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CORROSION MECHANISM OF ZIRCONIUM
AND ITS ALLOYS — DIFFUSION OF OXYGEN
IN ZIRCONIUM DIOXIDE

By
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July 27, 1962

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GENERAL ELECTRIC

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ABSTRACT

The diffusion rate of oxygen in anion-deficient zirconia, $\text{ZrO}_{1.994}$, has been determined by the interface migration of stoichiometric oxide and is represented by the equation

$$D = 0.055 \exp (-33,400 \pm 3100/RT).$$

A comparison was made with other processes which occur in the metal and the oxide. Excellent agreement was noted between activation energies of oxygen diffusion in $\text{ZrO}_{1.994}$ and those for parabolic or cubic oxidation in both air and water. It appears that oxygen diffusion in the oxide is rate-controlling during oxidation of the metal. The corrosion and oxidation behavior of zirconium and some alloys are discussed in terms of the oxide defect structure and the electrical conduction behavior in the oxide.

A speculative mechanism for corrosion transition to linear rates was suggested on the basis of preferential oxidation of a grain boundary metallic phase. The nature of this phase and of its formation and elimination are discussed.

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CORROSION MECHANISM OF ZIRCONIUM AND ITS ALLOYS - DIFFUSION OF OXYGEN IN ZIRCONIUM DIOXIDE

INTRODUCTION

Although the corrosion mechanism of zirconium and its alloys has been the subject of intensive research for a number of years, the corrosion process is still not completely understood. It has been generally accepted that the rate-controlling step appears to be the diffusion of oxygen through the protective oxide film to the oxide-metal interface, at which point the reaction takes place. Studies of the steam oxidation of zirconium have included many alloys containing both lower and higher valent solutes than the parent metal. The subsequent improvement or decrease in oxidation resistance has been attributed to the change in anion vacancies, according to the Wagner-Hauffe theories; the change in vacancy concentration therefore changed the diffusion rate of oxygen and thus the oxidation or corrosion rate. This approach has appeared very interesting and has shown that correlations exist, but unfortunately no data have been available for confirmation, and all treatments have therefore been speculative. It is the primary purpose of this report to present diffusion data for oxygen in the oxide and to relate the diffusivity to the defect structure.

Although zirconium dioxide is characterized by a white color in the stoichiometric condition, the oxide films which form on the metal during oxidation during the early stages of the process are usually black. The black color is due to non-stoichiometry, specifically due to anion vacancies, and may be attributed to the fact that the metal has a high solubility for oxygen. The pure metal (or alloy) is thermodynamically unstable in contact with the oxide, and solution of the oxide occurs in the metal substrate until saturation is achieved. Thus the metal represents an oxygen sink, and as long as it exists the color of the oxide should remain dark from the anion deficiency. In some cases white spots are observed; these may be attributed to cracks in the oxide film parallel to the surface, the cracks acting as a diffusion barrier to oxygen. It is this marked change in color of the oxides which has provided a basis for measurement of the diffusion coefficient of oxygen.

The usual methods of determining oxygen diffusion in oxides have been either by O^{18} exchange (and mass spectrographic analyses) or by manometric analysis of oxygen absorption into oxygen-efficient oxide particles. Each of these techniques has limitations such as experimental handling and analysis of the exchange method or uncertainties due to non-sphericity or non-uniformity of particle size in the manometric technique. It was thus decided to use an interface migration measurement to determine the diffusion coefficient. The interface in this case was not one existing between two phases but rather a constant concentration of oxygen which corresponded to a discrete color change.

Anion-deficient oxides were prepared by vacuum hot pressing. Rectangular slabs of the oxide were then exposed to either high purity oxygen or steam for various times, sectioned, and the rate of thickening of the stoichiometric layer was measured. The diffusion coefficient was then computed directly from these data, as shown in the Appendix.

EXPERIMENTAL PROCEDURES

Material

High purity TAM ZrO_2 was used, the analysis of which is listed in Table I. That particle size was determined by the BET method to be 0.08 micron.

