THE HIGH TEMPLEMMENTS OXIBUTION KINETICS OF ALGONIUM

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THE OXIDATION KINETICS OF ZIRCONIUM

AT 800° AND 850°C.

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An investigation of the parabolic-linear oxidation of Extremium at 800° and 850°C, is reported. It was found that irrespective of the oxygen concentration in the metal substrate, parabolic kinetics represent the growth of the initial compact oxide scale while linear kinetics represent the later stages of growth. Metallographic observations indicated a transition from a compact to compact plus percus oxide scale. Accompanying hardness measurements demonstrated that oxygen penetrated into the metal via a steady concentration profile during linear oxidation. An exponential solution of the diffusion equation fitted to the concentration profile gave evaluations of the exygen diffusion constant in the metal which are in good agreement with such evaluations from diffusion experiments. Several features of the oxidation kinetics of zirconium and titanium were correlated as further elucidation of the properties of metals in Foriodic Subgroup IVE.

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(111)

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CHAPPER I

INTRODUCTION 1

Due to the technological developments in different fields, like rocket and atomic reactor engineering, use of some less abundant metals at high temperatures has become very important. Zirconium is one of the important metals for reactor use. This thesis is concerned with an investigation of the oxidation kinetics of sirconium at high temperatures.

The mechanisms for oxidation of metals has been surveyed by Evans (1), Kubaschewski and Hopkins (2) and many other investigators. From the theoretical considerations of oxidation phenomena Wagner (3) developed a mathematical theory for "parabolic oxidation" in 1933. Later, Cabrera and Nott (4) published a theory which explains a number of relationships for the rate of growth of oxide scales. Evans (1) pointed out the existance of stress in oxide files and suggested an alternative formulation for the purabolic rate law. These theories have been expanded by others, and muny detailed experiments have been based on them.

Despite the considerable number of investigations that have been carried out on different metals and alloys, the general characteristics of exidation are not yet clear, and further detailed studies of the mechanisms involved are required. In this thesis, we are dealing with the exidation of metals in Periodic Subgroup IVD, titanium, zirconium

and hafnium. These metals follow very similar rate equations which can be attributed to the diffusion of oxygen in superficial dioxide films and scales (5-9). At intermediate temperatures, the kinetics follow logarithmic, cubic and parabolic equations in order of increasing exposure while, at high temperatures, the kinetics follow a paraboliclinear equation.

From common knowledge we know that most metals possess an "affinity" for oxygen; that is, the combination of oxygen and atmospheric pressure with almost all metals (encept possibly a few noble metals such as gold) results in a drop of free energy - so that the reaction is capable of occurring spontaneously. Thus the production of an oxide on the surface of a metal exposed to oxygen tends to isolate the metal from oxygen. The oxide film then can only grow by the movement of metal ions outward or oxygen inwards. Such movement is possible, in cases where the oxide contains interstitial metal or vacant lattice sites.

Smeltzer, Haering and Kirkaldy (10) have constructed a phenomenological theory to account functionally for the kinetics of oxidation at intermediate temperatures. It was based on the model that oxygen migrates through the oxide lattice and through low resistance paths of tempererily decreasing effectiveness under the influence of the oxygen gradient. The equation involves three parameters: the perabolic rate constant, the ratio of the diffusion constants for short circuit and lattice diffusion and the fraction of available oxygen sites lying within low resistance paths. The latter were assumed to decay in time as a first order rate process. These kinetics previously represented in temperal order by logarithmic, cubic and parabolic equations were represented in this theory

by a single exponential relation. It was demonstrated that this equation adequately represents the oxidation kinetics of titanium, zirconium and hafnium in the temperature range $300^{\circ}-600^{\circ}C$.

Parabolic oxidation is associated with the development of a compact scale and concurrent penetration of oxygen into the metal substrate. The change of parabolic to linear kinetics is brought about by complete or partial breakdown of compact oxide whereupon the oxygen distribution in the metal attains a steady configuration in a reference system moving with the oxide/metal interface (8). It has been reported for titanium that the scale becomes a completely porous envelope by compression mechanisms involving either exfoliation, blistering or cracking of the compact oxide at critical thicknesses or critical metallic oxygen contents (8, 11, 12). On the other hand, the transitions to linear oxidation kinetics for zirconium and hafnium appear to be brought about by formation of duplex scale consisting of adjacent porous and compact oxide layers (13, 9). Consequently, linear kinetics for these metals are probably controlled by the inward diffusion rate of oxygen through the remnant compact oxide layers.

To the present, it has not been demonstrated that the transition from parabolic to linear oxidation for zirconium is associated with the formation of a duplex scale. Results are reported here which confirm the viewpoint of duplex scale formation whore the scale consists of a compact inner layer overlain by a porous outer oxide layer. This porous outer layer provides no resistance to the direct contact of oxygen with the compact inner layer. Also, an oxide-metal diffusion model is advanced to account for the kinetics of oxidation. Our experimental observations confirm the validity of the diffusion model.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction

If a motal or alloy is brought in contact with oxygen, and if the thermodynamic conditions for a reaction are favourable, one can observe a more or less rapid reaction in which the reaction products appear as a surface layer. The mechanism and rate of surface layer formation vary depending upon experimental conditions. A very thin surface layer formed on a metal during exidation is generally compact, adherent and pore free. This is also observed if the reaction-product layer is of smaller molar volume than the atomic volume of the motallic phase, although the Pilling and Bedworth's rule (14) states that compact surface layer can only be expected if the ratio of molar volume of surface layer to metal is greater than one.

In the case of metal exidation by gaseous exygen, the nature and extent of particle transport depend upon the defect model of exide constituting the surface layer. For example, in the case of zine exidation the zine exide surface layer contains zine ions in interstitial lattice sites. Consequently, zine ions migrate through interstitial lattice sites together with free electrons towards the outer ZnO boundary. In case of copper exidation to cuprous exide, where copper ion vacancies and electron holes are formed due to a metal deficiency, outward migration of Cu ions and electrons takes place through vacancies and holes.

Conversely, anion migration will always be favoured whenever the anion sublattice is predominantly defective. This type of structure has been established for the dioxides of titanium, zirconium and hafnium where vacancies occur in the partial lattice structure of oxygen ions.

The rate of oxidation of a metal can be divided into different catagories: Parabolic, Cubic, Logarithmic, Inverse Logarithmic and Linear. These oxidation rate laws have been derived from assumptions of the structure of the oxide films. Two types of models have been commonly used. The first model assumes the growth of the compact film by the process for the diffusion of ions and electrons through lattice defects in the film. The second model is based on the assumption that the film is less perfect due to formation of blisters, cracks or pores which give preferential oxidation paths. It has been established that many metals oxidize too rapidly to be explained by lattice diffusion of reactants through the superficial oxide layer at relatively low and intermediate temperatures (1).

