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INITIAL OXIDATION OF TUNGSTEN AND TANTALUM

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

by

Doyle W. Rausch, B.Met.E.

* * * * *

The Ohio State University
1965

Approved by

Department of Metallurgical Engineering
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INTRODUCTION

Despite the attractive refractory aspects of the physical and mechanical properties of tungsten, tantalum, molybdenum, and niobium, the usefulness of these refractory metals at elevated temperatures is severely curtailed by their relatively poor oxidation resistance. As a result of the technological demand for high temperature materials in the past two decades, a great effort has been made to overcome this limitation. A large part of the effort has been application-directed (including alloy and coating development) and has brought limited success. The remaining effort has been aimed toward an understanding of the fundamental aspects of oxidation behavior\(^{(1,2,3)}\). The present work was motivated by this latter goal.

While the four refractory metals W, Ta, Mo, and Nb can be logically grouped together on the basis of their high melting points (which decrease in the order given along with atomic number), their crystal structure (body-centered cubic), and their unlimited mutual solubility in one another, it is advantageous to pair them on the basis of electronic configuration. Thus, W and Mo with six outer electrons (Group VI in the periodic chart), and Ta and Nb with five outer electrons (Group V) may be compared. Within each pair a remarkable similarity exists with respect to such properties as electrical resistivity, ductility, tensile strength, and solubility limit for interstitial elements. A marked dissimilarity between pairs is also noticed with respect to the same properties. Although the macroscopic (or gross) oxidation behavior of these metals has been
reported to be highly specific, there are striking similarities within each pair\(^{(2,3)}\). For example, over a wide range of oxygen pressures and substrate temperatures the susceptibility to oxidation in pure oxygen decreases in the order Mo, W, Nb, and Ta; and at high temperatures the tendency of the respective oxides to volatilize decreases in the same order. In both cases there is but a very small difference between the behavior of Nb and Ta. In view of this, tungsten and tantalum were selected for the initial studies in order to provide a degree of contrast.

A. Oxidation of Tungsten and Tantalum

Fundamental studies of the gaseous oxidation of metals are necessarily based upon equilibrium thermodynamics and structure of the phases involved in the reaction, and reaction kinetics and mechanisms. Without knowledge of the former, limited fundamental quantitative information can be obtained from kinetic studies (useful design parameters, of course, may be obtained). Relative to the equilibrium properties of more common metal-oxygen systems, the tungsten-oxygen and tantalum-oxygen systems are not well established. The excellent review given above\(^{(2)}\) describes this situation in some detail.

The phase diagram for the W-O system at one atmosphere total pressure\(^{(4)}\) indicates the stability of the four well-established oxide phases of composition \(\text{WO}_2\), \(\text{WO}_{2.72}\), \(\text{WO}_{2.9}\), and \(\text{WO}_3\) (i.e., \(\text{WO}_2\), \(\text{W}_{180.49}\), \(\text{W}_{20.58}\), and \(\text{WO}_3\), respectively). Although the homogeneity
ranges of these oxides are not well known(5), an allotropic transformation has been fairly well established for WO$_3$ between 700 and 750° C. The solubility of oxygen in tungsten is known to be quite low—on the order of 0.06 atomic per cent at 1700° C(6).

Even less is known about the Ta-O system. The stability and structure of the pentoxide Ta$_2$O$_5$ is well established, and an allotropic transformation has been observed at 1360° C. Other less well established suboxides at oxygen/metal atomic ratios of $\sim 1/4$, 1, $\sim 2$, and 2 have been observed under a variety of conditions. The conditions for stability of these oxides is not known. The solubility limit of O in Ta is known to be much greater than the corresponding solubility in W(5). Reported values fall in the range of 1 atomic per cent at 600° C to 2.9 atomic per cent at 1200° C.

Oxidation kinetics are usually studied by determining rate laws (i.e., specimen weight change as a function of time) for gross behavior and attempting to rationalize these results (along with pressure dependence) in terms of reaction mechanisms and defect structure of the oxidation product(3). The primary variables are usually substrate temperature, time, and oxygen pressure (with gas composition, i.e., the presence of gases other than oxygen, not always considered as a separate variable—but usually held constant). These studies on tungsten and tantalum oxidation have yielded a great deal of insight regarding overall oxidation mechanisms, and rate equations of important engineering significance covering large temperature and pressure ranges(7,8,9).
The above techniques have also produced much conflicting data regarding the oxidation of tungsten and tantalum. Even such basic characteristics as the shape of the rate curve or transition points are not without ambiguity. For example, one finds a number of studies which indicate that the oxidation behavior of tungsten between 600 and 1100° C in pure oxygen at pressures between 1 and 0.1 atmosphere is linear (non-protective)(10,11,12). Other studies, however, show oxidation rates to be parabolic (protective) initially and linear after longer exposure times for the same range of oxygen pressure and substrate temperature variables(4,13,14,15).

For tungsten substrates between 600 and 1100° C and oxygen pressures between 1 and 10⁻³ atmosphere, the parabolic rate is ascribed to the formation of suboxides by anion diffusion control, and the linear rate to conversion of suboxides to non-protective WO₃ at the oxide-gas interface. Between 400 and 600° C, the parabolic rate is generally observed(3).

The temperature effect above 1000° C has been summarized as follows(2): Between 1000 and 1500° C volatilization of the oxide diminishes its protective nature and leads to higher oxidation rates. Between 1500° C and 2000° C the oxidation rate continues to increase as oxide scales are not formed. Between 2000 and 2800° C the oxidation rate increases less rapidly with temperature. And above 2800° C the rate decreases with increasing temperature.

The oxygen pressure effect, too, is not without ambiguity. Most studies have been carried out in the pressure range of 1 to 10⁻³ atmosphere. For substrate temperatures under 600° C, the results
have been particularly difficult to rationalize. One example (14) is the decreasing weight gain per unit area (for a fixed time of the order of several hours) for oxygen pressures in the order: $1.3 \times 10^{-2}$, $3.5 \times 10^{-2}$, $1 \times 10^{-1}$, $7 \times 10^{-2}$, and $8 \times 10^{-3}$. For substrate temperatures above $600^\circ C$, the following pressure dependence has been reported: 680 to 1100° C, parabolic rate constant is proportional to the 0.4 power of pressure; 1500 to 2000° C, rate depends on the 0.6 power of pressure; 2000 to 2800° C, rate depends on the 0.8 power of pressure; and above 2800° C a linear dependency on pressure is observed.

Tantalum oxidation kinetics have been studied less extensively than tungsten. The rate laws for air or oxygen at pressures near atmospheric have been reported as follows (3): below 400° C, logarithmic, inverse logarithmic, and cubic; around 500° C, parabolic and parabolic-linear; and above 700° C, linear.

