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ELLIPSOMETRIC STUDY OF OXIDATION
KINETICS IN TITANIUM-ALUMINUM SYSTEM

by

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ELLIPSOMETRIC STUDY OF OXIDATION KINETICS IN

TITANIUM-ALUMINIUM SYSTEM

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TABLE OF CONTENTS

	Page
I. INTRODUCTION.....	1
II. THEORY OF OXIDATION REACTIONS.....	4
A. GENERAL.....	4
B. THIN FILM (TARNISHING) MODELS.....	4
1. <u>Reciprocal Logarithmic Model</u>	4
2. <u>Direct Logarithmic Model</u>	7
C. THICK FILM (SCALING) MODELS.....	8
D. EMPIRICAL RATE EQUATION.....	9
E. EFFECT OF ALLOYING ELEMENTS.....	11
III. EQUIPMENT AND MATERIALS.....	15
A. EQUIPMENT.....	15
1. <u>Ellipsometer</u>	15
2. <u>Test System</u>	17
B. MATERIALS.....	25
1. <u>Alloys</u>	25
2. <u>Oxygen</u>	27
IV. EXPERIMENTAL.....	28
A. PROCEDURE.....	28
B. PRELIMINARY VACUUM TESTS.....	29
C. TECHNIQUE OF PREPARATION AND MEASUREMENT..	29
D. CALCULATIONS.....	30
V. RESULTS.....	36
A. TIME-THICKNESS DATA.....	36
B. OPTICAL CONSTANTS.....	36
C. DISPERSION DATA.....	41

	Page
VI. KINETIC MODELS AND CORRELATIONS.....	44
A. EMPIRICAL RATE EXPRESSION.....	44
B. THIN FILM (TARNISHING) MODELS.....	44
VII. DISCUSSION.....	53
A. ERRORS IN CALCULATION OF THICKNESS.....	53
B. THIN FILM (TARNISHING) MODELS.....	55
C. EMPIRICAL RATE EQUATION.....	55
D. EFFECT OF ALLOY ADDITIONS.....	56
VIII. CONCLUSION.....	58
NOMENCLATURE.....	60
BIBLIOGRAPHY.....	63
APPENDICES	
I. KINETIC DATA, EXPERIMENTAL Δ, ψ , TIME, THICKNESS AND COMPUTED LOGARITHMIC RATE LAW VARIABLES, $\lambda = 5000 \text{ \AA}$, $\phi_0 = 79.756 \text{ deg}$	66
II. COMPARISON OF COMPLEX OPTICAL CONSTANTS OF Ti-Al ALLOYS BASED ON DISPERSION AND KINETIC MEASUREMENTS AT 5000 AND 5890 \AA	73
III. SUBSTRATE AND THIN FILM OXIDE FILM COMPLEX OPTICAL CONSTANTS OF Ti-Al ALLOYS FROM DISPERSION MEASUREMENTS AT ROOM TEMPERATURE.....	76
IV. EFFECT OF THICKNESS CHANGE ON CALCULATED COMPLEX OPTICAL CONSTANTS OF OXIDE FILM ON 0% Al ALLOY.....	85

LIST OF TABLES

Table	Title	Page
I.	TEST ALLOYS, CHEMICAL ANALYSIS	26
II.	EXTRA DRY GRADE OXYGEN, TYPICAL ANALYSIS	26
III.	RECIPROCAL LOGARITHMIC RATE MODEL CONSTANTS AND ACTIVATION ENERGY	52
IV.	DIRECT LOGARITHMIC RATE MODEL CONSTANTS AND BARRIER HEIGHT ENERGY	52

PREVIEW

LIST OF FIGURES

Figure	Title	Page
1.	Binary System Ti-0 and Ti-Al.....	13
2.	Ellipsometer Components.....	18
3.	Test System.....	21
4.	Disassembled Test Cell.....	22
5.	Test Cell and Sample Holder.....	23
6.	Assembled Test Cell.....	24
7.	Scheme for Calculation of Thickness.....	31
8.	Computed $\Delta\psi$ Calcomp Plot I. and Superimposed Data Points for 0.4% Al at 520°F.....	33
9.	Computed $\Delta\psi$ Calcomp Plot II. and Superimposed Data Points for 0.0% Al at 330°F.....	34
10.	Time-Thickness Profiles at 0% Al.....	37
11.	Time-Thickness Profiles at 23% Al.....	38
12.	Substrate Optical Constants versus Percent Al at 5890 Å.....	39
13.	Oxide Film Optical Constants versus Percent Al and Temperature (Equivalent Thickness) at 5000 Å.....	40
14.	Oxide Film Optical Constants versus Wavelength at 0% Al.....	42
15.	Oxide Film Optical Constants versus Wavelength at 23% Al.....	43
16.	Empirical Rate Constant and Reaction Index versus Percent Al.....	45
17.	Reciprocal and Direct Logarithmic Rate Models at 6% Al and 329°F.....	46
18.	Reciprocal Logarithmic Rate Models at 0% Al and 442°F.....	47