TABLE I
CHEMICAL ANALYSES OF ZrO_2

<u>Impurity</u>	<u>Amount</u>
SiO_2	0.15%
TiO_2	0.005
Fe_2O_3	0.003
MgO	0.03
HfO_2	0.02
Al_2O_3	0.005

Hot Pressing

Non-stoichiometric oxide bodies were prepared by hot pressing in graphite dies with graphite plungers in an induction-heated, vacuum hot press at the Metallurgical Products Department, General Electric Company, Detroit, Michigan. The die interior and plunger ends were coated with boron nitride to prevent reaction between oxide and graphite. Preliminary runs made on a laboratory press had shown that the zirconium carbide formed when no barrier was used. No evidence of reaction was detected with the coating. Two inch diameter pellets 2 to 3 inches high were pressed at 3000 psi and 2000 C. The pressure was maintained at temperature for 1/2 hour after plunger movement ceased.

The pellets were surface-ground after pressing and sectioned on a cut-off wheel into rectangular slabs. Density measurements were made by weighing in air and in CCl_4 . A value of 5.82 gm/cm^3 was determined for ZrO_2 .

Diffusion Anneals

The slabs were placed in a stream of flowing oxygen in a horizontal tube furnace at the desired temperature for various times. The oxygen was passed through a Drierite tower and calibrated orifice at 20 liters per hour and 25 mm Hg pressure.

The slabs were then sectioned transversely and mounted in Bakelite, ground through 600 grit silicon carbide paper, and polished with diamond abrasive on a Syntron polisher for four hours. The diffusion zones were photographed at 100X under polarized light on a Bausch and Lomb Research Metallograph.

The analysis of the diffusion in ZrO_2 presented a problem due to the extremely rapid grain boundary diffusion. The zirconia samples did not exhibit a uniform periphery of stoichiometric oxide around the anion-deficient structure. Rather, diffusion occurred down grain boundaries within one minute and was followed by the slower lateral diffusion of oxygen into the grains from the boundaries. The peripheral rings around individual grains were measured (at least 100 grains for each time-temperature condition) on the photomicrograph with an optical comparator.

The minimum thickness was taken as the true thickness under the assumption that a random plane of section would pass close to or through the diameter of at least one grain. At small values of the ratio of thickness to radius (assuming that the grains were nearly spherical), the error involved in this treatment was probably less than 2%. As would be expected, little difference was noted between the values of apparent thickness for low values of t/r compared to those noted for high values of t/r . Diffusion conditions were therefore selected which would give smaller values of the ratio. Figure 1 shows the relationship between true and apparent thicknesses of the diffusion zone as a function of the t/r ratio.

X-Ray Diffraction

Conventional techniques were employed to obtain diffraction patterns by the goniometer on flat surfaces of bulk samples. A G.E. XRD-5 was used with filtered copper radiation at 50 KV and 16 ma. A pulse height analyzer was used on the goniometer to reduce the background, and a traversing speed of 2.0 degrees per minute was employed.

Determination of Oxide Composition

A modified Sievert's type apparatus was used to measure the pressure decrease during oxidation of non-stoichiometric samples. The volume and pressure were selected to give a sensitivity of 6×10^{-4} gm oxygen per mm pressure drop. The system volume was 450 ml. A pressure of about 20 mm Hg was used with a sample size of 0.3-1.0 gm.

RESULTS AND DISCUSSION

Diffusion in Zirconium Oxide

The least squares fit of the zirconium oxide diffusion data to an Arrhenius plot is shown in Figure 2 and is represented by equation (1) for a 95% confidence level.

$$\text{Oxygen Diffusion in } \text{ZrO}_{1.994}: D = 0.055 \exp (-3,400 \pm 3,100 / RT) \quad (1)$$

The diffusion curve is compared in Figure 2 to the results obtained by Kingery et al ⁽¹⁾ for oxygen diffusion in stabilized zirconia ($\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$). These data are the only measurement reported in the literature to provide a comparison. The difference in diffusivity is not

Figure 1. DEVIATION OF APPARENT THICKNESS OF DIFFUSION LAYER FROM TRUE THICKNESS AS t/r RATIO INCREASES

Figure 2. OXYGEN ION DIFFUSION IN ZIRCONIUM OXIDES

too large considering the wide difference in composition and the different structure of the lattice, i.e. cubic instead of monoclinic.