The oxidation product formed below 400° C is reported to be initially amorphous. The crystalline form, obtained after aging for periods of days at 300 to 350° C, is identified as something other than $Ta_2O_5$ (presumably $TaO_y$ or $TaO_z$ with $y \sim 1/4$ and $z \sim 2$). Both dissolution of oxygen and nucleation and growth of suboxides are assumed to take place during the reaction in this temperature range. Above 500° C, the dissolution and suboxide reactions appear to be accompanied by formation of the pentoxide. Internal oxidation and platelet growth parallel to $\{320\}$ planes in the tantalum are characteristic of suboxide formation. The $Ta_2O_5$ is
apparently confined to the gas-oxide surface and is not protective. For oxygen pressures between 41 and $10^{-5}$ atmosphere the linear rate constant undergoes a transition around $750^\circ C$. The transition has been associated with instability of $\text{TaO}_2$ above $750^\circ C$ and a change in the rate determining reaction from $\text{TaO}_2 \rightarrow \text{Ta}_2\text{O}_5$ below $750^\circ C$ to $\text{TaO}_y \rightarrow \text{Ta}_2\text{O}_5$. The higher temperature linear rate constant is relatively insensitive to oxygen pressure up to at least $1400^\circ C$. Above $1000^\circ C$ only $\text{Ta}_2\text{O}_5$ has been observed.

Despite the shortcomings of the above work, several potentially important ideas emerge. It appears as though further progress toward a fundamental understanding of oxidation mechanisms depends upon recognition of several other variables in addition to pressure, temperature, and time. Among the more important of these variables are: substrate crystallography, interface reactions, and nucleation and growth in general.

B. Oxidation in the Initial Stages

In view of the difficulties inherent in obtaining reliable experimental data and analyzing the results of complex metal-oxygen systems such as W-O and Ta-O, it is not surprising that very little attention has been directed to the initial stages of oxidation reactions. The fact that very few general theories attempt to describe any oxidation mechanism for films thinner than about $100 \, \AA$ reflects both the lack of meaningful experimental data and the possible highly specific nature of such reactions. Before discussing
the results of several studies dealing with the initial oxygen reaction on tungsten, significant insight may be gained from a brief review of the initial oxidation of other metals.

Much of the experimental work which has been carried out suffers from

1) a lack of positive definition of the initial metallic substrate,
2) a difficulty in observing surface structure in fine enough detail,
3) an inability to achieve a sufficiently low reaction rate so that the initial stages can truly be studied (for even at oxygen pressures as low as $10^{-6}$ torr a monolayer of gas may be adsorbed in a matter of seconds), and
4) the presence of unknown gases other than oxygen.

Despite these difficulties and the resulting uncertainty in interpretation, a number of potentially important observations have been made. The kinetics of the initial reaction on copper(16) and magnesium(17) at relatively low temperatures have been studied in some detail.

The reaction is characterized by three distinct stages: incubation, nucleation and lateral growth, and after impingement and complete surface coverage, bulk growth perpendicular to the surface. The nuclei or microcrystallites form on a more-or-less undefined "film", and appear simultaneously on a given crystallographic
plane. The constancy of nuclei density with increasing reaction time and the decrease in nuclei density with increased substrate temperature (at constant pressure) lead to the concept that each nucleus is surrounded by a "zone of influence" in which another nucleus is not likely to form. The extent of such a zone depends upon the rate of surface diffusion, rate of desorption, and rate of adsorption. The kinetics are markedly dependent upon crystallography. Other studies on copper(18), barium(19), iron(20), and nickel(21) are generally consistent with this characterization of the oxidation process, even though gross contamination of the initial substrate was undoubtedly present.

The role of substrate dislocations in the initial oxidation process is not well understood. However, it appears that certain impurities may be required in the dislocations in order for them to act as preferred nucleation sites.

The experimental work on the kinetics of the initial oxygen-substrate reactions on tungsten have dealt primarily with oxygen adsorption and mobility on atomically clean tungsten. Since these studies have been reviewed elsewhere(22,23) only the pertinent experimental details and general results will be mentioned here.

Two of the experimental methods which have been used in the studies of oxygen adsorption on tungsten are field emission microscopy (electron and ion), and flash filament techniques(24,25,26,27,28). These experiments have generally involved the deposition of oxygen on the substrate at room temperature or below, and the subsequent reaction of the covered
substrate in ultra-high vacuum (10^{-9} \text{ mm Hg to several orders of magnitude lower}) at temperatures between 4^\circ \text{ C} \text{ and } \sim 2000^\circ \text{ K}. \text{ Mobility experiments have usually been carried out below room temperature, while desorption experiments employed higher substrate temperatures. Desorption experiments aim to relate desorption temperature with pressure rise in the vacuum system as the reaction takes place, or change in the electronic work function of the various crystallographic planes on the substrate.}

It has been reported that two chemisorbed monatomic layers are formed below room temperature. About 80 per cent of the first layer is formed without activation and is generally immobile. This layer is characterized by a variation in coverage (i.e., surface density of adsorbed species) and binding energy with crystallography. The average binding energy of the first layer is about 160 \text{ Kcal per mole} (subject to a 20 per cent variation). This layer is also stable under high vacuum to about 1000^\circ \text{ C}. \text{ Each tungsten atom in the surface is believed to contact only one oxygen atom, with each oxygen atom contacting several tungsten atoms. Such an arrangement permits a second, less-tightly bound, chemisorbed layer on planes other than the most densely packed \{110\} in body-centered cubic. The second layer is considerably less stable and is desorbed above 300^\circ \text{ C in high vacuum.}}

\text{Additional molecular oxygen may be accommodated in a physisorbed state at low temperatures, but even the complete second chemisorbed layer seems to be formed with difficulty at room temperature (i.e., relatively high oxygen pressures are necessary).}
At substrate temperatures slightly above room temperature undissociated oxygen is believed to be slowly taken up by the chemisorbed layer in a manner resembling "slow oxidation". Mobility within the chemisorbed layer is observed at 130° C and above. Oxidation and desorption apparently take place simultaneously above 300° C in the ultra-high vacuum environment.

The relatively new technique of low energy electron diffraction has also been used to study the oxygen-substrate reaction at relatively low temperatures(29). The early work with tungsten \{110\} planes and adsorption at room temperature is in agreement with conclusions of the previously mentioned work. Only a single layer is reported on this plane after long exposures to pressures as high as 1 torr. The binding energy is apparently high enough to prevent significant desorption in ultra-high vacuum at temperatures below 1500° C. The structure of the monolayer, however, is thought to be comprised of oxygen atoms arranged exactly like that of the metal atoms in the underlying substrate. The formation of the monolayer may involve oxygen and metal atoms exchanging positions, but once the monolayer is formed, oxygen atoms appear to regain the outermost positions.

These same techniques have given much less information regarding the initial reactions occurring on oxygen-covered tantalum substrates in ultra-high vacuum(30,31), although interesting morphological observations have been made with low energy electron diffraction(32,33).
In most of the above studies, differentiation between oxidation and adsorption has been difficult. And nucleation phenomena had not been emphasized prior to a preliminary report on the present work(34).