19.	Reciprocal Logarithmic Rate Models at 12% Al and 522°F.....	48
20.	Debye Length and Activation Energy versus Percent Al and Temperature.....	49
21.	Energy of Activation versus Percent Al Based on Reciprocal Logarithmic Model.....	50

PREVIEW

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I. INTRODUCTION

The oxidation kinetics of many pure metals has been studied at high temperatures and the mechanism of oxidation is reasonably well understood. At low temperatures, below 300-400°C, the oxidation kinetics of many metals is not as well defined because of the lack of sensitivity for measuring extremely thin films and the attendant difficulty in relating the data to a single growth mechanism. Studies reported on commercial alloys, while useful for specific applications, are not amenable to quantitative comparison because of the complicating effects of several components. The purpose of this investigation has been to study the oxidation behavior of pure metal (titanium) at 325°F, 440°F and 520°F and determine the effect of a second component (Aluminum) in solid solution alloys at the same temperatures. The titanium-aluminum system was chosen because of the high mutual solid solubility of these elements and because of commercial interest in titanium base alloys for space applications.

The most common method for determining the oxidation kinetics of metals and alloys is to measure the weight change with time using a microgravimetric balance. Such measurements were initiated primarily by Gulbransen^{1,2} in about 1950 and were used by Gulbransen and Andrews to study the oxidation of pure titanium. The sensitivity for weight gain measurement was reported to be equivalent to an oxide thickness of about 20 Å. This sensitivity is inadequate for

measurement of very small thickness changes prevailing at lower temperatures because the experimental points are found to be somewhat scattered.³

Reviews on the application of ellipsometry to oxidation corrosion processes have been presented by Kruger and Hayfield and White.⁴ Based on experience in the Electrical Materials Laboratory at the University of Nebraska and the General Mills Research Department,⁵ a preliminary study was made to determine whether the high sensitivity of ellipsometry, equivalent to less than 0.2 \AA , could be used to study the very small oxide thickness changes on titanium alloys at low temperature. Ellipsometry was found to be feasible and a detailed study was initiated.

The oxidation rate of pure titanium can be expressed by several different rate equations depending on temperature, film thickness and time. Sample preparation, polishing, metal impurity, gas impurity and oxygen solubility must also be considered. The literature shows that the oxidation follows either a direct logarithmic [$x = A \ln(t) + B$] or cubic ($x^3 = At + B$) relationship below 300°C . A transition to parabolic ($x^2 = At$) occurs between 300° and 600°C ; and a final transition to linear ($x = At$) occurs above 1000°C .^{2,3,6}

Addition of a second component increases the number of factors that must be considered. The alloying element may have

1. different affinities than the base metal for oxygen

2. mutual solubility in the base metal and oxide
3. varying diffusion rates in the base metal and oxide
4. an effect on composition and structure of the oxide as oxidation proceeds.

At relatively high temperatures (700-900°C), small amounts of elements of higher valence than titanium (tungsten, niobium, molybdenum) decrease the extent of oxidation.^{3,7} Chromium increases the oxidation rate for chromium contents below 17 wt% although aluminum has little effect. Silicon, vanadium, iron and other alloying additions have been studied, although no systematic low temperature study of a binary titanium base alloy has been found in the literature.

In discussing the effects of alloying additions on oxidation, Stringer⁸ concludes that a more detailed and systematic study of the oxidation of alloys is needed than has been made in the past. It is hoped this study will contribute to an understanding of binary alloy oxidation as well as define oxidation parameters specific to the Ti-Al system at low temperature.

II. THEORY OF OXIDATION REACTIONS

A. GENERAL

It is customary to treat separately the oxidation of metals at low temperature (below about 300°C) and that at high temperature since the oxide film thicknesses are different in magnitude. The present study deals with thin film processes below about 200 Å.

The process of oxide growth involves the outward migration of metal ions or the inward migration of oxygen ions and is related to the presence of lattice defects.⁹ For purposes of this study, defects are generally defined as vacancies (vacant positions) on otherwise occupied lattice sites, interstitial atoms at positions in the interstices between lattice sites, and misplaced atoms.