2.2 Theories on Metal Oxidation

Several theories have been published to explain the various growth equations. Some are related to only a portion of the time or range of temperature and some to only a few metals.

2.2 (a) WAGNER THEORY OF PARABOLIC OXID FION

This theory (15, 16) is confined to surface reactions that follow the parabolic rate equation and for which diffusion in the oxide lattice is the rate determining step. The theory is based on the transport mechanism of ions and electrons in semi-conductors. Electrical conductivity in semi-conductors is due mainly to the movement of electrons botween electron defects, the number of which is equivalent to the number of ion defects in the lattice. However, the slower transport rate of ions is generally the rate determining step in an oxidation reaction. Thus, a concentration gradient of ions is established and the oxidation rate is controlled by the diffusion rate of metallic or oxygen ions through the superficial oxide layer.

A useful approximation to the equation for parabolic oxidation may be derived as follows. Assuming that an electrical field does not exist across the oxide film, the ion current is,

$$J = -D \frac{dc}{dx}$$
(1)

where D is the diffusion coefficient and de is the concentration gradient of interstitial ions, cation or anion vacancies. Thus the rate of film growth is,

$$\frac{dx}{dt} = JS = -D \quad \frac{dc}{dx} \tag{2}$$

if 52 is the volume of oxide per ion. Since the concentration gradient is inversely proportional to the film thickness, integration gives the equation of the parabolic law,

$$x^2 = k_1 t + k_2$$

where $k_1 = 20 (n_1 - n_2)$ and $k_2 = 0$

Here, n_1 and n_2 are the numbers of interstitial ions or vacancies per cubic centimeter at the oxide/oxygen and oxide/metal interfaces.

There have been many variations and developments of this basic theory as pointed out by Kubaschewski and Hopkins (17). The significance of these equations is not that they provide a method of predicting oxidation rates but if the rate equations agree with experimental results, the underlying assumptions concerning the oxidation mechanism may be supported.

2.2 (b) CABRERA AND MOTT THEORY

Cabrera and Mott (4) have presented a theory of oxidation to explain each of the various rate equations, and in order to do so, divided the scales into three thickness ranges; thick scales, films, and very thin films. For thick scales in which electronic neutrality may be maintained, they developed expressions for the parabolic oxidation of metals forming metal-deficit and metal-encess oxide scales. It is generally considered that their main contribution was made in the field of very thin films. (100% or less). They postulated that the oxide film may behave as an electrical dipole layer due to the rapid transport of electrons across the film to form oxygen ions from adsorbed oxygen. The velocity of the drift of the ions than becomes dependent upon the electrical field strength and metallic ions escaping from the metal surface may, in fact, be directly pulled across the film to react at the oxide/oxygen interface. This type of oxide growth may exist only up to a limiting file thickness. Reactions of this type follow an inverse logarithmic law of oxidation and many metals oxidize at room temperature by this relationship.

2.3 Oxidation in General for Subgroup IVB Notels

Titanium and hafnium,like sirconium, exhibit unusually high solubilities for oxygen. These metals of Periodic Subgroup IVB possess similar chemical characteristics. In this literature review, titanium and hafnium will be considered with zirconium in order to correlate their similar exidation characteristic and also to facilitate clearer understanding of zirconium exidation.

2.4 Oxidation of Titanium

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Fast (18) in 1938 and Ehrlich (19) in 1941 found that oxygen forms a solid solution with titanium beneath the oxide scale. In 1949 Gulbransen and Andrew (20) showed that after an "initial period" the oxidation reaction in the temperature range $250^{\circ}-600^{\circ}$ C for the period of two hours followed a parabolic growth equation.

Alexander and Pidgeon (21) concluded from their oxidation experiments over the temperature range 250°-550°C, that two mechanisms are involved in the oxidation process:

(a) The formation of their film.

(b) The solution of oxygen in the metal.

Below 300°C the first mechanism is predominant and oxygen absorption is limited. The reaction in this case followed a logarithmic growth equation. Above 450°C the oxidation of titanium involved solution of oxygen in the metal by a diffusion controlled process, and again a logarithmic equation best fitted their results.

In 1953 Waber, Sturdy and Wise (22) confirmed the investigation of Alexander and Pidgeon. They suggested that the break in Arrhenius plot reported by Gulbranson and Andrew (20), at 350°C was due to a change from the logarithmic to the parabolic equation.

Jenkins (23) then showed that for titanium the oxide formation occurs at the scale/metal interface. The scales formed in the temperature range 600°-925°C were porous. He established the cxygen gradient in the metal by microhardness measurements and from these results suggested a mechanism for the oxidation of titanium at high temperatures. Oxygen diffused into the metal core but the oxidation rate was controlled by diffusion in the scale. He also suggested that the transformation of the initial parabolic to linear growth occurs when the thickness of scale is built up to a thickness beyond which it can not exist without rupture.

Examination of the oxidation of saturated and unsaturated titanium specimens in the temperature range $300^{\circ}-1200^{\circ}$ C by Simmad, Spilners and Katz (24) has shown that initial oxidation rates were parabolic irrespective of the oxygen content of the metal. The parabolic rates, however, were lower for the specimens saturated with oxygen.

In further study of the oxidation of titanium, using an accurate volumetric method, Jenkins (25) checked the kinetic reaction obtained between 650° and 950°C. He found that the parabolic growth changed abruptly to a linear growth at decreasing time with increasing temperature. Further abrupt changes were found to occur at irregular intervals after long oxidizing times. In discussing his results, Jenkins, using an analytical method put forward by Wagner, showed that reaction at either the gas/scale interface or the scale/metal interface were unlikely to be controlled reactions. Therefore, the rate of diffusion of oxygen in the scale and metal core was assumed to control the oxidation rate.

Kinna and Knorr (26) suggested for their experimental results carried at 800°, 1000° and 1200°C that at the beginning of oxidation rutile is formed, through which titanium ions diffuse outwards and oxygen ions diffuse inwards, forming a titanium-oxygen colid solution in the core. After several hours, the outer layer of rutile becomes dense and on its under surface a layer of porous oxide forms.

Kofstad, Hauffe, and Kjollesdale (27) found four different growth equations from their investigations; logarithmic below 300°C, cubic from 300°C to 600°C, parabolic from 600°C to 850°C, and parabolic and linear above 850°C. The initial growth equation observed at any temperature eventually changed into a growth equation corresponding to the higher temperature level. They assumed that the diffusion of oxygen ions through the scale was the rate determining step-below 1000°C, and suggested that the logarithmic growth equation resulted from an oxide film formation, governed perhaps, by a Nott type mechanism. The cubic growth equation was assumed to be associated with the diffusion of oxygen into the metal core and the parabolic growth equation was interpreted in terms of the usual Wagner high temperature mechanism. Linear growth resulted when cracks were found due to stresses in the oxide scale and, at this stage of oxidation, a phase boundary resction became the rate determining reaction.