C. The Present Work

Compared with the field emission work described above (namely, oxygen deposition at low temperatures and subsequent heating in the absence of gaseous oxygen), the present work is concerned primarily with the course of reaction on tungsten and tantalum substrates above room temperature with oxygen from the gas phase (i.e., conditions under which appreciable oxidation is expected).

The field electron emission microscope is well suited for such a study because of the following reasons.

1) Electron emission is dependent upon crystallography and is extremely sensitive to surface contamination.

2) Atomically clean and reproducible surfaces can be achieved on tungsten and tantalum emitter-substrates by heating to temperatures between $2000^\circ$ and $2600^\circ$ C.

3) All major crystallographic planes are present on the approximately hemispherical emitter substrate.

4) High magnification and resolution are readily achieved. The inherent resolution in the depth dimension is less than one atomic layer, and about $20 \AA$ in the lateral dimensions.
5) Observations can be easily made during the course of the reaction since the reaction takes place in the microscope.

The most serious shortcoming of the field electron emission technique involves the relatively limited extent of a given crystallographic structure and the resulting difficulty in obtaining rate measurements.
II. EXPERIMENTAL EQUIPMENT AND TECHNIQUE

A. Field Emission Microscope

Since its invention by E. W. Müller in 1937, field emission microscopy has been developed to the point of being a fairly simple technique. In view of the abundance of published reviews covering operating principles and techniques(35,36), only a brief description is given here.

Field emission is accomplished by the tunneling of electrons through a field-deformed potential barrier at the surface of the specimen. Electric fields of the order of $10^7 \text{ V/cm}$ are sufficient for appreciable emission. While in principle, it is possible to obtain such emission from macroscopic surfaces, relatively low voltage is capable of producing the high field if the specimen surface is highly curved. Accordingly, field emission specimens are usually in the form of fine wires containing a highly curved tip. Potentials of several kilovolts are sufficient to produce adequate emission from tips of about $1000\,\AA$ radius. The ultra-high vacuum requirement of the field emission microscope results from the occurrence of gaseous ionization and discharge when relatively high pressures of gas encounter such high electric fields. Resolution of the microscope is about $20\,\AA$ in lateral directions on the surface and is much less than a monolayer of adsorbate in a perpendicular direction to the tip surface. Magnifications of the order of $10^6$ are possible.
The microscope used in this work consisted of an ultra-high vacuum system, the emission tube, and a reaction gas system. The reaction gas system and pressure measuring technique will be described in the next section.

The ultra-high vacuum system was all pyrex beyond the roughing pump, and was comprised of the following components connected in series: roughing pump; three-stage, oil diffusion pump; vacuum stop-cock with outlet to the atmosphere; steel-ball, pyrex-seat valve; zeolite trap; Bayard-Alpert ionization gauge (WL-5966); liquid nitrogen trap; ground-glass, seat valve (totally enclosed and containing a steel slug for manual operation with magnet); Veeco ionization gauge (RG-75) with thoriated filament; and titanium gettering tube. The last three of these components are represented schematically in Figure 1 and designated respectively by V, IG, and G.

The field emission tube was constructed of a 250-ml round-bottom pyrex flask and a four-lead press-seal as shown in Figure 1. The heating loop (HL) or tip support loop was spot welded to two of the four tungsten leads in order to provide a resistive heating circuit for the tip (T) and to serve as the external cathode connection. The remaining two leads in the press seal were used as potential sensing leads for monitoring the temperature of a small section of the heating loop extending about 1/16 inch on both sides of the tip. The anode consisted of a thin deposit of tin oxide with an external tungsten lead (A). A thin coating of calcium tungstate deposited over the anode from a nitrocellulose vehicle and
A - ANODE
G - GETTER
HL - HEATING LOOP
IG - IONIZATION GAUGE
L - LEAK VALVE
S - SCREEN
T - Emitter Tip
V - Glass Valve

FIGURE 1. DIAGRAM OF ULTRA HIGH VACUUM SECTION OF FIELD EMISSION SYSTEM
heated to 450° C served as the fluorescent screen (S). Reaction gases were admitted to the field emission tube through a 7 mm diameter pyrex tube leading from a Granville-Phillips leak valve (L).

The heating loop, potential leads, and tip were all made of the same metal in a particular experimental run, so as to eliminate likely sources of foreign matter (e.g., volatile oxides) during high temperature reactions. Potential leads were fabricated from 3 or 4 mil wire, the heating loops from 10 or 15 mil wire, and tips from 5 or 10 mil wire. Tungsten tips were etched in 1 n NaOH or KOH (carbonate-free) with a carbon electrode at several volts a.c. Best results for tantalum were obtained by oxidizing the wire for a few seconds in air at a temperature of about 1300° C prior to etching. Etching was carried out in a solution of concentrated H\textsubscript{2}SO\textsubscript{4} covered by a layer of 40% HF in a polyethylene container. Both platinum and tantalum were used for the second electrode, and etching was completed in several minutes with a potential difference of 5 to 10 volts d.c.

The vacuum technique employed after joining the emission tube to the vacuum system consisted of the following operations: initial pump-down, leak test, bake-out of entire system beyond ball valve to a temperature above 400° C for several hours, leak test, outgas all metal parts, deposit gettering material. This technique routinely produced vacua between 0.8 and 4 x 10\textsuperscript{-9} torr without the use of liquid nitrogen traps except for leak testing. These pressures were extremely stable over periods of days (and in one
instance two weeks) without attention. The above operations were carried out with all valves open and the inlet port to the Granville-Phillips valve sealed.

For electron emission, high positive voltage was applied to the screen (or anode) by a N.J.E. HP-5 power supply while maintaining the tip at ground. Applied voltages were measured with a potentiometer (L & N 8690) across a 5000 ohm (1%) resistor. The RCA WV-84C microammeter was used for emission current measurements. The accuracy specification for this instrument is ± 5%.

Tip heating was achieved by resistive heating of the support loop. For this purpose a twelve-volt storage battery was placed in series with the support loop and variable resistors. The potential drop across the 1/8-inch long section of the support loop was recorded continuously, and control was achieved manually.

Emission patterns were photographed with a Polaroid camera using the Polaroid close-up lens and 4000-speed film.

The temperature of the tip was determined from the potential drop across the sensing leads as follows. The electrical resistance of the section of the support loop between the leads was measured potentiometrically as a function of temperature as determined by an N.B.S.-calibrated optical pyrometer with close-up lens. Resistance values measured between room temperature and 800°C were assigned temperatures based on the known variation of resistivity with temperature(37,38). Optical pyrometer measurements were corrected for the emissivity of tungsten or tantalum according to the data given by DMIC(39). Corrections for absorption in the glass wall of the
emission tube were based on subsequent temperature measurements made with and without a portion of the emission tube wall in the path of vision. If evaporation films were not present on the emission tube wall, the correction due to absorption was apparently smaller than the uncertainty arising from visual color matching of the pyrometer filament and emitter tip. A final correction was applied to these temperatures in order to account for the temperature gradient between the heating loop and the end of the emission tip. This calculation has been made (40) for a tungsten tip containing an included angle of 1° and a length of 1/2 mm. The corrections reported were:

-2° at 900° C, -20° at 1700° C, and -86° at 2500° C. The corresponding corrections for tantalum tips (accounting for the difference in thermal conductivity of tungsten and tantalum) are: -1°, -15°, and -77°.