The significance of lattice defects is illustrated⁷ by comparing ΔF° (Al_2O_3) and ΔF° (Cu_2O) with oxidation constants at 600°C. The oxidation constant ($3 \times 10^{-11} \text{ gm}^2/\text{cm}^4\text{-hr}$) for aluminum oxidation is five orders of magnitude less than it is for copper oxidation even though ΔF° (Cu_2O) is 165 Kcal mole⁻¹ more positive than ΔF° (Al_2O_3). The reason that the least noble metal (Al_2O_3) reacts slowest with oxygen is because the defect concentration is smaller in Al_2O_3 than in Cu_2O and fewer paths are available for diffusion through it.

B. THIN FILM (TARNISHING) PROCESSES

1. Reciprocal Logarithmic Model

In thin film processes at low temperatures, the

extent of oxidation is greater than would be expected from ordinary diffusion in a concentration gradient because of the low ion diffusion coefficients. In the theory developed by Mott and Cabrera,^{3,7,10,11} it is proposed that oxygen atoms are adsorbed on the oxide surface and that electrons pass from metal to the adsorbed oxygen and establish equilibrium between them. An electric field thus existing across the oxide film is responsible for pulling the ions through the film.

Assuming that the potential gradient is electrical in character and provided that temperature remains constant, the rate of oxide film growth will decrease with time since the potential gradient decreases as the thickness increases. In the absence of an electrical field, the chance of an ion possessing the minimum requisite energy to move across an energy barrier will be the same in all directions and will be equal to $\exp(-U/kT)$. In the presence of a potential gradient, the chance of movement in one direction will increase to $\exp [(-U+K_1/x)/kT]$ by an amount equivalent to the increase in potential gradient K_1/x , while the chance of movement in the opposite direction will decrease to $\exp [(-U-K_1/x)/kT]$ by the same factor. Therefore, according to this model, the net movement will be proportional to $A' [\exp (K_1/xkT) - \exp (-K_1/xkT)]$ where $A' = \exp (-U/kT)$. The growth rate of the oxide film is then proportional to the effective movement:

$$\frac{dx}{dt} = A' [\exp (K_1/xkT) - \exp (-K_1/xkT)] \quad (1)$$

A limiting case of this equation is realized at low temperature since the vacant sites are less mobile and the chance of their movement in the absence of help from a potential gradient is negligible. For thin oxide films, the potential gradient is large so that movement can be neglected in the direction against the gradient and equation (1) then simplifies to

$$\frac{dx}{dt} = A' \exp(K_1/xkT) \quad (2)$$

Defining the potential barrier K_1/x as $zedV/2x$ and the Debye length x_0 as $zedV/2kT$, the rate equation becomes

$$\frac{dx}{dt} = A' \exp(x_0/x) \quad (3)$$

In terms of the experimental variables, the activation energy⁷ is given by

$$E = \frac{zedV}{x} = \frac{x_0}{x} (2kT) \quad (4)$$

In order to solve differential equation (3), Hauffe⁷ multiplies the term on the right by $x_0/(x_0+2x)$ for the case where $x_0 > 2x$ (verified experimentally). The equation may then be rewritten

$$\frac{dx}{dt} = \left(\frac{A' x_0}{x_0 + 2x} \right) \exp(x_0/x) \quad (5)$$

By separating variables and integrating, the reciprocal logarithmic equation is

$$\frac{1}{x} = \frac{2}{x_0} \ln(A'x_0)^{-\frac{1}{2}} + \frac{1}{x_0} \ln [x^2/(t+t_0)] \quad (6)$$

Since this equation is linear in $1/x$ and $\ln[x^2/(t+t_0)]$, its validity can be determined graphically.

2. Direct Logarithmic Model

Below 300-400°F, the conductivity of an oxide may be too low for ion movement to be the controlling step. In this case, electron tunneling may be used to explain the electron-transfer. As opposed to an ion requiring a kinetic energy of $1/2 mv^2$ to surmount an energy barrier, an electron has a finite probability of passing through the energy barrier even if the kinetic energy is less than the potential energy at the top of the barrier.

For a perpendicular energy barrier, the proportion of electrons passing across it is given by $\exp(-4\pi x\sqrt{2mQ}/h)$.^{3,7} If the oxidation rate is controlled by the rate at which electrons can pass across it, the rate equation is then given by

$$\frac{dx}{dt} = A'' \exp(-x/x'_0) \quad (7)$$

$$\text{where } x'_0 = h/(4\pi\sqrt{2mQ}) \quad (7a)$$

Kubaschewski and Hopkins³ integrate equation (7) and assume $A''/x'_0 \approx 1$ to obtain equation (8):

$$x = x'_0 \ln(t) - c \quad (8)$$

Hauffe and Ilschner^{3,12}, using the original idea of Mott¹³, indicated that curves of equations (6) and (8) will intersect if superimposed on the same plot.⁹ If the intersection occurs at an experimentally accessible point, control by electron passage may be expected in the very early stages of oxidation followed by ion passage at greater thicknesses. That is, the direct logarithmic equation will be obeyed at very small thicknesses and the reciprocal logarithmic equation will be obeyed at slightly greater thicknesses.