Wallwork, ... (23) has concluded from his study of the oxidation of titanium at high temperature that oxygen dissolves in the metal lattice to form a gradient beneath the scale. The oxidation process is governed by the movement of this gradient, and growth may be parabolic and linear, consecutively, for high temperatures of oxidation. The establishment of a "steady gradient" coincided with the transition of the growth equation from a parabolic to linear oxidation. In his experiments he could not establish that linear growth was controlled by diffusion in the oxide scale. He also found that the oxide had seven percent percent percent was linear instead of parabolic as expected. He suggested more accurate work to establish that linear oxidation is associated with the diffusion pro-

The oxidation of titanium in the temperature range 850°-1000°C has been recently investigated by Stringer (11). The initial parabolic rate was superseded by a second parabolic rate, considerably more rapid than the first. In general, the lower the temperature, the longer before the first parabolic rate law broke down. He determined the partition of oxygen between the scale-forming and oxygen solution reactions. The proportion of oxygen entering the metal remained constant at about 45 percent during the first parabolic section. As the relative amounts of oxygen in the metal and scale remained constant during the initial parabolic stage, both the formation of scale and solution of oxygen separately must be parabolic. After the break-away the proportion dropped until by the time the second parabola was established only about 5 percent of the total oxygen absorbed was present in the motal. For this stage of oxidation, the most probable step for the control of the kinetic appeared to be gaugeous diffusion of oxygen through the porcus scale.

2.5 Oxidation of Hafnium

Vory little information has been published about the oxidation of hafnium. Smeltzer and Simnad (9) investigated the oxidation kinetics in the temperature range 350°-1200°C. Although information is not available on the solubility of oxygen in hafnium, they noted that oxygen dissolved in the metal phase beneath scales on oxidized specimens. The kinetics followed the parabolic relationship in the temperature range 350°-800°C after an initial deviation. In this early stage of oxidation, the kinetics would be represented by a logarithmic equation. Thus the

rate of scale growth in the temperature range 350°-300°C followed a logarithmic plus parabolic equation for the investigated exposure periods. Between 900 and 1200°C, the growth equations were parabolic after an initial deviation and became linear during long periods of oxidation. Although they were unable to measure the weight increases in the early stages of oxidation, the authors suggested that in their temperature range the initial period might also be described by a logarithmic equation. In interpreting their results, the authors suggested that the rate controlling process was the diffusion of oxygen through the scale, and that a linear growth equation was obtained when porous oxide formed over a compact layer which had grown to a maximum thickness. X-ray diffraction showed that the scale was monoclinic hafnic. Utilizing radio-active markers, scale growth was shown to occur by the inward diffusion of oxygen.

Wellwork and Jenkins (8) have studied several features of the parabolic-linear exidation kinetics of hafmium. They established the formation of a duplex scale. Adherent compact gray exide was formed below perous exide and establishment of the steady exygen gradient in the metal coincided with the change from a parabolic to a linear growth equation.

2.6 Oxidation of Zirconium

According to Cubicio (29, 30) the zirconium dissolves larger amounts of oxygen than titanium, Lintton (31) established that oxygen penetrated into the metal during oxidation. The effect of oxygen additions on the lattice constants of zirconium was investigated by Treco (32). He found

that the lattice expanded linearly with increasing amount of oxygen. Also, the hardness of zirconium was increased in direct proportion to the increasing amounts of dissolved oxygen.

liayes and Roberson (33, 34) found, in 1948-49, that on heating zirconium in air in the temperature range 425 to 1360°C, a marked increase in the exidation rate occurred near 900°C. In 1949. Gulbransen and Andrew (35), using a microbalance, determined the growth equation for the oxidation of "abraded" samples in pure oxygen in the temperature range 200°-435°C for periods of 120 minutes. Their results were best fitted to a parabolic growth equation. In 1951, Cubiciott (30) investigated the temperature range 600°-900°C and found that a parabolic rate equation was followed for periods up to two hours but noted that a small deviation towards a linear relationship occurred at 920°C in this period. In the same year Phalnikar and Baldwin (36) reported a parabolic oxidation relationship for zirconium heated in air until a white scale formed. They reported an enormous increased rate when white scale appeared. Belle and Mallet (37) reported in 1954, however, that in the temperature range 575°-950°C the results were best fitted to a cubic equation. Charles, Earnatt and Gulbransen (38) also showed that in the temperature range 350°C and 450°C for the periods of 400 hours the results were fitted to a cubic equation. Kendall (39) found that for prolonged periods of exposure in the temperature range of 500°-700°C the parabolic oxidation changes to linear.

As shown by Belle and Mallet (37) specimens oxidized at 575°C do not exhibit oxygen penetration in the metal phase. At the higher temperature of 875°C oxygen did penetrate into the metal phase. In 1959, Wallwork (25) studied the high temperature exidation properties of zirconium and found the following facts. Strongly adherent gray compact exides with some visable perosity were formed with white ridges showing the edges. Gray scales, when stripped from the metal and heated in exygen, turned white. There were no layering in the scale structure. Both the white and gray forms of scale were shown by x-ray diffraction to be monoclinic. The exidation kinetics at 850°C followed a parabolic plus linear rate equation with the change occurring in the vicinity of 24 hours. The exygen penetration reached a "steady gradient" after 24 hours. Thus the establishment of the steady gradient coincided with the change from the parabolic to linear relationship. He concluded that the scale was non-protective and that the exidation process was controlled by the interstititial diffusion of exygen in the metal phase.

In 1961, Cox (40) discussed the mechanism of oxide film growth and breakdown on zirconium. He has suggested that, in the initial period at least, two mechanisms of film growth are operating simultaneously₂ and after breakaway there is indefinite linear growth. From the nature of the breakaway process at high temperature, he has suggested that at a critical film thickness, cracking of the film occurs due to stressees set up in it during growth. These stresses may result from the high Ft-lling-Badworth ratio of 1.56.

CHAPTER III

THEORETICAL CONSIDERATIONS

The following processes have been considered for the paraboliclinear exidation kinetics of sirconium. It is proposed that the growth of compact scale during parabolic exidation is due to the reaction of the metal with only a part of the exygen which diffuses through the exide lattice. The remainder of the exygen dissolves in the metal substruce. At a critical compact scale thickness, a duplex scale consisting of percus and compact excle layers develops by breakdown of the compact exide at its outer surface. During the linear growth, a compact layer of scale is always present on the surface of the metal. Forous exide is assumed to offer no resistance to exygen migration towards core metal. Hence, linear exidation may be associated with continuous percus exide formation; and with the diffusion of exygen across the inner compact layer of constant thickness to react with the metal. During this period of linear growth, exygen is not further taken up by the metal.