The probable error in temperature measurements arising from the use of the above data and the optical pyrometer may be evaluated in terms of individual uncertainties \(E_i\) due to:

a) pyrometer calibration at N.B.S. \(E_a\)
b) emissivity data \(E_b\)
c) radiation absorption \(E_c\)
d) visual color comparison \(E_d\)
e) gradient along tip \(E_e\).

Since these uncertainties are a function of temperature, Table 1 lists estimated values at two temperatures in the range of primary interest in this work. The probable error \(E_p\) is given by (41):

\[
E_p = \left( \sum_{i=1}^{\infty} E_i^2 \right)^{1/2}.
\]
### TABLE 1. ESTIMATED UNCERTAINTIES IN TEMPERATURE MEASUREMENT

<table>
<thead>
<tr>
<th>Individual Uncertainty</th>
<th>Value in °C at 900° C</th>
<th>Value in °C at 1700° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$</td>
<td>±4</td>
<td>±5</td>
</tr>
<tr>
<td>$E_b$</td>
<td>±10</td>
<td>±18</td>
</tr>
<tr>
<td>$E_c$</td>
<td>±5</td>
<td>±10</td>
</tr>
<tr>
<td>$E_d$</td>
<td>±5</td>
<td>±10</td>
</tr>
<tr>
<td>$E_e$</td>
<td>±1</td>
<td>±10</td>
</tr>
</tbody>
</table>
The probable errors at 900° C and 1700° C are then ± 13° C and ± 25° C, respectively.

B. Reaction Gas System and Pressure Measurement

It was apparent from the onset of this work that a number of well developed techniques were available for introducing reaction gases into ultra-high vacuum systems(42,43,44,45). The techniques which had been used to admit oxygen to field emission tubes included (a) diffusion through a heated silver membrane, (b) evaporation of oxygen condensed by immersing the entire (sealed-off) emission tube in liquid helium, (c) decomposition of heated copper oxide, and (d) effusion from a heated bead of oxygen-saturated silver. All of these techniques served conveniently to establish a stable oxygen pressure over relatively long periods of time in a static vacuum system.

Preliminary experiments in the present work, however, pointed to several difficulties inherent in the anticipated kinetic studies. For example, a stable oxygen pressure would be of use only if observations could be made during the course of the reaction. Such observations would be useful providing the high electric field necessary for imaging had a relatively small effect on the events taking place on the surface. Furthermore, at the anticipated high substrate temperatures thermal radiation could greatly exceed the emission from imaging electrons.
Initial experiments carried out with a static oxygen pressure and the constant electric field needed for continuous viewing indicated that drastic field-induced surface rearrangement occurred on substrates heated to 600° C and above (600° C is not necessarily the lower limit). Unusual build-ups on surfaces heated to elevated temperatures in the presence of high electric fields have also been observed by others (see Ref. 46 for example). The extent of this phenomenon seems strongly dependent upon substrate temperature.

In view of this difficulty, two courses of action became apparent. First, a pulsed electric field could be applied during the reaction, thus diminishing the field effects; or, the reaction could be interrupted at convenient intervals and the field applied after the substrate had been cooled and oxygen pressure reduced. While the latter technique appeared quite promising, the conventional methods for introducing oxygen into the emission tube did not offer the rapid response required.

Accordingly, it was decided to attempt the development of a molecular beam technique featuring rapid response. Several ideas were considered, the most promising of which were (a) the use of a Knudsen cell containing condensed oxygen and constructed as part of the emission tube, (b) the incorporation of an oxygen-saturated silver bead with external heating leads in a side arm connected to the emission tube, and (c) the connection of a mechanical leak valve to the emission tube for admission of oxygen from an external
reservoir. Rapid response was to be achieved by operating the vacuum system in a dynamic way (i.e., an "open" system through the pumps).

The initial efforts involved the use of a pyrex side arm (22 mm tubing about 6 inches long) containing an oxygen-saturated silver bead on a platinum heating loop. The side arm was connected to the emission tube by a short length of 1 mm capillary tubing aligned with its axis intercepting the emission tip. The silver bead was positioned so that an optical path did not exist between it and the tip. During operation, the side arm was submerged in liquid nitrogen. These experiments established the beam nature of the oxygen leak, the rapid response of the technique (due to the large pressure gradient within the system), and the limited capacity of silver beads saturated with oxygen before bakeout.

In order to remedy this latter difficulty, the side arm was replaced by a Granville-Phillips valve (9100 Series) connected to a tank of research-grade oxygen through copper tubing. A mechanical vacuum pump and a zeolite trap were connected to the copper tubing with an all-metal needle valve in order to provide a means of flushing the line after the initial connection was made. During experimental runs, the oxygen was leaked through the Granville-Phillips valve from a line pressure of about 3 psig.

Despite the many conveniences associated with this beam technique, the primary difficulty lies in determining the oxygen pressure at the tip. The tip itself is exposed to a flux gradient
resulting from its geometry, and a large pressure gradient exists between the tip and the ionization gauge.

The flux gradients existing over the tip surface are due to (a) the effusion distribution from the inlet and (b) the shape of the tip itself. The second of these factors gives rise to a shadowing effect on the side of the tip not facing the beam. The shadowing effect is observable in the emission patterns of reactions carried out with tungsten tips at temperatures below room temperature and with tantalum tips at temperatures below about 250° C. In fact, only reactions carried out below these temperatures show visible evidence in the emission patterns of either of the above flux gradients. This means that either surface diffusion obviates the effects of the gradients on surface reactions at the higher temperatures, or that the surface reactions are insensitive to the gradients. The evidence to be presented in this paper will support the former interpretation.

It is necessary, however, to establish the relation between measured pressure at the ionization gauge, $P_g$, and the oxygen pressure equivalence of the flux in the vicinity of the tip, $P_{O_2}$. This may be accomplished by comparing emission patterns obtained as a function of time at constant substrate temperature and constant oxygen flux using the Granville-Phillips (G-P) valve technique with emission patterns resulting from the reaction taking place when the pressure of the entire vacuum system is raised by the addition of oxygen.
through the vacuum stopcock while the system is closed to the pumps through the ball and glass valves. That is, two sets of experiments are required—dynamic and static. In the static experiments it is presumed that pressure gradients do not exist, and hence $P_g$ after being corrected for the gauge sensitivity (47) to oxygen, $P_{g_0}$, will be identical to $P_{02}$. In this connection, it should be noted that only ionization gauges employing relatively low filament temperatures (such as the RG-75 with a thoria-coated iridium filament as used in this work) can be used in oxygen without appreciable production of foreign gases (48,49). On the other hand, $P_{g_c}$ will differ from $P_{02}$ in the dynamic experiments by a factor $n$, which is itself a function of $P_{g_c}$. The problem of pressure determination is then one of determining $n$.