Second Phase in Zirconium Oxide

A grain boundary network of a white phase was observed in the hot-pressed oxide. A small amount of the white phase was also observed as discrete particles within the grains. Initially, x-ray diffraction failed to show any lines other than monoclinic ZrO_2 . Repeated attempts finally yielded several lines other than the oxide which were indexed as oxygen-saturated alpha zirconium. The remaining lines of the oxygen-saturated phase had been shifted sufficiently by the approximately 30 a/o oxygen in solution so that they overlapped the oxide lines and made identification difficult.

Thermodynamic calculations indicated that under equilibrium conditions zirconia was reduced by carbon vapor to form Zr and carbon monoxide at temperatures above 2200 C. The first pressings were made at 2300 C, hence the reaction was very probable. The carbon vapor pressure at this temperature was about 10^{-3} mm, the source of carbon being the die and plunger. Subsequent hot pressing at 2000 C reduced the amount of alpha zirconium significantly but did not eliminate it entirely due to dynamic conditions, i.e., a dynamic vacuum which continuously removed CO gas. A long time anneal of 68 hours at 1900 C of the metal-containing oxide resulted in almost entire elimination of the phase by diffusion of zirconium to the surface and evaporation (determined by x-ray analysis of a thin coating of zirconium on the oxide surface). Only heat-treated oxide bodies were used for diffusion experiments. The structure of a hot-pressed sample and the effect of subsequent heat treatment at 1900 C are shown in Figure 3.

The significance of the grain boundary phase lies in the fact that it will oxidize preferentially with a concomitant increase in volume of about 10-12 percent. The volume increase is sufficient to shatter the oxide sample as shown in Figure 4 which illustrates the catastrophic effect by the oxidation of the grain boundary phase in an as-pressed sample. Although the heat treatment did not entirely eliminate the grain boundary phase, the amount present was sufficiently small to prevent shattering of

17X

Intergranular failure in zirconium oxide.

50X

Figure 3. DIFFUSION IN HEAT-TREATED OXIDE

100X

As-pressed zirconium oxide.

Bright field.

100X

Polarized light.

100X

Heat-treated zirconium oxide, 68 hours at 1900°C.

Figure 4. MICROSTRUCTURE OF ZIRCONIUM OXIDE
CONTAINING OXYGEN-SATURATED, α -Zr

the samples. The very rapid oxidation and diffusion of oxygen in this phase resulted in a nearly complete penetration of the grain boundaries by oxygen in less than one minute. Bulk diffusion into the grains then proceeded from the grain boundaries which provided a source of oxygen. The effect of the boundary penetration is shown in Figure 4-b.

Comparison of Activation Energies

A comparison of activation energies for various processes is shown in Table VI. Gulbransen and Andrew⁽²⁾ used a microbalance technique over the range of 200-425 C and observed a parabolic rate law with an activation energy of 18.2 kcal/mole. McAdam and Geil⁽³⁾ measured oxidation by changes in temper colors over the range of 200-350 C and obtained an activation energy of 35 kcal/mole, assuming that a parabolic rate law was followed. Cubicciotti⁽⁵⁾ employed volumetric methods over the range of 600-900 C and observed parabolic behavior with an activation energy of 32.0 kcal/mole. His data fit an extrapolated line through the data of Gulbransen and Andrew with a break in the curve between 400 and 500 C.

Belle and Mallett⁽⁷⁾ observed a cubic rate law from 575-950 C for short times with an activation energy of 47.2 kcal/mol. Later work by Charles, Barnartt, and Gulbransen⁽⁶⁾ at 350 and 450 C was used with Gulbransen and Andrew's earlier data,⁽²⁾ assuming a cubic rate law for the early work and gave a value of Q of 38.0.