This diffusion model is illustrated in figure 1. The total thickness of the duplex scale designated, ϵ , for time, t, has developed by inward migration of oxygen. The oxygen interfacial concentrations in the oxide and metal phases, which may be determined from the metal-oxygen phase diagram, are designated C_0^S , C_0^{II} and C_0^L . The initial oxygen concentration in the metal C_0^{I} is assumed to be negligible.

This model for growth of compact oxide with concurrent solution



of oxygen in the metal corresponds to a model advanced by Wagner (41) for diffusion in a two-phase system. He has demonstrated that diffusion theory in terms of constants $D_0^{\rm I}$ and $D_0^{\rm II}$ for metal and oxide, respectively, lead to a parabolic growth law. It will be demonstrated subsequently that the oxygen uptake of metal amounts to only from 15 to 30 percent of the total in the temperature range $300^{\circ}-850^{\circ}C$. Accordingly, it is assumed that a constant oxygen gradient in the oxide serves as a good first approximation to obtain the low gradient expression for the parabolic growth law of compact oxide,

$$x^{2} = k_{p}^{II}t$$
 (1)

where $k_{p}^{II} = 2 \mathfrak{D}_{o}^{II} (C_{o}^{S} - C_{o}^{II})$

Here, as the volume of oxide per g oxygen ion and C_0^5 and C_0^{II} are the oxygen concentrations (g/cc) in the oxide/oxygen and oxide/metal inter-faces, respectively.

(2)

From the model it is possible to evaluate the parameters for linear oxidation. During this stage of porous oxide formation, the metal interface and oxygen profile in the metal move inward at a constant rate. Thus an extension of the analyses carried cut by Tiller et al (42) and Wagner (43) for diffusion in a phase where the boundary migrates at a constant rate may be applied. With the help of Fick's law, $J_x = -D(\frac{do}{dx})_x$ or $J_{x+dx} = -D(\frac{dc}{dx})_{x+dx}$ the net flow in the volume element, from Tiller's formula is $D(\frac{d^2c}{dx^2})$ per unit volume. If K_L is the linear rate constant in cm/sec, the total flow out is $K_L(\frac{dc}{dx})$. Then the diffusion equation for a steady state concentration distribution in a system moving at a velocity K_L is,

$$D \frac{d^2 c}{dx^2} + K_L(\frac{dc}{dx}) = 0 \text{ or } \frac{d^2 c}{dx^2} + \frac{K_L}{D} \frac{dc}{dx} = 0 \quad (3)$$

The solution for this equation can be obtained by putting $c = e^{i\pi k}$

$$\frac{dc}{dx} = me^{i2x}$$
(i)
$$\frac{d^2c}{dx^2} = m^2 e^{i2x}$$
(ii)

Putting values (i) and (ii) in (3)

x = 0, $C_0^I = A + B$

m(Dm + R) = 0

$$Da^2 + Ra = 0 \qquad (111)$$

or

$$m = 0 \qquad (iv)$$

$$m = \frac{K_L}{D} \qquad (v)$$

$$-K_L D \times C = A \cdot c + B$$

$$x = \alpha , C_0 = B$$

When

The appropriate solution for the metal phase with distance $x = x^*$ measured from the oxide/metal interface is,

$$C^{\mathbf{I}}(\mathbf{x}^{\bullet}) = (C_{\mathbf{o}}^{\mathbf{I}} - C_{\mathbf{o}}^{\bullet}) \exp\left(-\frac{K_{\mathbf{I}}}{D_{\mathbf{o}}^{\mathbf{I}}}\mathbf{x}^{\bullet}\right) + C_{\mathbf{o}} \qquad (l_{i})$$

and for the compact oxide phase with distance x = x'' measured from the oxide/ges interface if,

$$C^{II}(x'') = (C_{o}^{e} - C_{o}) \exp(-\frac{K_{I}}{D_{o}^{II}}x'') + C_{o}^{e}$$
 (5)

A fit of equation (4) to the oxygen penetration curve within the metal will be used to give an estimate of D_0^T for comparison with independent values in the literature as a check on the linear growth model for the metal.

The uptake of oxygen by the motal before onset of linear oxidation may first be evaluated. This encunt is therefore.

$$\begin{pmatrix} \underline{AM} \\ \underline{A} \end{pmatrix}_{\text{metal}} = \int_{0}^{\infty} C^{\mathbf{I}} dx' - \int_{0}^{\infty} C_{\mathbf{0}}^{\mathbf{I}} dx' \qquad (6)$$

$$= \int_{0}^{\infty} (C^{\mathbf{I}} - C_{\mathbf{0}}^{\mathbf{I}}) \exp(-\frac{K_{\mathbf{I}}}{D_{\mathbf{0}}^{\mathbf{I}}} x') dx' + \int_{0}^{\infty} C_{\mathbf{0}}^{\mathbf{I}} dx' - \int_{0}^{\infty} C_{\mathbf{0}}^{\mathbf{I}} dx'$$

$$\approx \frac{D^{\mathbf{I}}}{K_{\mathbf{I}}} (C_{\mathbf{0}}^{\mathbf{I}}) \qquad (7)$$

if the initial metallic concentration of oxygen (C_0) is assumed to be negligible.

As a second consideration, an expression for the parabolic constant of compact scale growth (K_p^{II}) in terms of the linear rate constant (K_L) can be evaluated. The boundary condition at the oxide/metal interface gives,

$$C_{o}^{\text{II}} - C_{o}^{\alpha} = (C_{o}^{s} - C_{o}^{\alpha}) \exp\left(-\frac{L_{L}}{D_{o}^{\text{II}}} \mathbf{x}_{o}^{\prime\prime}\right)$$
(8)

while the mass balance gives,

$$\begin{pmatrix} C_{o}^{II} - C_{o}^{I} \end{pmatrix} K_{L} = D_{o}^{I} \begin{pmatrix} \frac{\partial C^{I}}{\partial x} \end{pmatrix}_{x^{*} = o} = -D_{o}^{II} \begin{pmatrix} \frac{\partial C^{II}}{\partial x} \end{pmatrix}_{x^{''} = x^{''}}$$

$$\begin{pmatrix} C_{o}^{II} - C_{o}^{*} = \begin{pmatrix} C_{o}^{S} - C_{o}^{\infty} \end{pmatrix} \exp\left(-\frac{K_{L}}{D_{o}^{II}} x_{o}^{''}\right) \qquad (10)$$

or

Comparison with equation (8) shows that for a solution to exist one has to set,

$$C_{o}^{a_{0}} = C_{o}^{\dagger}$$
(11)

There is one further condition which must be imposed on the two solutions and that is the mass balance at the oxygen/oxide interface,

$$(C_{o}^{S} - C_{o}) K_{I} = -D^{II}(\frac{\partial C}{\partial x})_{x''=0} = (C_{o}^{S} - C_{o}^{\infty}) + (C_{o}^{S} - C_{o}^{*})$$
 (12)

where C_0 is the atmospheric oxygen concentration. Hence, for the steady solution to exist it must be that,

$$C_{0} = C_{0}^{\dagger}$$
(13)

There was no need to achieve this condition in the experiments since both C_0 and C_0' are sufficiently small to be set equal to zero, thus obtaining effective equality. For example, the oxygen concentration in an atmosphere at S.T.P. is 1.43 x 10⁻³ g./cc. This concentration would correspond to a metallic impurity oxygen content of only 0.02 weight percent. Moreover, C_0^3 is such larger than C_0 because the oxygen concontration of stoichicmetric zirconium dioxide is 1.49 gm/cc.

