2 pressure) are presented in Fig. 6. Stabilization of the potential roughly corresponds to stabilization of the R_e/R_i value. When steady conditions at the oxide/gas and metal/oxide interfaces are reached, an unchanging electric field is established.^{19,20} Presumably, a constant R_e/R_i value also indicates achievement of steady-state conditions.

Fig. 6. Development of a Potential across the Growing Oxide at 550 and 700°C

IV. INFLUENCE OF OXYGEN PARTIAL PRESSURE ON THE POTENTIAL ACROSS THE OXIDE

During zirconium oxidation in dry oxygen an electric field is established and a potential across the growing scale can be recorded.² Presumably, this electric field is dependent upon the defect structure of the growing oxide. Defect concentration will depend upon oxygen partial pressure, p_{O_2} . The oxygen-vacancy concentration presumably will depend on p_{O_2} and, because of the requirements for at least approximate local electrical neutrality, the conduction-electron concentration (and conductivity) will also depend on p_{O_2} .

The electrical potential associated with the field also might vary with p_{O_2} ; for, when oxygen is evacuated from the system, the potential drops to zero.³ The present measurements were made to observe the relationship between p_{O_2} and the potential developed during oxidation.

The experimental setup was similar to that described elsewhere.³ A zirconium specimen was placed on platinum powder in order to maintain a steady electrical contact without interrupting the oxidation process. The experiments were performed in the Ainsworth automatic balance.

Oxygen partial pressure was quickly changed at certain times during zirconium oxidation, such that each new pressure was maintained constant for a few minutes in order to reach steady-state conditions and stabilization of potential.

Potential measurements were difficult to reproduce because of irreproducibility of contacting conditions from run to run. However, the potential was stable for any particular run and remained constant after stabilization. Results of potentials recorded with a changing p_{O_2} are presented in Fig. 7. The potential was practically independent of p_{O_2} in the pressure range from 1 to 400 mm. However, at pressures below 1 mm the potential decreased with decreasing p_{O_2} and increased when p_{O_2} was increased.

Fig. 7. Potential Dependence upon Oxygen Partial Pressure at 700°C

Similar experiments at 550°C (see Fig. 8) and 800°C (see Fig. 9) also showed a dependence of the potential upon p_{O_2} . At 550°C the changes

Fig. 8. Potential Dependence upon Oxygen Partial Pressure at 550°C

Fig. 9. Potential Dependence upon Oxygen Partial Pressure at 800°C

in the potential with changing p_{O_2} were larger than at 700°C; potential was independent of p_{O_2} between 10 and 400 mm. At 800°C, observed potentials were sensitive to p_{O_2} over the entire pressure range used. The effect was maximum at the lowest pressures (see Fig. 9).

When the system for the experiment whose results are reported in Fig. 9 was evacuated at about 57 min after start, the potential quickly decayed to zero. However, at about 187 min, a more gradual decline was observed. How much of this phenomenon is attributable to relatively slow outgassing of the thicker oxide film is not known.

V. LOW-PRESSURE OXIDATION

Numerous investigators have found the kinetics of zirconium oxidation to be practically independent of p_{O_2} ; ^{3,22-25} however, their investigations have covered mostly the pressure range between 1 and 400 mm. This range corresponds approximately to the plateau on the curve of E vs p_{O_2} . Thus, an unchanging electric field corresponds to an independence of oxidation rate upon p_{O_2} . A question immediately arises: do changes in the electric field across the growing oxide scale at lower partial pressures of oxygen correspond to a change in oxidation kinetics?

Accordingly, a study of zirconium oxidation at a lower pressure was undertaken. The lower limits of p_{O_2} were restricted by the total volume of our experimental system, for oxygen consumption at low initial p_{O_2} will reduce considerably the p_{O_2} in the system. The conditions were

"static" (rather "nonflow") where no fresh inlet of oxygen was available. In our "static" system an extensive thermal convection takes place since the high-temperature zone occupies only a small fraction of the total volume of the automatic balance system.

Results of oxidation at 700°C and 0.04 to 0.025 mm O₂ are presented in Fig. 10, where they are compared with a run in the pressure-independent region.