The data available for water or steam corrosion are limited. Chirigos and Thomas⁽⁸⁾ determined the activation energy for corrosion of crystal bar zirconium in high pressure water by plotting log of the weight gain at 100 days against reciprocal temperature, giving a value of 11.4 kcal/mole. However, on the same plot of $\log \text{mg/dm}^2$ vs. $1/T$ values of the exponent in the relationship $\Delta w = kt^n$ were shown to vary between 0.33 and about 0.25. A replot of the data was made using the cubic rate constant instead of the incorrect linear constant, and a new value of 33.4 kcal/mole was determined for Q. This value is identical with that determined for self-diffusion of oxygen in the oxide and is strong evidence for the oxygen diffusion step being the rate-controlling process during corrosion in water.

Process	Material	Temp. Range °C	Rate Law	Activation Energy, kcal/mole	Reference
Oxidation of Zr	Zr	200-425 C	parabolic	18.2	2
Oxidation of Zr	Zr	200-350	assumed parabolic	35	3
Oxidation of Zr	Zircaloy-2	400-700	parabolic	28.6	4
Oxidation of Zr	Zr	600-900	parabolic	32.0	5
Oxidation of Zr	Zr	350-650	cubic	38.0	6
Oxidation of Zr	Zr	575-950	Cubic	47.2	7
Oxidation in H ₂ O (l) *	Zr	260-360	cubic	33.4	8
Diffusion of oxygen	alpha-Zircaloy-2	1000-1500 **	parabolic	41.0	9
Diffusion of oxygen	beta-Zircaloy-2	1000-1500	parabolic	28.2	9
Diffusion of oxygen	alpha-Zr	400-585	parabolic	51.8	10
Diffusion of oxygen	ZrO _{1.975}	500-650	parabolic	58.0	11
Diffusion of oxygen	Zr _{0.85} Ca _{0.15} O _{1.85}	700-1000	parabolic	28.1	1
Diffusion of oxygen	ZrO _{1.994}	700-1000	parabolic	33.4	This study

* High pressure, 2000 psi, compared to oxidation in O₂. Value of 11.4 kcal reported for Q, however, the data were plotted as log mg/dm² vs. 1/T. A replot of log (mg/dm²)³ vs. 1/T gives 33.4 kcal for Q.

** Determined in oxygen-stabilized α (α not stable in this range).

TABLE VI

A SUMMARY AND COMPARISON OF VARIOUS PROCESSES OCCURRING DURING OXIDATION OF ZIRCONIUM

The diffusion of oxygen in Zircaloy-2 metal has been reported to have activation energies of 41.0 and 28.2 kcal/mole in alpha and beta zirconium, respectively, ⁽⁹⁾ whereas Pemsler ⁽¹⁰⁾ has determined an activation energy of 51.8 kcal/mole for oxygen diffusion in alpha zirconium.

One other process should be mentioned which closely parallels this study. Aronson ⁽¹¹⁾ oxidized non-stoichiometric zirconium dioxide powder, $ZrO_{1.975}$, following the reaction gravimetrically on a coil spring balance having a sensitivity of 1.50 mm/mg. The sample size was 0.3 gm, and the B.E.T. surface area was $4.2 \text{ m}^2/\text{gm}$. Parabolic weight gain curves were observed over the temperature range of 500 to 650 C, with a value of 58.0 kcal/mole determined for the activation energy. Aronson stated that the rate constant for the oxidation process would ordinarily be a simple diffusion coefficient of oxygen in the non-stoichiometric oxide; but, due to the ionic transport, which has been shown to occur in zirconia, he suggests that the rate constant was a complex parameter related to both oxygen and electron diffusion.