An expression can now be obtained for the parabolic rate constant (K_p^{II}) for compact scale growth in terms of the linear rate constant (K_L) by solving equation (5).

If the oxide phase is considered as a semi-infinite plate moving with a gradient constant with time

$$C_{(x)}^{II} = (C_0^S - C_0) \exp \left(-\frac{K_I}{D_0^{II}} x''\right) + C_0$$

When the thickness of compact scale is maximum $X'' = X_c''$

$$C_{x_{o}}^{II} = (C_{o}^{B} - C_{o}^{\infty}) \exp \left(-\frac{K_{L}}{D_{o}^{II}} x_{o}^{"}\right) + C_{o}^{\infty}$$

Taking $C_{o}^{\infty} = C_{o} = C$ and neglecting the value of C_{o}
$$\frac{C_{o}^{II}}{C_{o}^{S}} = \exp \left(-\frac{K_{L}}{D_{o}^{II}} x_{o}^{"}\right)$$

or,

 $K_{\rm L} x_{\rm o}^{\rm H} = D_{\rm o}^{\rm II} \ln \frac{C_{\rm o}^{\rm S}}{C_{\rm o}^{\rm II}} - D_{\rm o}^{\rm II} \left(\frac{C_{\rm o}^{\rm S} - C_{\rm o}^{\rm II}}{C_{\rm o}^{\rm II}}\right)$ (14)

or,

$$K_{L} x_{0}^{"} C_{0}^{II} = D_{0}^{II} (C_{0}^{S} - C_{0}^{II})$$
 (15)

The left hand side can be evaluated empirically from the linear rate data and the phase diagram. It can be substituted into the expression for the parabolic rate constant, equation (2), to give an independent value of this parameter for comparison with the directly determined value. This serves as a check on the linear growth model for the oxide.

This analysis will be applied incofar as possible to the high

temperature oxidation of zirconium. A test of the model based upon independent calculations of the parabolic and linear rate constants cannot be carried out owing to the absence of diffusion and concentration data for zirconium diozide. Accordingly, a further investigation has been made on the kinetics of oxidation, scale structures and oxygen gradients in the metal in order to gain substantiating experimental findings for testing the scale-metal diffusion model by equations (4), (7) and (15).

CHAPTER IV

EXPERIMENTAL APPARATUS AND METHODS

4.1 Oxidation Apparatus

A diagram of the apparatus used for the measurements of oxidation rates is illustrated in figure 2, showing the pyrex glass vacuum system, furnace and spiral spring balance arrangement.

4.1 (a) VACUUM SYSTEM

The vacuum system used was of conventional design and consisted of a mechanical pump (1), a two stage oil diffusion pump (2), oxygen storage flashs (3) and cold traps (4), placed in such a way as to protect the metal specimens from moisture, oil vapour or mercury vapour. The vacuum was measured with a McLeod gauge. The vacuum system could maintain the assembly at a pressure of 10^{-6} mm Hg.

4.1 (b) FURNACE

The furnace (5) was of simple construction. The heating element consisted of michrome wire wound around a mullite tube and then covered by a layer of refractory pasts. This furnace was capable of operating at 1000°C for long periods of time. The hot spot of the furnace was about two inches in length and about 6 inches below the top of the furnace. The oxidation temperature was measured by two chromel-alumel thermocouples placed between the furnace wall and mullite reaction tube of the assembly. One of the thermocouples was connected to a Philips controller-recorder and the other to a potentiometer. The controllerrecorder was coupled with a mercury relay switch and powerstat allowing



Schematic Diagram of the Oxidation Apparatus

temperatures to be controlled to $\pm 2^{\circ}C$.

4.1 (c) BALANCE ARRANGEMENT

A McBain type spiral spring balance (44) was used for oxidation measurements. Cathetometer measurements of spring elongation were reproducible to 0.01 cm; this corresponded to a reproducibility of 0.3 mg for a specimen weighing 0.7 gm.

4.1 (d) OXIDATION PROCEDURE

All specimens were annealed before oxidation. Once a specimen was in place, the system was exacuated to 10^{-6} nm of mercury. The temperature of the furnace was brought to about 700° C and the specimen was annealed for two hours at this temperature. The furnace was then adjusted to desired oxidation temperature which was either 800° or 850° C. When the temperature of the furnace was steady, oxygen was admitted to the combustion tube. The oxygen pressure for all tests was maintained slightly below atmospheric (750 mm Hg).

Several of the oxidized specimens were prepared for metallographic examination and microhardness measurements. After oxidation of a specimen had proceeded for the required number of hours, the system was exacuated to 10^{-6} mm Hg pressure, and the furnace shut off to allow the specimen to cool in vacuum. After the furnace had cooled, air was admitted to the system and the specimen was removed. A specimen for hardness measurements was cooled by raising it to the top of the combustion tube by means of the glass winch.

For the study of the growth rates of specimens containing oxygen, two types of experiments were carried out. In the first set of experiments, specimens oxidized to the range of linear growth were removed from the furnace after cooling in situ. The oxide layer was removed from the specimen and then replaced on the spring balance. The furnace tube was then evacuated to 10^{-6} mm Hg pressure and the furnace heated to 850° C. Cxygen was then admitted to the tube for recuidation of the specimen. The weight gain was recorded with time. In the second set of experiments, this specimens 0.25% mm thick, were exidized at 750 mm Hg pressure at oxygen atmosphere to a weight gain of about 300 atom percent for saturation of the specimen in the alpha phase as taken from the constitutional diagram of the sircondum-oxygen system (45). The furnace was then evacuated and the oxidized specimen annealed for 100 hours for the formation of saturated alpha-solid colution by the diffusion of oxygen from the oxide layer to the metal core. After this annealing process, the opecimen was oxidized at 850° C and 750 mm of Hg pressure for growth rate determination.

4.2 Sample Material and Surface Proparation

The sirconium metal prepared by the indide process was received as 0.04 and 0.125-in gauge sheet. Specimens approximately 5 mm thick and about 10 mm square were prepared by abrasion with silicon carbide papers to a 4/0 fineness for the microhardness tests. For the oxidation kinetics measurements the specimens were about 1 mm thick. Some of the specimens were propared by chemical etching after polishing on papers. The colution (5 percent HF, 40 percent HNO₃ and the rest water) for polishing the specimen by etching was found to produce a smooth surface.