Two types of reactions need to be considered. Let Type I be a reaction characterized by rate control due to mass transport of the oxygen, but otherwise not dependent upon oxygen pressure over a significant range of pressure. If this reaction is allowed to proceed to the same extent in both the dynamic and static experiments (as identified by emission patterns), then the accumulation of oxygen in both experiments will have been the same. It follows that the product of flux and time (or the pressure equivalence of the flux and time) will be equal for both experiments, i.e.,

$$P_{02} \Delta t' = P_{02} \Delta t = n P_g \Delta t$$

(2)

where the primed quantities refer to the static experiment and unprimed quantities, to the dynamic experiment. $\Delta t$ is the length of
time of the reaction (say, beginning with a clean substrate), and 
n contains the correction for gauge sensitivity to oxygen. For 
Type I reactions, equation (2) demands only that the products of the 
$p_{02}$ and $\Delta t$ terms be equal. In this case one measures $p_{02}'$, $\Delta t'$, $p_g$, 
and $\Delta t$; and calculates $n$.

The second type of reaction, Type II, may be characterized 
by rate control due to mass transport of oxygen as in Type I, but in 
addition the reaction product is in some identifiable way dependent 
upon pressure. In this case, Equation (1) is applicable if $p_{02}'$ is 
identical to $p_{02}$, and $\Delta t'$ is identical to $\Delta t$. A relatively greater 
experimental effort is required for this type of reaction since one 
cannot a priori select $p_{02}'$ and $p_g$ such that $\Delta t'$ and $\Delta t$ are equal.

For both tungsten and tantalum substrates at temperatures 
under $\sim 900^\circ C$ and oxygen pressures under $10^{-4}$ torr, it will become 
apparent that the initial reactions are of Type II. Since $n$ depends 
primarily on the geometry of the emission tube assembly, it must be 
redetermined each time a tip is replaced or a new emission tube is 
constructed. Typical values of $n$ are given in Table 2. The major 
uncertainty associated with such values of $n$ is the result of an 
uncertainty in the determination of $p_{02}'$. Since the estimated un-
certainty in $p_{02}'$ is about plus or minus 50%, the estimated uncertainty 
in $n$ is likewise plus or minus 50%. This uncertainty increases 
greatly for $p_g < 7 \times 10^{-9}$ torr.
TABLE 2. TYPICAL VALUES OF $n$
(Residual gas pressure: $2 \times 10^{-9}$ torr)

<table>
<thead>
<tr>
<th>$P_g$ (torr)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$7 \times 10^{-9}$</td>
<td>70</td>
</tr>
<tr>
<td>$5 \times 10^{-8}$</td>
<td>30</td>
</tr>
<tr>
<td>$5 \times 10^{-7}$</td>
<td>8</td>
</tr>
<tr>
<td>$5 \times 10^{-6}$</td>
<td>8</td>
</tr>
</tbody>
</table>

C. Reaction Materials

The substrate (emitter tip) was fabricated from either G.E. 218 tungsten or National Research Corporation tantalum wire. Typical chemical analyses are given in Table 3.

Mathieson research-grade oxygen was used as the reaction gas. A typical analysis in parts per million is $N_2 < 400$, $A < 100$, $H_2 < 50$, $CO_2 < 10$, $CO < 10$, $NO < 1$, dew point of $-100^\circ F$, and remainder oxygen.
TABLE 3. TYPICAL CHEMICAL ANALYSES OF SUBSTRATE MATERIALS IN PARTS PER MILLION OF IMPURITY

<table>
<thead>
<tr>
<th>Tungsten (50)</th>
<th>Tantalum (51)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe, 20</td>
<td>Fe, 40</td>
</tr>
<tr>
<td>Mo, 40</td>
<td>Cr, 20</td>
</tr>
<tr>
<td>C, 60</td>
<td>Ni, 30</td>
</tr>
<tr>
<td>Other individual metallics &lt; 10</td>
<td>Nb, 50</td>
</tr>
<tr>
<td>Total all impurities &lt; 500</td>
<td>O₂, &lt; 100</td>
</tr>
<tr>
<td></td>
<td>C, &lt; 100</td>
</tr>
<tr>
<td></td>
<td>H₂, &lt; 100</td>
</tr>
<tr>
<td></td>
<td>N₂, &lt; 100</td>
</tr>
<tr>
<td></td>
<td>Total others  &lt; 60</td>
</tr>
</tbody>
</table>
D. Operational Scheme

After completing the preliminary substrate temperature and oxygen pressure calibrations, oxygen-substrate reactions were carried out and studied in the following manner (the listing is chronological).

1) The substrate was cleaned by heating to temperatures above 2000°C until the characteristic clean emission pattern\(^{52,53}\) was obtained and photographed.

2) Emission current and applied voltage measurements were made at room temperature or below; and the applied voltage turned off.

3) Simultaneously the substrate was heated to the reaction temperature and oxygen was admitted at the pressure of interest. Both pressure and temperature were recorded by strip recorders operated at a speed of one-fifth of an inch per minute.

4) After the reaction had proceeded for the desired length of time, the substrate was cooled to room temperature or below and the oxygen beam turned off simultaneously.

5) The emission voltage was now applied and the resulting pattern photographed. The applied voltage and emission current were measured, and the voltage turned off.

6) Steps 3, 4, and 5 were repeated until further changes in the emission patterns could not be detected.
Subsidiary experiments starting with the cleaned substrate were necessary in order to ascertain the effect of heating or cooling and oxygen pressure change during Steps 3 and 4 (i.e., end effects) and residual gases during Step 5. The over-all effect of interrupting a given reaction for observation and photography was so small it could not be detected if the background or residual gas pressure was under $5 \times 10^{-9}$ torr, the time required to carry out Step 5 was on the order of a minute, and the substrate was not cooled below ambient temperature. For example, consider a reaction beginning with a clean substrate divided into three time intervals $\Delta t_1$, $\Delta t_2$, and $\Delta t_3$ such that the substrate temperature, $T$ and oxygen pressure, $P$ are constant during each interval. Furthermore, let $P_r$ be the residual gas pressure and $T_a$ be the ambient temperature or unheated substrate temperature. If during $\Delta t_1$, $T = T_1$ and $P = P_1$; during $\Delta t_2$, $T = T_a$ and $P = P_r$; and during $\Delta t_3$, $T = T_1$, and $P = P_1$ (where $\frac{P_1}{P_r} > 10$ and $T_1 > T_a$), this composite reaction is found to be equivalent to a single reaction of $\Delta t = \Delta t_1 + \Delta t_3$, $T = T_1$, and $P = P_1$ providing $P_r < 5 \times 10^{-9}$ torr and $\Delta t_2 \approx$ one minute. In this example, $\Delta t_2$ corresponds to Step 5.