There was less oxidation at the lower p_{O_2} during the initial stages; with continued oxidation, the weight gain of the corresponding higher-pressure run (point C) was reached. Location of this point and the initial difference in weight gains varied from one run to another, but the same effect was obtained in each of a considerable number of runs.

Fig. 10. Low-pressure Oxidation of Zirconium at 700°C

The phenomena may be explained by considering the rapid oxidation and high oxygen consumption at the early stages of zirconium oxidation at 700°C. The surface concentration of oxygen ions increases with p_{O_2} . At high temperatures and low p_{O_2} , when transport of oxygen molecules to the site of reaction becomes insufficient, there may be a significant decrease in oxygen concentration in the chemisorbed layer. Though the calculated number of molecules striking the surface exceeds the amount of oxygen needed for oxidation, the sticking probability is not known.

In the independent-of- p_{O_2} region the number of active sites available for chemisorption depends on structure, temperature, and surface properties. Oxygen concentration in the chemisorbed layer is independent of oxygen pressure, since the rate-controlling process is the transfer of charged particles through the oxide. But at higher temperatures and lower p_{O_2} , the transport of oxygen molecules to the reaction site might become the rate-controlling step. At the beginning of oxidation the number of sticking oxygen molecules is not sufficient to provide a "saturated" oxygen layer (as in a regular run*). The amount of oxidation is therefore smaller. The thickening of oxide film retards the oxidation, and a point is reached

* A run in which oxygen pressure is between 1 and 400 mm.

where we are again in the "pressure-independent" region. At this point the true film thicknesses are not simply proportional to weight gain. Since ZrO_2 dissolution into the metal is expected to proceed at the same rate for the lower-pressure as for the regular run, the film thickness for the lower-pressure run will be less than suggested by the comparative weight gains. At the time when oxygen supply no longer limits reaction rate, oxidation will be more rapid at the lower pressure than at the corresponding time during a regular run. This can be observed from oxidation results presented in Fig. 10:

the oxidation rate constant of portion OD (Run No. 158) is smaller than that of the corresponding portion OD' (regular run), but portion DC (Run No. 158) exhibits a higher oxidation rate constant than for D'C portion of a regular run.

An analogous investigation was undertaken for zirconium oxidation at 550 and 800°C. At 550°C, in order to obtain sufficient weight gains, larger samples (than for 700°C) were employed since the oxidation rate at 550°C is lower than at 700°C. In oxidation experiments performed at a pressure higher than 0.1 mm, the scattering of results at 550°C was more significant than at 700°C, and possible small variations in oxidation kinetics were difficult to observe. For pressures lower than 0.1 mm, however, the effect was very appreciable (see Fig. 11). Initial oxidation was slower for Run No. 172 (initial $p_{\text{O}_2} = 0.026$ mm) than for Run No. 177 (initial $p_{\text{O}_2} = 0.033$ mm). Similar to the results at 700°C, the weight gain at lower pressures gradually approached the regular run, and points C and D could be distinguished (see Fig. 10). The slope of the oxidation curve at the initial stages showed a dependence between linear and parabolic, being closer to linear.

Fig. 11. Low-pressure Oxidation of Zirconium at 550°C

Oxidation results for 800°C are presented in Fig. 12, and the phenomena observed are similar to those at 550 and 700°C. The same mechanism, presumably, is applicable at 800°C, although the contributions of different influencing factors probably are different.

Fig. 12. Low-pressure Oxidation of Zirconium at 800°C

All the results of lower-pressure oxidation suggest that one of the influential factors is the rate of arrival of oxygen at the reaction site. An oxidation rate dependence close to linear would be expected for this case. Analysis of the oxidation kinetics based on gravimetric data for the first few minutes of oxidation was difficult, so volumetric techniques were applied for a more accurate study of the early stages of oxidation.

The decrease in oxygen pressure during oxygen consumption at low pressure was continuously recorded. A small volume of oxygen was transferred rapidly from a storage vessel to the evacuated system containing the annealed specimen at reaction temperature. Blank experiments showed that steady-state conditions were reached in less than 20 sec after the start of gas admission, and reliable data were obtained from this time on. The zero point was obtained by extrapolation under the assumption of linearity in the 0-20-sec region.