4.3 Motallographic Mounting and Polishing

A great deal of difficulty was encountered both in mounting and polishing the specimens. During mounting, the oxide tended to break

away from the motal. Also, the great difference in hardness between the metal and oxide played a detrimental role as edges readily rounded under the most careful conditions of polishing.

4.5 (a) MOUNTING

The specimens for the hardness measurements and metallographic study of the scale, were mounted on edge using a cold setting polyester resin. The specimens were first given a few thin cents of the cold mounting material in order to help prevent the oxide from being pulled away from the metal by mount shrinkage during setting. The specimens were mounted in vacuum to minimize the number of pores in the mount_as the carry over of compounds from one stage of polishing to another caused severe scratching. The vacuum mounting was accomplished by placing the apparatus, shown in figure 3 in a vacuum desiccator.

This apparatus was placed in the desiccator in a position such that the handle of the crucible arm was against the inside wall of the desiccator. Thus, the crucible could be tipped by means of a magnet placed against the outside wall. The crucible was filled with mounting material and the desiccator was then evacuated with a mechanical pump. The mounting material was then poured into the mould which contained the specimen. The mold was made out of plastic tubing and the specimen was held on its edge for mounting by means of a wire stand. The mould was polished along with the mounted specimen. Maquid mounting material with hardener was found to produce better mounts in vacuum.

4.5 (b) POLISHING

Oxidized spectments for metallographic examination and microhardness measurements were abraded by hand after cold mounting on 220,





Vacuum Mounting Apparatus

320, 400 and 600 silicon carbide papers with flowing water as lubricant. This was followed by hand polishing on silk cloths using 6, 1 and 1/4-p diamond paste with lapping oil lubricant. Final polishing was done on polishing wheels using 0.3 and 0.1-p alumina slurries.

4.3 (c) HARDNESS MEASUREMENTS

Hardness measurements were employed as a measure of oxygen concontration in the metal substrate. Indentation measurements were made adjacent to the metal/oxide surface at a known distance using a Vickers microhardness unit. Five hardness scanswere determined for each oxidized specimen and the arithmetical averages taken for the determination. Individual measurements were reproducible within \pm 10 percent.

CHAPT IR V

EXPERIMENTAL REGULZS

The results of the oxidation tests on weight gain measurements are presented in conjunction with the microhardness determinations and metallographic examinations.

5.1 The Scales

The oxidized specimens produced during this series of experiments for the periods up to 40-50 hours had shiny gray-black scales with white ridges showing on the edges. Metallographic examination of these scales showed that they were dense without any porosity. They adhered strongly to the metal. Detached gray oxide from the metal turned white on heating in air or oxygen. Layering, of the type reported in titanium (28) scales, was not observed in any of the scales on zirconium.

The photomicrographs in figures 4-5 exhibit coveral features of the scales produced by exidation at 350°C for different exposure times. As illustrated by the photomicrograph in figure 4, the scale produced upon an exposure of 20 hours is uniform and free of any detectable pores.

The photomicrograph in figure 5 shows an inside gray oxide layer and an outside thin porcus layer of oxide formed by oxidation of a specimen at 350°C for 80 hours. The scale is considerably thicker but still uniform. As shown in figure 6, this uniformity vanishes for longer periods of oxidation.

Microhardness examinations were undertaken to establish whether a duplex scale was formed during linear exidation. The scale developed











Specimen oxidized for 100 hours at 850°C; X 187.5



Figure 8 Specimen saturated with oxygen and exposed for 30 hours at 850°C; X 240 during linear oxidation appeared to be composed of an outer porous oxide overlying the remnant gray compact oxide (figure 7-9). The external appearance of the white oxide is shown in figure 7. Its surface exhibits a network of cracks. The original abracion scratches have persisted because oxidation proceeded by inward migration of oxygen. The breakaway of an oxide section from the surface of specimen (the lower right hand corner of this photomicrograph) has exhibited the underlying compact gray oxide. A number of localized white areas were noticed on the gray oxide before the whole surface became covered with white oxide. Forous oxide growth appeared to be initiated by localized attack associated with crack formation as shown in figure 8.

Some of the specimens with gray oxide were heated in air for a short time to gain additional observations on the characteristics of white oxide formation. It was found that white oxide readily formed at gracks formed in the oxide due to thermal shock upon quenching of oxidized specimens. This characteristic is illustrated by the photomicrograph in figure 10. White oxide formation is also shown in areas derived of thermal cracks. Consequently, the gray oxide scales on several oxidized specimens were emanined to find if possible, the approximate grain size of oxide in the scale. For this purpose the oxide scales were otched in hydrofluoric acid and then examined under microscope. Very usuall surface cracks were found to exist in the oxide which appeared to follow grain boundaries (figure 11). However, it was not possible to definitely establish that these cracks followed grain boundaries and that these cracks served as the localized areas for white oxide formation.

5.2 Microhardness Testa

In order to determine the oxygen gradients in the metal, microhardness measurements were made on specimens oxidized at 350°C for exposures of 24, 35, 48, 60, 83 and 100 hours. The results of these experiments are illustrated in figure 12 and figure 13. Figure 12 shows the gradual increase of hardness as exygen penetrates inwards due to longer exidution periods. Within experimental accuracy, the concentration of exygen as a function of distance in the metal is defined by a steady configuration during linear exidation (figure 13).

5.3 Oxidation Measurements

Neasurements were made of the oxidation rates of as-received motal, the metal containing sufficient oxygen for the establishment of a steady state gradient, and the motal saturated with oxygen. The methods for preparing the specimens and measuring these oxidation rates have been presented in the section Oxidation Procedure, 4.1 (d). In figure 14, a photomicrograph is illustrated of a typical surface after preparation by the abrasion method. There are abrasion scrutches, which have been shown to remain on the outer surface of compact oxide (figure 7). A photomicrograph is shown in figure 15 of the surface of an oxidized specimen after removal of the oxide by stripping and a subsequent light abrasion. In this case the surface is very irregular.

5.4 Oxidation Rates of the As-Received Netal

In figure 16, results are shown of experiments at 800° and 850°C for long oxidation exposures. Here, the weight gains of zirconium specimens, mg oxygen/cm², have been plotted vs time in hours. The oxidation rates continuously decreased for exposures to approximately 60 hours after



Figure 9

The Corner of an Oxidized Specimen. After exposure for 80 hours at 850°C; X 187.



Figure 10

White oxide formed at the cracks in the gray oxide after re-oxidation of specimen in air at 850°C. (Photomicrographs taken under polarized light at magnification of 150 X.)