The observed relative insensitivity of the reactions to interruptions permits the use of composite data obtained from consecutive time intervals at constant oxygen pressure and substrate temperature to represent the course of the oxygen-substrate reaction as a function of the accumulated time at elevated substrate temperature and oxygen pressure.
III. RESULTS AND DISCUSSION

A. Introduction

One of the conveniences inherent in the field emission technique is the relative ease with which a reproducible atomically clean substrate can be obtained on refractory metals. Figure 2 shows the emission patterns for clean tungsten and tantalum respectively as established by this work and many previous investigations (24,25). The patterns in Figure 2 are oriented to coincide with the orthographic projection of crystallographic poles occurring on a [110] oriented b.c.c. single crystal. The identification of two symmetry elements permits the indexing of all other positions. The planes which are predominant in the field emission patterns (i.e., the more densely packed low-index planes) are designated by the filled-in symbols on the orthographic projection.

In contrast to the "clean patterns" given in Figure 2 which exhibit a relatively gradual variation in emission intensity from region to region, the patterns of rather heavily oxidized tungsten and tantalum substrates are given in Figure 3. These patterns resulted from an exposure of several minutes to oxygen pressures at the upper limit of the present experimental technique (about 5 x 10^{-5} torr). The reactions were carried out on initially clean substrates heated to 800° C. A significant feature of these patterns is the existence of highly localized discontinuities in emission intensity characteristic
FIGURE 2. COMPARISON OF EMISSION PATTERNS FROM CLEAN TUNGSTEN (UPPER LEFT) AND TANTALUM (LOWER LEFT) SINGLE CRYSTAL EMITTER-SUBSTRATES AND THE STANDARD $[110]$ CUBIC PROJECTION.
Magnification is 120,000 and 100,000 respectively.
FIGURE 3. EMISSION PATTERNS FROM HIGHLY OXIDIZED TANTALUM (LEFT) AND TUNGSTEN (RIGHT) SUBSTRATES
Both substrates had been exposed to oxygen at ~10^{-5} torr for several minutes. Substrate temperature (T_s) was 800° C in both cases. Magnification is 60,000 X for tantalum and 80,000 X for tungsten.
of most crystallographic regions* on the substrate. Tungsten tips exposed to oxygen in the field ion microscope at the same pressure and substrate temperature have been found to contain (upon stripping the surface layers by high field evaporation) a multitude of pits extending to about 20 Å deep(52). The pits were not characteristic of adsorption reactions (i.e., did not appear in lower pressure reactions) and were, therefore, assumed to result from preferential evaporation of oxide microcrystallites extending into the substrate.

Other field emission studies have revealed highly localized discontinuities in emission intensity after reactions have taken place on the substrate which could lead to the formation of microcrystals(53,54,55,56,23,25). Such microcrystals function as individual emitters, and as a result of their small radius of curvature, give rise to the well-known field enhancement effect.

Interpretation of emission patterns is complicated, however, since other kinds of reactions on the substrate may also lead to a degree of discontinuous emission intensity (usually less sharply defined though) and patterns exhibiting a "mottled" appearance(57,58,59,60,25). We shall encounter examples of this mottling in the present work even at substrate temperatures around 30°C (a temperature at which presumably only adsorption takes place).

A rather simple solution has been suggested for the above paradox(23) related to adsorption, desorption, and oxidation. Discontinuities in emission intensity as a result of field enhancement

*The discontinuous nature of emission intensity in the bright {111} regions on tungsten is only partially visible in the photograph due to the extremely high emission level of these regions.
accompanying desorption should disappear upon increasing the gas supply function to the substrate, while a similar result should not necessarily be observed if the discontinuities result from microcrystals on the surface. In the above experiments adsorption of oxygen led to an increase in average work function of the substrate while field enhancement resulting from oxidation had the reverse effect. Thus, differentiation between the adsorbed and oxidized state was possible. Since these experiments generally involved the exposure of the substrate to oxygen at substrate temperatures of 30° C or below and then heating such an "oxygenated" substrate to higher temperatures in the absence of gas phase oxygen. Simultaneous adsorption effects were usually not present.

In the experiments of the present work, however, all three surface processes (adsorption, desorption, and oxidation) take place simultaneously under the majority of experimental conditions imposed, and thus differentiation between the three becomes more complex. We shall see in the following sections that field enhancement arises in some crystallographic regions of the substrate while simultaneous adsorption in other regions prevents a net decrease in average work function. This means that an average work function criterion for the existence of microcrystals on the surface is usually ambiguous and difficult to use.

Nevertheless, it will be possible to distinguish between oxidation (crystallite formation) and desorption and/or adsorption on
the basis of thermal stability of the surface product. Surfaces or crystallographic regions giving rise to the "mottled" emission will be found to lose the mottling features very rapidly upon heating in the absence of gas phase oxygen*, and in most cases regain the mottled appearance after re-exposure to gaseous oxygen. However, sharply defined discontinuities in emission intensity such as exist in Figure 3 are generally stable during prolonged heating in the absence of gas phase oxygen. And re-exposure to gaseous oxygen seems not to alter the appearance of these regions. In both of the above circumstances we refer to "isothermal" reactions. (They are isothermal in the sense that the temperature of the substrate is held constant except during the period of viewing.)

This basis for differentiation between the part processes of adsorption, desorption, and oxidation (or microcrystal formation) is thus largely visual, but requires subsidiary experiments and heat treatments. In the discussion that follows, the terms "mottled" and "adsorbed state" will be used interchangeably, with the former term referring to the emission pattern and the latter to the corresponding substrate. Likewise, the terms "highly localized discontinuities in emission intensity" (or "highly localized enhancement") and "oxide microcrystals" will be used synonymously, referring respectively to the emission pattern and the corresponding substrate.

*Examples of these features along with further discussion will be given in the next section, e.g., Figures 4 and 5.
Finally, it should be noted that the analysis of a given state of the substrate usually requires viewing the emission pattern at various emission current levels. The photographs to be presented in the following, however, will correspond to a single emission current level for all patterns in a sequence (except when otherwise noted), and will demonstrate primarily the gross features of the crystallographic distribution of emission.

B. Tungsten-Oxygen Reactions

Although the interaction of oxygen on substrates at low temperatures has been studied by others (see INTRODUCTION) several low temperature experiments will be discussed for comparative purposes.