Oxidation results obtained by volumetric methods are presented in Figs. 13 and 14 (for 550°C) and Fig. 15 (for 700°C). The plots in Figs. 14 and 15 exhibit no sharp transition point of deviation from linear dependence. If the linearity corresponds to dissolution of the chemisorbed oxygen, oversaturation, and the presence of nonprotective oxide, then a "crystallization" point may give a sharp transition from linearity. This "induction" period has been observed for a number of metals at low pressures.

Fig. 13. Low-pressure Oxidation of Zirconium at 550°C (Volumetric Techniques)

Fig. 14. Early Stages of Zirconium Oxidation at 550°C (Volumetric Techniques)

Fig. 15. Early Stages of Zirconium Oxidation at 700°C (Volumetric Techniques)

A closer examination of Run Nos. 198 and 202 (see Fig. 15) shows the transition from linearity occurring for approximately the same amount of consumed oxygen.

The linearity found in volumetric measurements can be interpreted as supporting the assumption that the oxygen arrival at the reaction site determines the reaction rate at low pressures.

VI. OXIDATION OF ZIRCONIUM WITH A VAPOR-DEPOSITED GOLD FILM

A study of oxidation of zirconium bearing a vapor-deposited gold film was initiated in order to employ zirconium that would oxidize faster than pure zirconium with no film on it. Extension of low-pressure behavior to higher pressures was expected. The reported data³ seemed to support the choice. A number of experiments have been performed at 700°C; the results are presented in Fig. 16. At 400 mm pressure, the presence of 400 Å of gold decreased the oxidation rate by a factor of about 2; however, increasing the gold layer to 6400 Å (experiment from Ref. 3, incorrectly reported as 200 Å of gold) caused an increase in rate by a factor of about 6 for short exposures (an increase of three times over uncoated zirconium).

Fig. 16. Oxidation of Zirconium with an Evaporated Gold Film (at 700°C)

For the two specimens bearing the 400-Å gold layer, the oxygen pressure was changed periodically during the runs. At each pressure change, the system first was briefly evacuated to provide the buoyancy correction. In all cases, the oxidation rate increased when the pressure was increased and decreased when the pressure was decreased. In all cases, after the first pressure change at about 130 min, the rate was approximately constant for each constant-pressure period. The oxidation rates reproduced well for the two specimens at the two pressures for which comparison could be made readily. In contrast to these observations, the specimen started at 400 mm oxidized substantially less (during the initial period) than the one started at an oxygen pressure of 100 mm.

It can only be speculated that galvanic acceleration of oxidation occurred when the original film was so thick that only a small fraction of it diffused into the zirconium. As judged by appearance, essentially all of the thinner (400 Å) gold layer diffused into the base metal during the preliminary 2 hr of vacuum annealing and the 5 hr of oxidation exposure. Presumably the inverse dependence on pressure was observed during the early stages of diffusion. By the time of the first evacuation and readmission of oxygen (at a new pressure), perhaps diffusion had reached the stage that no further major change could be expected. Specimens in this latter condition apparently could be used to study linear, pressure-dependent oxidation at pressures as high as about an atmosphere. This extension of the study is yet to be made.

VII. ELECTRICAL MEASUREMENTS IN ZIRCONIUM REACTIONS WITH NITROGEN, CARBON DIOXIDE, AND WATER VAPOR

Electrical and electrochemical measurements were extended to zirconium oxidation in carbon dioxide, nitrogen, and water vapors.

The experimental setup previously described was used for recording potentials and measuring oxidation rates. Resistances were determined from the E-vs-I slope by applying small currents to samples resting on platinum powder. Although this method of resistance measurement is not very accurate and has to be followed by a measurement in a molten carbonate bath, it was accepted for a gross method of resistance measurements and proved to be useful when significant changes of resistance occurred.

High-purity nitrogen was dried by passage through anhydrous CaSO_4 before admission to the system. High-purity CO_2 was dried by passage through P_2O_5 . Water-vapor admission was carried out by bubbling pure argon through water of quite high purity.

Weight gains of zirconium exposed to nitrogen at 900°C are plotted in Fig. 17. No potential was observed in zirconium nitriding for a 1450-min run at 900°C . The resistance of the nitride film was lower by two orders of magnitude than that of an equivalent oxide film. Admission of oxygen at 3 mm pressure to the system containing 100 mm nitrogen at 900°C (when a considerable nitride film was present) resulted in the immediate appearance of a large potential (-1.08 V) across the film on zirconium and an increase in resistance by two orders of magnitude (from 10^3 to $10^5\ \Omega$). The values of the resistance and potential then gradually declined.