Figure 11

Cracks in Gray Oxide Surface after etching by HF (X 540). The specimen had been exposed in oxygen for 2^{l_1} hours at 850°C.





Microhardness determinations of zirconium specimens oxidized for 60, 83, and 100 hours at 850°C and 750 mm Hg pressure.





Figure 14

Surface of specimen prepared by abrasion. X240



Figure 15

Surface obtained by removal of oxide for re-oxidation. X240

which the specimens oxidized at constant rates. As will be demonstrated, these periods of decreasing and constant rates corresponded to the stages of parabolic and linear oxidation.

5.5 Effect of Caygon Concentration in Zirconium on Oxidation Rates

To test the possible role of the initial metal oxygen concentration in determining the oxidation kinetics, a series of auxiliary short-time experiments consisting of exposures to 12 hours at 850° C were carried out. As datum experiments, the oxidation kinetics of three as-received specimens containing negligible oxygen contents were determined. The result of these tests are illustrated in figure 17 by parabolic plots, (gn oxygen/ cm²)² vs time since, after exposures of approximately 3 hours, the kinetics obeyed a parabolic relationship.

The following experiment was then carried out in duplicate. A specimen was oxidized for 60 hours at 350° C for establishment of the steady configuration of oxygen in metal. After removal from the balance, the scale was chipped from metal surface. The specimen was then lightly abraded on 4/0 silicon carbide paper to remove adhering oxide and replaced in the balance assembly for re-oxidation at 850° C. The oxidation kinetics, figure 18, could still be represented by parabolic plots although their reproducibility was poor. These variations were probably due to non-uniformity of the lightly abraded surfaces (shown in figure 15) from which oxide had been chipped.

Oxidation tests were then carried out on 0.022 on thick specimens with oxygen contents approaching saturation values. To attain this condition, a specimen was oxidized at 850° C until its weight gain corresponded to 5.0 mg/cm² (the saturation value from the phase diagram is





Figure 17 Oxidation of zirconium at 850° C at 750 mm Hg pressure.

Re-oxidation at 850°C in oxygen at 750 mm Hg pressure of zirconium specimen after removal of compact oxide scale.



5.1 mg/cm²) (41). The balance assembly was then subjected to vacuum and specimen annealed for 100 hours so that the oxide would dissolve in the metal. This time was sufficient to rediscolve most of the oxide and approximately homogenize the oxygen in the metal. The results for reoxidation of two such specimens are illustrated by the parabolic plots in figure 19. In agreement with the preceeding tests, the specimens oxidized by parabolic kinetics following brief exposure times.

5.6 Atomic Structure of Scales

The existence of three crystallographic forms: cubic, tetragonal and monoclinic have been reported by different investigators. Both the gray and white oxide structures were examined separately by x-ray analysis. Parameters were calculated from the diffraction lines and then related to the published parameters for different forms of sirconium oxide. Only the monoclinic structure was identified. It was not possible to measure a difference in the parameters between the gray monoclinic and white monoclinic structures.



CHAPTER VI

DISCUSSION

In this section, the experimental findings are correlated incofar as possible to show that the growth of a duplex scale, consisting of inner compact and outer porous oxide layer determines the paraboliclinear oxidation kinetics. The influence of the compact layer on the oxidation kinetics after establishment of the "steady gradient" of oxygen in metal is also discussed to demonstrate that the linear kinetics are due to the steady diffusion of oxygen through a compact scale of constant thickness. Also, several oxidation features common to zircenium and titanium are discussed in order to further elucidate behaviour of metals in Periodic Subgroup IVB in oxidizing environments.

The experiments have demonstrated that parabolic oxidation occurs before onset of linear oxidation irrespective of the metallic oxygen contents. This oxidation behaviour was illustrated by the plots in figure 16 for specimens exposed in oxygen for long exposures at 800° and 850° C and the plots of oxidation data for relatively short exposures at 850° C in figure 17 - 19. In table 1, the evaluations are recorded of the parabolic constants at 850° C from the plots in figures 17 - 19 for the as-received metal, for the metal containing sufficient oxygen for establishment of the steady gradient, and for the metal saturated with oxygen. These evaluations are of the same order of magnitude.

One cannot formulate conclusions as to the relative amounts of oxygen consumed by oxide formation and solution in the metal from these

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TABLE I

Metal Parabolic Constant Temperature oc (z.oxygen)²/ca⁴-sec 2.3×10^{-10} 8000 Received metal 7.5×10^{-10} 8500 Received metal 7.2 x 10⁻¹⁰ 6.4×10^{-10} 9.2 x 10⁻¹⁰ 8500 Metal with 1.7 x 10⁻⁹ oxygen sufficient to establish gradient before linear oxidation 8500 1.2 x 10⁻⁹ Metal saturated 1.2 x 10⁻⁹ with oxygen

Parabolic Oxidation Constants for Zirconius

evaluations because the oxygen saturated specimens oxidized at the most rapid rate. This effect has also been established by Ostagen and Kofstad (46). For the specimens of their tests, linear oxidation occurred in the time periods reported here for parabolic oxidation. From figure (13), it can be seen that the reporducibility of the results for the weight gain in case of reoxidation were not good. This effect may be due to the surface roughness of the specimens prepared by the removal of oxide scale. The photomicrographs in figures 14 and 15 have shown the extreme roughness of these surfaces compared to those surfaces prepared by abrasion.

The total uptake of oxygen by the metal during oxidation may be evaluated if equation (7) accounts for the amount of dissolved oxygen in the metal during linear oxidation. This amount may then be compared with the total uptake of oxygen during parabolic oxidation. The average values of the ratio $(K_{\rm I}/D_0^{\rm I})$ at 850° and 800°C are 108 and 271 respectively (table II). These values were calculated from the data presented in figures 13 and 16. The consumption of oxygen by the metal is therefore 4.8×10^{-3} and 1.7×10^{-3} gm/cm². Since the total uptakes of oxygen before onset of linear oxidation are 1.6×10^{-2} and 1.0×10^{-2} gm/cm² at 850° and 800°C, respectively (figure 16), oxygen solution accounts for 30 and 17 percent of the oxygen consumed during parabolic oxidation. One may therefore conclude that oxygen weight-gain kinetics of zirconium at temperatures to 850°C are mainly associated with scale growth.