In Mott's original model, the very early stage of oxidation was in the domain where electron transport occurred by tunneling. Within the very early stage he predicted parabolic behavior followed by direct logarithmic behavior. Fromhold¹⁴ compared experimental data from several sources with Mott's predictions and showed that at the temperatures of concern in the present study, the parabolic stage occurs in a fraction of a second to a limiting thickness of about 20 Å. For this reason, the initial parabolic equation was not considered.

C. THICK FILM (SCALING) MODELS

At higher temperatures, an oxide scale forms rapidly on the surface. However, in contrast to lower temperatures, the oxidation mechanism depends upon whether

1. the oxide is a liquid or a solid
2. the oxide partially evaporates
3. the oxide is compact or porous
4. oxygen dissolves appreciably in the base metal²

Compact oxide scales act as barriers to concentration diffusion. Thus the Wagner theory applies because volume diffusion of reaction ions (or corresponding defects) is the rate controlling step. Metal ions diffuse outward or oxygen ions diffuse inward while respective cation and anion vacancies migrate in opposite directions.²

At fairly high temperature, x will quickly become sufficiently large so that terms containing x^{-3} and higher may be neglected in the Taylor series expansion of equation (1). This results in equation (9) which leads, upon integration, to the parabolic scaling equation (10):

$$\frac{dx}{dt} = 2A'K_1/xkT = K_2/x \quad (9)$$

$$x^2 = 2K_2t + K_3 \quad (10)$$

The form of parabolic equation (10) is the same as that derived by Mott for the very initial stages of tarnishing oxidation although the mechanism is entirely different.

D. EMPIRICAL RATE EQUATION

Lustman and Mehl¹⁷ found that oxidation data, when analyzed by plotting logarithm of oxide thickness versus logarithm of time, followed a power law such as equation (11):

$$x^{\ell} = A_1 t \quad (11)$$

An expression similar to equation (11) can be obtained by assuming a rate equation of the form given by (12). Taking

the logarithm of equation (12), a plot of $\ln(dx/dt)$ versus $\ln(x)$ gives the slope n and y intercept $\ln(A)$ in accordance with equation (13):

$$\frac{dx}{dt} = Ax^n \quad (12)$$

$$\ln(dx/dt) = \ln(A) + n\ln(x) \quad (13)$$

A comparison of constants given by equations (11), (12), and (13) can be made by integration of equation (12):

$$x^\ell = A_1 t + A_2$$

$$\text{where } \ell = 1-n \text{ and } A_1 = A(1-n) \quad (14)$$

This type of analysis provides a rapid means for determining the approximate value of ℓ prior to further analysis of the data. Values of ℓ near one, two or three over a temperature range suggest a linear, parabolic or cubic oxidation mechanism. Upon determination of the mechanism by this empirical method, a detailed analysis can then be made to determine A_1 .

The constant A_1 may be correlated analogously with conventional chemical reaction models to follow the Arrhenius equation (15)

$$A_1 = A_0 \exp(-E/RT) \quad (15)$$

A plot of $\ln(A_1)$ versus $1/T$ gives a straight line of slope $-E/R$ from which an equivalent value of E may be determined. However, n must be constant at all temperature levels for such a correlation. Another interesting method for obtaining an equivalent value of E uses a more general rate expression given by equation (16):

$$\frac{dx}{dt} = A_0 [\exp(-E/RT)] f(x) \quad (16)$$

An equivalent value of E is obtained by comparing the rates at the same oxide thickness at two different temperatures as can be shown by equation (17):

$$\frac{dx/dt_1}{dx/dt_2} = \exp[(E/R) (\frac{1}{T_1} - \frac{1}{T_2})] \quad (17)$$

B. EFFECT OF ALLOYING ELEMENTS

The effect of an alloy addition on the rate of oxidation may be interpreted from the valence of alloying elements and their effect on lattice defects, the relative magnitude of free energies of the oxides and the solubilities of the metallic components in metal phases as well as in oxide phases.

As a rule, oxidation layers on metals are of the semi-conducting type and can be characterized as either n-type or p-type. A p-type oxide has a deficit of metal whereas an n-type oxide has an excess of metal. In the n-type oxides, either the excess cations and equivalent electrons exist on