Fig. 17. Zirconium Nitriding at 900°C and 100 mm P_{N_2}

Zirconium oxidation in CO_2 at 750°C and 100 mm p_{CO_2} is shown in Fig. 18. The resistance of the zirconium oxide film formed in CO_2 was lower than in oxygen. A very low potential (-3 to -5 mV) developed only after formation of a relatively thick film. Admission of oxygen to the Zr- CO_2 system caused an immediate rise of the potential up to -0.7 V. The potential then slowly decreased upon further oxidation.

Fig. 18. Oxidation of Zirconium in CO_2 at 750°C and 100 mm Pressure

When zirconium was oxidized in an Ar + H_2O vapor mixture, a potential of about -0.2 to -0.25 V, considerably lower than in oxygen, developed. Resistance was about the same as in oxygen oxidation. Oxygen admission again caused an increase in potential, while the resistance remained practically unchanged.

Evidently, development of a relatively high potential, which indicates an establishment of a strong electric field across the oxide, is typical for oxygen oxidation of zirconium. Of the atmospheres tested, the greatest potential developed in oxygen. The electrical measurements can support certain assumptions regarding the reactions occurring when oxygen was admitted to a system of zirconium plus reacting gas. Zirconium nitride is formed according to the gross reaction

When a relatively small amount of oxygen is added, a potential immediately appears and the resistance increases sharply, perhaps because of ZrO_2 formation in the reaction

There is question whether the ZrO_2 uniformly covers the surface of $\text{Zr} + \text{ZrN}$ or whether oxygen diffuses through the porous nitride to the metal surface to form a uniform thin film of $\text{ZrO}_{2-\delta}$. The observed decay in potential and resistance suggest that more than a single reaction is occurring. Probably some secondary process occurs, or the oxide that has formed diffuses into the nitride to make a "mixed" film, in which oxygen and nitrogen ions are incorporated into the crystal lattice of the film.

In a CO_2 atmosphere, a film consisting mainly of zirconium oxide is formed. The predominant gross process occurring is

A small amount of carbon is also formed and is incorporated into the oxide. The carbon formation reaction may be (as was proved by Hussey and Smeltzer²⁷ in their experiments with C^{14}) the dissociation of the formed carbon monoxide by disproportionation:

The resistance of the oxide formed in CO_2 was found to be lower than that of the oxygen-formed oxide. Small amounts of carbon incorporated into the oxide lattice or the different structure of the oxide may be the cause. The recorded potential, much lower than in oxygen oxidation, reflects an entirely different mechanism during oxidation in CO_2 . The rise in potential when small amounts of oxygen are admitted indicates reaction of oxygen with the previous oxidation product and/or the metal. The analogous (to the CO_2) phenomena that occurred in argon saturated with water vapor can be interpreted in a similar manner.

Thus, electrical measurements are a valuable tool in studying the mechanisms of film formation in these environments.

VIII. SUMMARY AND CONCLUSIONS

1. Zirconium oxidation in oxygen at 550, 700, and 800°C does not follow any known simple rate expression. Data fell between the lines for parabolic and cubic laws on a log-log plot, but not on a straight line.
2. Oxidation kinetics are practically independent of p_{O_2} in the pressure range from 1 to 400 mm.
3. Measurements of oxide-film resistance at different stages of oxidation, followed by R_e and R_i calculation, indicate predominantly electronic control during most of the reaction, with significant retardation by the

ionic process at the very early stages. This change is interpreted as being caused by transformation of the initially formed tetragonal zirconia to the monoclinic modification.