An evaluation cannot be made of the parabolic oxidation constant in the absence of data for the oxygen diffusion constant and phase boundary compositions for zirconium dioxide. Nevertheless, it is

TABLE II

Evaluations of Linear Oxidation Rate Constants and of Oxygen Diffusion Constants for Zirconium and Titanium and a Comparison of These Values to These Obtained from Diffusion Penetration Experiments (references in brackets)

Meta	l Temperature °C	Exposure Times for Crygen Gradient Esta- blishment hours	к <mark>1</mark> /Э	к _L <u>к. сокугал</u> сп ² -зес	D (oxidation) cm ² /sec	D (diffusion) cm ² /sec
Z	r 800		271	1.3x10 ⁻⁸		2.9x10 ⁻¹⁰ (52)
1						6.7x10 ⁻¹⁰ (50)
	850	60 - 100	72	2.6::10-3	2.420-10	8.7x10 ⁻¹⁰ (52)
		2 [!] 4 - 72	143(47)		1.2::10-10	9.40210 ⁻¹⁰ (50)
1	1 750	36-48	365(6)	1.9×10 ⁻⁸ (1)	3.0x10 ⁻¹¹	4.11210-10 (48)
						1,1x10 ⁻¹¹ (8)
						3x10 ⁻¹¹ (51)
	850	24-48	144(6)	1.1:10-7(7)	4.6x10-10	1.8x10 ⁻⁹ (48)
				1.6x10 ⁻⁷ (8)	6.3x10 ⁻¹⁰	1.2::10 ⁻¹⁰ (8)
1						4.1x10 ⁻¹⁰ (51)

possible to test whether steady state diffusion conditions exist in the metal and compact oxide layer during linear oxidation. For this type of oxidation, equation (4) and (15) describe the limiting penetration curve for oxygen in the metal and the conditions for duplex scale formation.

To perform this test for the oxygen gradient in the metal it is assumed that the hardness determinations of the metal are directly proportional to its oxygen concentrations. That such an assumption is reasonable is borne out by hardness measurements of Treco and Roo, Palmor and Open (47, 48) on zirconium and titanium oxygen solid solutions respectively. Accordingly, equation (4) for the concentration gradient of oxygen in the metal during linear oxidation is expressed in the form,

$$\log (H_{x} - H_{o}) = \log (H_{o}^{I} - H_{o}) - (\frac{T_{L}}{D_{o}^{I}} \log_{10} e)_{x}$$
 (16)

where H_x , H_o^T and H_o are the microhardness determinations within the metal substrate at distance x from the metal/oxide interface, at the metal/oxide interface, and at a distance beyond the penetration of the oxygen gradient, respectively.

The microhardness measurements, figure 12, have shown that the oxygen gradient changes during the parabolic growth. The steady state formation of the oxygen gradient during linear oxidation can be seen from the microhardness measurements illustrated in figure 15. These latter determinations and those reported by Wallwork and Jenkins (3) for titanium are plotted according to the above relationship in figure 20. The exponential relationship represents the penetration data only to a good first approximation, perhaps due to the failure of the

Figure 20

Microhardness determinations plotted according to equation (16), log ($H_x - H_0$) vs. x, for zirconium and titanium oxidized to range of linear oxidation

- Upper curve: hardness gradient in zirconium after exposures of 60, 80 and 100 hours in oxygen at 750 mm. Hg. pressure at 850°C.
- Lower curve: hardness gradients in titanium after exposures of 24-48 hours in oxygen at 760 mm. Ng. pressure at 750° and 850°C. Determinations by Wallwork and Jenkins⁽⁸⁾.



assumption of linearity between concentration and hardness. Hevertheless, the slope of these curves near the interface should give a good estimate of the ratio, $K_{\rm L}/D_0^{\rm I}$, for comparison with independently measured values.

The values of the oxygen diffusion constants calculated from this exidation data for zirconium and titanium and a comparison of these values with those reported in the literature from diffusion penetrution anneal experiments are recorded in table II. For zirconium, an additional determination is also included from an analysis of unpublished exidation results obtained by Wallwork (49). The comparison lies in all cases within experimental error, thus confirming the essential correctness of that part of the diffusion model which refers to the metal substrate.

The consistency of the linear oxidation kinetics with diffusion conditions of the duplex scale model may be demonstrated by employing equation (15) to calculate the parabolic constant, equation (2), for growth of compact oxide. Since the oxygen uptakes for compact scale growth are 8.5×10^{-3} and 1.12×10^{-2} ga/cm² at 800° and 850° C, the values of parabolic constants are 2.3×10^{-10} and 5×10^{-10} ga²/cm⁴/coc, respectively. These values, which are in close agreement with the experimental parabolic constants for the as-received metal (table I), substantiate the consideration that steady state diffusion conditions are satisfied in the inner compact layer during linear oxidation.

While diffusion accounts for the kinetics of oxygen migration during the linear oxidation of zirconium, the primary controlling process providing one of the boundary conditions for diffusion is associated with the mechanical phenomena which maintains a constant thickness of

compact oxide. The metallographic observations do not give information on the mechanism of surface-crack formation. It can be noted from the micrographs of figures 6 - 10 that porous white oxide is formed from compact gray oxide by exfoliation from initiating cracks.

The examinations of the external surfaces of oxide scales produced on specimens by oxidizing for different lengths of time have shown that white oxide was formed on the surface of gray oxide at different points, which in time spread and covered the whole surface of gray oxide with white porous oxide. Compact oxide, which was internately bonded to the metal, remained gray due to a relatively larger oxygen vacancy concentration. The detached oxide was white because its composition approached that for the oxygen-rich oxide equilibrated with oxygen. In this respect, the parabolic-linear oxidation kinetics of zirconium differ from those for titanium. For this latter metal, the controlling step for linear oxidation appears to be determined by reaction parameters at oxide/metal interface brought into play by a complete breakdown of oxide to a porous scale at a critical thickness (4, 7, 8).

CONCLUSION

From the literature review, theoretical considerations and experimental findings, this thesis can be concluded as follows:

1. The exidation of zirconium in exygen at atmospheric pressure follow a parabolic linear growth equation at 800° and 850°C.

2. Irrespective of the oxygen concentration in the metal substrate, parabolic kinetics represent the growth of the initial compact oxide scale while linear kinetics represent the later stages of growth. The transition from parabolic to linear oxidation for zirconium is associated with the formation of a duplex scale consisting of compact and percus oxide layers.

3. The gray compact oxide is formed during parabolic oxidation the inward migration of oxygen to the oxide metal interface. During this stage of the oxidation reaction, oxygen is dissolved in the metal substrate.

4. At a critical thickness of the compact oxide, a steady concentration gradient of oxygen in the metal substrate is established upon onset of linear oxidation kinetics. An exponential solution of the diffusion equation fitted to the concentration profile can be used to evaluate the oxygen diffusion constant in the metal.

5. The oxide formed on the surface of gray oxide during linear growth is white and porous. The structure of both gray and white oxide are monoclinic.

6. The thickness of the compact gray oxide remains constant during linear oxidation by its conversion to white porous oxide. This oxide offered no resistance to the migration of oxygen from gas phase to porous oxide/compact oxide interface.

7. The white porous oxide appeared to form at cracks on the gray oxide surface and then spread by an exfoliating cracking type mechanism. It was impossible to show by chemical etching experiments with hydrofluoric acid whether these cracks occurred at grain boundaries in the compact oxide

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