Figure 4 gives a sequence of patterns resulting from oxygen being adsorbed on the initially clean tungsten substrate at room temperature. Note the relatively rapid darkening (i.e., increase in work function) of the regions between the \( [110] \) and \( [211] \) poles after just one minute of reaction. Mottling effects are apparent in the patterns shown for reaction times of six minutes and longer. And finally, the last two patterns in this sequence show that a saturated state is being approached. It has been shown that this state is relatively insensitive to oxygen pressure over the range of pressures to be employed in the present work. Flash filament work and desorption experiments\((18,19,20,21)\) indicate that this saturated state corresponds approximately to the two most tightly bound chemisorbed layers thought
FIGURE 4. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR SUBSTRATE TEMPERATURE \( (T_s) \) OF 30°C AND OXYGEN PRESSURE \( (P_{O_2}) \) OF \( 7 \times 10^{-8} \) TORR

Symbols (below) representing reaction time at temperature \( (t \text{ in minutes}) \) and applied voltage \( (V \text{ in K volts}) \) are in positions corresponding to patterns above. \( 100,000 \times \)

- \( t = 0, \ V = 5.0 \)
- \( t = 11, \ V = 7.2 \)
- \( t = 1, \ V = 5.4 \)
- \( t = 16, \ V = 7.6 \)
- \( t = 6, \ V = 6.6 \)
- \( t = 31, \ V = 7.7 \)
to exist on W. The desorption experiments have involved heating the saturated substrate to higher temperatures in the absence of gaseous oxygen. Some resulting patterns are given in Figure 5 for successive heatings of two minutes each at increasing temperatures. The first two patterns in Figure 5 are associated with the most tightly bound chemisorbed layer. Above 1000° C only a portion of this layer is stable on the substrate. Near 1800° C and above, only a very small fraction of this layer yet exists, and finally the clean substrate is observed after heating to about 2000° C. Note the disappearance of the mottling so pronounced in Figure 4.

Returning again to gaseous oxygen-substrate reactions, little change is noticed in the course of reaction at higher substrate temperatures up to about 500° C. Figure 6 shows the sequence of emission pattern changes associated with the reaction at 400° C. Note the similarity to Figure 4. The saturated state of Figure 6 is similar enough to that obtained at room temperature, that the same desorption patterns result upon heating to higher temperatures in the absence of gaseous oxygen.

For substrate temperatures above 500° C, the gaseous O₂-substrate reaction changes markedly. Figures 7 and 8 (excluding the last pattern in Figure 8) show the reaction path for a substrate temperature of 600° C and O₂ pressures of 2 x 10⁻⁶ and 2 x 10⁻⁵ torr, respectively. Although localized emission discontinuities are not apparent in the pattern corresponding to the "saturated state" of
FIGURE 5. DESORPTION OF SATURATED STATE OF FIGURE 4

The saturated state in this instance corresponded to an applied voltage of 7.3 K volts. 80,000 X

plus 2 min. at 800° C
(V = 6.5)

plus 2 min. at 1000° C
(V = 6.4)

plus 2 min. at 1200° C
(V = 5.8)

plus 2 min. at 1400° C
(V = 5.1)
FIGURE 6. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_s = 400^\circ \text{C}$, $P_{O_2} = 7 \times 10^{-8} \text{ TORR}$

$100,000 \times$

$t = 0, V = 5.0$  $t = 10, V = 6.8$  $t = 20, V = 7.5$

$t = 30, V = 7.8$  $t = 40, V = 7.9$
FIGURE 7. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_0 = 600^\circ$ C, $P_{O_2} = 8 \times 10^{-6}$ TORR 90,000 X

$t = 0, V = 5.3$  
$t = 0.25, V = 6.8$  
$t = 2.5, V = 7.9$  
$t = 10, V = 7.9$
FIGURE 8. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_g = 600^\circ$ C,
$P_{O_2} = 2 \times 10^{-5}$ TORR; AND EFFECT OF SUBSEQUENT
INCREASE IN $T_g$ IN ABSENCE OF GASEOUS OXYGEN
90,000 X

$t = 0, \ V = 4.7$

$t = 22, \ V = 9.6$

$t = 0.5, \ V = 6.3$

plus 7.5 minutes at
$T_g = 900^\circ$ C, $V = 9.0$
Figure 7, they start to emerge at higher pressures in the \{111\} region as shown in Figure 8 after 22 minutes. A rather interesting result is noticed if the apparently "saturated state" of Figure 8 is heated to a higher temperature in the absence of gaseous oxygen. Highly localized discontinuities in emission intensity become noticeable on substrate regions which were previously devoid of appreciable emission (e.g., \{100\} regions). The last photo in Figure 8 is an example of this behavior. This pattern was obtained after heating the substrate for an additional 7.5 minutes at 900° C in the absence of gaseous oxygen and remained virtually unchanged after 5 additional minutes at 900° C. The distribution of discontinuities in emission intensity (resulting from microcrystals in this case in view of the high temperature stability) will be seen to resemble the distribution obtained by oxidizing at 900° C to 1000° C in the presence of gas phase oxygen. This rather curious result might be associated in some way with the transformation of WO$_3$ around 750° C, except that similar results are also obtained when substrates saturated at 500° C are heated to temperatures below 700° C in the absence of gas-phase oxygen.

Returning again to gas-phase reactions, one notices only slight changes in the course of events as initially clean substrates are reacted at somewhat higher temperatures. As an example, the reaction on tungsten at 700° C and oxygen at 10$^{-5}$ torr is shown in Figure 9. Highly localized enhancement becomes a bit more pronounced in the \{111\} regions than was observed in Figure 8 but the effect
FIGURE 9. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_g = 700^\circ$ C,
$P_{O_2} = 1 \times 10^{-5}$ TORR  85,000 X

$t = 0, V = 6.5$  
$t = 1, V = 8.8$  
$t = 0.3, V = 8.6$  
$t = 2, V = 8.9$
is not large. The state of the surface given in the last photograph in Figure 9 remains apparently unaltered even after continuing the reaction for more than 30 additional minutes.

A graphical view of the general differences in the rates of reaction at 600° and 700° C for several low pressures which did not produce oxide microcrystals is given in Figures 10 and 11, in which the fractional increase in applied voltage to yield a constant emission current, $V$, is plotted as a function of time. In these figures $V_i$ is the initial voltage. Note that the general shape of the curves indicate a decreasing rate of approach to equilibrium as a function of time. Subject to the limitations inherent in assuming a proportionality between work function changes, or applied voltage changes, and coverage(61,62), the curves suggest an approach to equilibrium according to the solution of the rate expression giving the net rate of accumulation on the surface as equal to the impingement rate minus the desorption rate (since bulk diffusion into tungsten is known to be small):

$$\frac{dC}{dt} = I - C \nu_d \exp\left(-\frac{\Delta G_d'}{kT}\right)$$

(3)

where $C$ is the surface concentration, $I$ the impingement flux, $\nu_d$ the vibrational frequency of adsorbed atoms normal to the substrate, and $\Delta G_d'$ the corresponding activational free energy for desorption. Since the solution to (3) is given by

$$\frac{C}{C_0} = 1 - e^{-\beta t}$$

(4)
FIGURE 10. FRACTIONAL INCREASE IN APPLIED VOLTAGE VS. TIME (FOR NON-OXIDIZING CONDITIONS AND $T = 600^\circ$C)
Oxygen pressures are given for each curve.
Figure 11. Fractional increase in applied voltage vs. time (for non-oxidizing conditions and $T_s = 700^\circ$ C).
Oxygen pressures are given for each curve.
where $C_o$ is the equilibrium value and $\beta$ the desorption probability term in (3), $\Delta G_d^i$ can be estimated from the data in Figures 10 and 11. With the assumption that

$$\frac{C}{C_o} = \left( \frac{\Delta V}{V_i} \right) / \left( \frac{\Delta V}{V_i} \right)_{\text{max}}, \tag{5}$$

then

$$e^{-\beta t} = 1 - \left( \frac{\Delta V}{V_i} \right) / \left( \frac{\Delta V}{V_i} \right)_{\text{max}}. \tag{6}$$

If the log of the right side of Equation 6 is plotted versus $t$ and $V_d$ taken as $10^{12}$, $\Delta G_d^i$ is calculated from the slope to be 60 (± 10%) kcal/mole.*

One notes that the activational energies for desorption determined by heating an "oxygenated" tungsten substrate in the absence of appreciable gas-phase oxygen lie in the range of 130 to 120 kcal/mole(63). If activational entropies are not responsible for this discrepancy, different states of binding may be involved (i.e., higher coverages may exist in the present experiments).