4. The electric field across the growing oxide is dependent upon p_{O_2} in the low-pressure range, a phenomenon that is in accord with predictions based on a varying defect structure.
5. The variations in the electric field with p_{O_2} correspond to a change in oxidation kinetics at lower p_{O_2} : initial oxidation was slower; eventually the weight gain becomes equal to that of a regular run.
6. Volumetric techniques are useful in an accurate study of the early stages of oxidation. Linear dependence was found for the initial period of oxidation.
7. Results for low-pressure oxidation are believed to indicate that the process is controlled by the rate of arrival of oxygen at the reaction site. Another interpretation of early linearity involves an "induction" period, during which an "oversaturated" solution of oxygen in the metal and a nonprotective oxide forms. A protective oxide film forms subsequently.
8. The rate of oxidation of zirconium bearing a vapor-deposited gold film was found to depend upon the thickness of the gold layer and p_{O_2} . At a gold thickness of 400 Å it appeared possible to provide circumstances in which pressure-dependent linear oxidation rates of zirconium could be studied for long periods of time and pressures as high as 600 mm.
9. No measurable potential was produced in high-temperature nitriding of zirconium. Electrical measurements indicate that even small amounts of oxygen added to a $Zr + N_2$ system react with zirconium and/or zirconium nitride to yield the oxide.
10. A low potential (10 to 25 mV) was recorded in CO_2 oxidation, supposedly because of a different (than in oxygen oxidation) mechanism and surface process. Resistance measurements and results of admission of a small amount of oxygen indicate that a different oxidation product probably is formed during CO_2 oxidation.

REFERENCES AND BIBLIOGRAPHY

1. L. D. Kirkbride and D. E. Thomas, WAPD-T-308 (1956).
2. R. D. Misch and G. W. Iseler, ANL-6434 (1961).
3. D. H. Bradhurst, J. E. Draley, and C. J. Van Drunen, *J. Electrochem. Soc.* 112, 1171 (1965).
4. H. H. Uhlig, 2nd Intern. Con. of Metallic Corrosion, New York, March 1963, p. 1.
5. C. M. Schwartz, D. A. Vaughan, and G. G. Cocks, BMI-793 (1952).
6. I. I. Korobkov and D. V. Ignatov, *Dokl. Ak. Nauk SSSR (Russ.)* 120, 527 (1958).
7. D. E. Whitney, *J. Am. Ceram. Soc.* 45, 612 (1962).
8. W. L. Baun, *Science* 140, 1330 (1963).
9. F. W. Vahldiek, L. B. Robinson, and C. T. Lynch, *Science* 142, 1059 (1963).
10. J. E. Bailey, *Proc. Roy. Soc. (London)* A279, 395 (1964).
11. D. K. Smith and H. W. Newkirk, *Acta Cryst.* 18, 983 (1965).
12. K. S. Mazdiyasni, C. T. Lynch, and S. Smith, *J. Am. Ceram. Soc.* 48, 372 (1965).
13. R. C. Garvie, *J. Phys. Chem.* 69, 4, 1238 (1965).
14. M. Denoux, *C. R. Head Sci. Paris* 260, 5003 (1965).
15. J. P. Pemsler, Presented at Electrochem. Soc. Meeting, Oct. 10-14, 1965, Buffalo, New York.
16. R. W. Vest and N. M. Tallan, *J. Am. Ceram. Soc.* 48(9), 472 (1965).
17. T. Homma, *Rep. Inst. Ind. Sc. Univ. Tokyo* 15, 3, Sev. 102 (Dec 1965).
18. A. Krauth and N. Meyer, *Ber. Deut. Ker. Ges.* 42(3), 61 (1965).
19. A. T. Fromhold, Jr., *J. Phys. Chem. Solids* 24, 1081 (1963).
20. A. T. Fromhold, Jr., *J. Phys. Chem. Solids* 24, 1309 (1963).
21. H. H. Baumbach and C. Wagner, *Z. physik. Chem.* B22, 199 (1933).
22. A. Guillot and A. M. Anthony, *Rev. Hautes Temp. Refr.* 1, 325-329 (Oct-Dec 1965).
23. H. A. Porte, V. G. Schnizlein, R. C. Vogel, and D. F. Fisher, *J. Electrochem. Soc.* 107, 506 (1960).
24. G. R. Wallwork, W. W. Smeltzer, and C. J. Rosa, *Acta Met.* 12, 409 (1964).
25. D. Cubiccioto, *J. Am. Chem. Soc.* 72, 4138-4141 (1959).
26. K. Hauffe and H. J. Engell, *Z. Elektrochem.* 56(4), 366 (1956).
27. R. J. Hussey and W. W. Smeltzer, *J. Electrochem. Soc.* 112(6), 554 (1965).