There is some agreement with the value obtained in this work, 33.4 kcal/mole, with Kingery's value of 28.1 for oxygen diffusion in $Zr_{0.85}Ca_{0.15}O_{1.85}$ and those for parabolic oxidation, 35.0 and 32.0 kcal/mole, and Charles value of 38.0 for cubic oxidation. The values reported for oxygen diffusion in alpha zirconium generally appear too high to warrant serious consideration as a rate-controlling step for oxidation of the metal, and the cubic rate law determined by Belle and Mallett appears to have a value out of line with those mentioned.

It is difficult to account for the rather large difference between Aronson's value and that measured in this work. Belle and co-workers ⁽¹²⁾ found a large difference in activation energies for oxygen diffusion in stoichiometric UO_2 and $UO_{2.063}$, the values being 65.3 and 29.7 kcal/mole, respectively. This difference was attributed to excess interstitial oxygen in the non-stoichiometric oxide which moved in combination with a lattice atom, the lattice ion moving into an available interstitial site and the interstitial ion moving into the vacated lattice site. The higher activation energy and slower diffusion for stoichiometric oxide was

attributed to thermally induced Frenkel defects, the mobility of the vacancy being small compared to the mobility of the interstitial oxygen ion. The higher activation energy contained a term for the formation of the Frenkel defect as well as the movement of the defect.

An analogous line of approach can be used to explain the difference in activation energies between Aronson's results and this study. Let us assume, as in the case of uranium dioxide, that the activation energy consists of two terms. In this case they are the energy to cause movement of the defects in the neutral lattice and the energy to move defects through a space charge layer. The number of defects over-all is fixed by the composition, increasing with increasing departure from stoichiometry. However, when very small particles (about 2×10^{-5} cm) are used, space charge effects on the surface will change the defect concentration in the layer due to chemisorption, according to Hauffe.⁽¹³⁾ Chemisorption of oxygen in n-type oxides results in a surface depletion of electrons to form the space charge layer.

Hauffe has shown that the mass flow is equal to the product of mobility-mass density-electrochemical potential gradient, and that mass transport in the space charge layer will be considerably less than in the neutral interior.

The free energy across the boundary layer is determined by chemical and electrical potentials and was shown by Hauffe to decrease for electrons and to increase for ions in p-type oxides. By analogy it is possible to show that an additional energy term will be required to penetrate the boundary layer in n-type oxides.

Extrapolation of the diffusion coefficient to 500 C indicates that it is higher by three orders of magnitude than Aronson's rate constant. If the diffusion coefficient were related to the rate constant by some simple relation such as $k = 4D$ as given by Moore and Selikson,⁽¹⁴⁾ it would not be possible to account for the large differences unless a surface layer effect predominated. The agreement between Kingery's data,⁽¹⁾ determined on particles of about 2×10^{-2} cm diameter, and this study (considering the difference in composition and crystal structure) indicate that this is so.

Defect Structure of Zirconium Oxide

Zirconia has been classified as an anion-deficient oxide⁽¹⁵⁾ but exhibits ionic conductivity at high temperatures instead of electronic. The anion-deficient structure results in the formation of some Zr^{+3} ions to maintain electrical neutrality, two ions being formed for each vacancy. Excess electrons are usually introduced into the lattice to form an n-type semiconductor, however, the ionic conductivity of zirconia suggests that the electrons are not free and are trapped by oxygen vacancies. The formation of conduction electrons can be expressed according to Kingery⁽¹⁾ by equation (2).

Filling of normally vacant lattice sites to form electron holes is given by (4).

where:

$\oplus$ = electron hole.

The mass action equation, assuming that interaction effects are small, is then given by (5).

$$K = \frac{C_{e^{-}}^2 P_{O_2}^{1/2} C_{\square_{O^{-2}}}}{C_{O^{-2}}} \quad (5)$$

Since the concentration of lattice atoms and oxygen vacancies is fixed by composition, the concentration of excess electrons is proportional to pressure

$$C_e = kP^{-1/4}. \quad (6)$$

The total conductivity is equal to that contributed by excess electrons, electron holes, and ionic species as given in (7).

$$\sigma = \sigma_{ion} + F u_e C_e + F u_{\oplus} C_{\oplus} \quad (7)$$

where: F = Faraday constant

u = mobility

If conduction by either electrons or holes occurs, there should be a relationship between conductivity and pressure as indicated in equation (8).

$$\sigma = \sigma_{\text{ion}} + k_1 P_{\text{O}_2}^{-1/4} + k_1 P_{\text{O}_2}^{+1/4} \quad (8)$$

Kingery has established that the conductivity was independent of pressure at both 1427 and 1627 C over 10 orders of magnitude of pressure; therefore, conduction is entirely ionic.

Kiukkola and Wagner⁽¹⁵⁾ also showed that ionic conduction prevailed at 1000 C. Kingery's diffusion coefficients were determined from conductivity measurements at high temperatures and directly by O^{18} exchange from 700-1000 C. The curves coincided for all practical purposes, thus leading to the conclusion that ionic conductivity occurred at even 700 C. There are no data at lower temperatures (400 C) which would be applicable to corrosion processes in steam.

The oxides employed in this study exhibited an electrical resistivity of about 10^{-1} ohm-cm at room temperature which would be several orders of magnitude lower than the stabilized variety at this temperature. Assuming that ionic conduction prevails at low temperatures in the highly anion-deficient structure, $\text{ZrO}_{1.994}$, we may conclude that the number of oxygen vacancies is indeed very large and that the mobility is high.

Oxidation Kinetics

Most oxidation reactions do not follow rigorously a parabolic rate law. Generally, a lower value of the exponent in the relation $\Delta w = kt^u$ corresponding to a cubic or quartic rate law is observed. There are no simple models for either of these rate laws as in the case of simple diffusion control in parabolic rate laws. However, it is recognized that during the initial stages of oxidation of metals a logarithmic rate law is followed which is indicative of a high electric field in the film and field-induced tunneling of cations, even though the film may be anion-deficient.

A change from logarithmic to parabolic rates eventually occurs when the film thickens. This does not preclude the formation of space-charge layers on the surface of the oxide⁽¹³⁾ which would then influence the chemisorption of oxygen. At best the oxidation process is complex, and there is no assurance that other stages are not contributing to the

observed rates.

The kinetics of the formation of stoichiometric zirconia on the anion-deficient bulk oxides clearly followed a parabolic rate law as determined by both the interface migration measurements and by the absorption of oxygen in the Seivert's apparatus. There was thus no ambiguity as has been observed so often in the case of zirconium alloy oxidation in either steam or oxygen.

Corrosion Transition

The transition from parabolic (or cubic) to linear rate laws during corrosion of zirconium alloys is well documented⁽¹⁷⁻²⁰⁾ but has never been satisfactorily explained. It is proposed to offer a highly speculative cause of transition rather than to reiterate the past work which is well known.

The presence of the metallic phase in the oxide which oxidized preferentially to cause the shattering shown in Figure 3 offers an interesting possibility for breakdown in oxide films formed during oxidation or corrosion. The monoclinic oxide has a favorable Pilling-Bedworth ratio, 1.56, and should not necessarily break down at some given film thickness. Experimental data show that the weight gain (or thickness) at which transition occurs is not the same at various temperatures, thus precluding a critical stress for breakdown.⁽¹⁷⁻²⁰⁾

Gebhardt et al⁽¹⁶⁾ noticed the formation of metallic zirconium in zirconium dioxide in their study of the zirconium-oxygen system. Metallic zirconium formed in the oxide when the samples were heated above the eutectoid temperature, 1830 K, and subsequently cooled below the eutectoid. The metallic phase also formed during oxidation of zirconium wires at temperatures above the eutectoid. The structures obtained in either case were similar to those observed in the present study. If alloying additions which became oxidized and thereby dissolved in the oxide film decreased the eutectoid temperature sufficiently, a thin film of metallic zirconium would form in the grain boundaries of the oxide film upon cooling; subsequent oxidation upon reheating of the grain boundary phase would then result in breakdown and cracking in the oxide. It is difficult, however, to envision how these

elements could reduce the eutectoid temperature by some 1000 C to enable the metallic film to form. It is interesting to note though, that the alloying elements in zirconium which are most harmful on the corrosion resistance are those which are the strongest reducing agents, carbon, aluminum, titanium, and silicon. It would be of great importance to ascertain their effect on the phase relations existing in each of the respective ternary systems zirconium-oxygen- alloying addition. It should also prove beneficial to investigate more thoroughly the microstructure of oxide films on these alloys.

Bulk Oxide Behavior Compared to Thin Film Behavior

The logical question of differences which might exist between the properties of bulk oxides versus those in thin films must be considered. Thin films of oxide on zirconium are in biaxial compression. The effect of the state of stress on diffusion is not too large and at best would be a second order correction. It would be desirable of course to measure diffusion directly on the films and thus eliminate ambiguity which might arise from studies on bulk oxides.

The assumption that little difference exists between bulk oxides and thin film oxides has been substantiated by Wagner⁽²¹⁾ with his work on film growth of Ag_2S on silver, by Moore and Selikson who studied self-diffusion of copper in bulk Cu_2O ⁽¹⁴⁾ and obtained similar results to those obtained in thin films of Cu_2O by Bardeen, Brattain, and Shockley.⁽²²⁾

CONCLUSIONS

1. The activation energy for oxygen diffusion in $\text{ZrO}_{1.994}$ was determined to be 33.4 kcal/mole by measurements within individual grains.
2. The activation energy agreed very closely with values for the parabolic oxidation of zirconium in oxygen and in some cases with the value for oxidation according to a cubic rate law. The corrosion of crystal bar zirconium in water followed a cubic rate law and had an activation energy identical to that determined for oxygen diffusion in the anion-deficient zirconium oxide.

3. A grain boundary network of oxygen-saturated alpha zirconium formed during hot pressing and was almost entirely removed by subsequent vaporization in vacuum at 1900 C.
4. Oxidation of the as-pressed oxides resulted in preferential oxidation of the metallic phase with an associated volume change which caused intergranular shattering of the oxide. Heat-treated samples still exhibited an overwhelming propensity to very rapid grain boundary diffusion followed by slower lateral diffusion into the oxide grains.
5. A speculative mechanism for corrosion transition was suggested based on the presence of a thin film of a metallic phase in grain boundaries. The presence of alloying constituents in the oxide was offered as a means of lowering the eutectoid temperature in the zirconium-oxygen system.
6. A large difference in activation energies existed between this study and that for oxidation of non-stoichiometric $\text{ZrO}_{1.975}$ according to Aronson.⁽¹¹⁾ The difference was attributed to space charge effects in the very fine powders (about 2×10^{-5} cm diameter) used by Aronson. The space charge layer required an additional energy term for penetration by both electrons and oxygen vacancies.

APPENDIX

DETERMINATION OF DIFFUSION COEFFICIENTS

The relationship

$$x^2 = KDt \quad (9)$$

was found to fit the migration of the interface during diffusion anneals,

where: x = thickness of stoichiometric layer

K = constant

D = coefficient of diffusion

t = time (seconds)

Evaluation of the constant K can be obtained from the upper limit of the integral in the following diffusion equation. ⁽²³⁾

$$C = \frac{C_0}{2} \left[1 - \frac{2}{\pi^{1/2}} \int_0^{\frac{x}{2(Dt)^{1/2}}} e^{-z^2} \cdot dz \right] \quad (10)$$

C = concentration of diffusion specie at time t and distance x

C_0 = original concentration in solvent

x = distance from boundary, cm

t = time, seconds

z = integration variable

As discussed by Zaplatynsky, ⁽²⁴⁾ C is considered to be constant in view of the fact that a phase boundary does not exist, only a change in stoichiometry over a very small distance. The above integral gives a value of 4 for K which was used in equation (1) to evaluate the diffusion coefficients.

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