Figures 10 and 11 also demonstrate a more rapid approach to "equilibrium" as pressure is increased at constant temperature and the higher coverages obtained at lower temperature under constant pressure.

Another difference between reactions on substrates at 600° and 700° C is that somewhat lower oxygen pressures are required to

*Only the data up to about 90% of the apparent completion have been used in this calculation since uncertainties in $\Delta V$ become influential beyond this level.
initiate the formation of microcrystals on the surface at $700^\circ$ C. This effect becomes even more pronounced as reaction temperature increases.

Figures 12 and 13 are representative of the reaction path on substrates at $800^\circ$ C. With oxygen at the lower pressure shown ($9 \times 10^{-8}$ torr), oxidation is seen to commence after about five minutes and is most pronounced in the \{111\} regions. This pressure, however, is over one order of magnitude lower than the apparent minimum pressure required for oxidation at $700^\circ$ C.

As pressure is increased, Figure 13, the adsorption stages (or incubation time for oxide nucleation) becomes so short that oxide microcrystals are apparent after reacting for only a half minute. As the reaction proceeds, new microcrystals appear (particularly in the \{100\} regions) and one can actually measure this rate of appearance. The final state of the surface shown in this sequence after a reaction of 60 minutes is similar to that of Figure 3 ($P_{O_2} = 1 \times 10^{-5}$ torr) with the exception of the one highly emitting single spot in the \{110\} region.

Spots such as the one in Figure 3 are frequently encountered in the 750-1000$^\circ$ C temperature range when oxygen pressures are above $\sim 5 \times 10^{-6}$ torr. The intensity of the individual spot relative to other regions of the substrate often increases rapidly as a function of reaction time—a phenomenon related to whisker-like growth(53,54).
FIGURE 12. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_s = 800^\circ$ C,
$P_{O_2} = 9 \times 10^{-8}$ TORR 100,000 X

$t = 0, V = 5.3$

$t = 0.5, V = 6.0$

$t = 5, V = 7.9$

$t = 15, V = 8.1$
FIGURE 13. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_s = 800^\circ$ C,
$P_{O_2} = 1 \times 10^{-6}$ TORR 100,000 X

$t = 0$, $V = 5.3$  
$t = 0.5$, $V = 8.7$  
$t = 2.5$, $V = 9.6$  
$t = 60$, $V = 9.4$
away from the substrate. As such growth takes place, the effectiveness of the substrate in decreasing the field at the extended tip is decreased. Increasing relative emission results. Despite the phenomenal strength that these whiskers apparently possess in order to withstand the extremely high field stress, rupture frequently occurs as the whisker is broken or pulled off the substrate. Often, this is accompanied by loss of the substrate emitter tip itself. The above behavior in high pressure reactions, in effect, has limited many reactions to rather short times (i.e., much shorter than desired).

The rather curious lack of highly localized enhancement in certain regions (primarily \{110\} in this instance) is at present, only partially understood. The several possibilities are that—

1) oxide is not present in these regions;

2) the oxide structure is such that the emission is at a very much lower level than in other regions; and

3) the nucleation or growth characteristics favor relatively low emission.

In view of the nearly metallic electrical conductivity of the tungsten oxides(64), the known low oxygen adsorption capacity of the \{110\} region, and the almost negligible density of pits found in this region in the field ion microscope examinations mentioned earlier(52), the first possibility seems very likely.
One should understand that the great difference in the relative amount of current coming from two regions showing enhancement (e.g., \(\{111\}\) and \(\{100\}\)) may not bear at all on the relative coverage.

Figure 14 gives the fractional voltage increment as a function of time. Even though the lower pressure curves resemble those obtained at 600° and 700° C, since substantial enhancement is present even during the earliest measurement, analysis is rather futile. Note that the curve for the highest pressure not only seems to exhibit a peak, but behaves rather erratically.

As substrate temperature is increased above about 850° C, the extent of the regions exhibiting discontinuities in emission is found to decrease for a given pressure. Figures 15, 16, and 17 give the patterns for isothermal reactions at substrate temperatures of 900° C. The emitter in this particular run contained two tips.

The apparent extent of the oxidized regions decrease even more as substrate temperatures are increased (Figures 18, 19, 20, 21). Finally for substrate temperatures in the 1400° C range, localized enhancement cannot be detected even for reactions employing the highest pressures (\(\sim 5 \times 10^{-5}\) torr). This corresponds to the temperature range in which \(\text{WO}_3\) undergoes melting.

As substrate temperatures are increased even further, the emission patterns, devoid of localized enhancement even at highest pressures, resemble those obtained from surfaces undergoing desorption in the absence of gas phase oxygen(23,25), i.e., oxide microcrystals cannot be detected.
Field enhancement was observed in all patterns. (Oxygen pressures are given for each curve.)
FIGURE 15. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_b = 900^\circ$ C,
$P_{O_2} = 5 \times 10^{-7}$ TORR 90,000 X

$t = 0, V = 7.1$
$t = 5, V = 10.9$
$t = 1.5, V = 10.4$
$t = 10, V = 10.0$
FIGURE 16. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_g = 900^\circ$ C, $P_{O_2} = 2 \times 10^{-6}$ TORR 90,000 X

$t = 0, \, V = 7.0$

$t = 20, \, V = 9.6$

$t = 2.5, \, V = 10.3$

$t = 60, \, V = 9.5$
FIGURE 17. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_s = 900^\circ$ C, $P_{O_2} = 2 \times 10^{-5}$ TORR 90,000 X

$t = 0, V = 7.0$  
$t = 3, V = 9.3$  
$t = 5, V = 8.8$  
$t = 1, V = 10.1$
FIGURE 18. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_e = 1000^\circ$ C, $P_{O_2} = 1 \times 10^{-7}$ TORR  90,000 X

$t = 0, V = 5.5$

$t = 1.5, V = 6.7$

$t = 4.5, V = 6.6$

$t = 5.5, V = 6.6$
FIGURE 19. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_s = 1000^\circ$ C,
$P_{O_2} = 2 \times 10^{-6}$ TORR  90,000 X

- $t = 0, V = 5.5$
- $t = 4.5, V = 6.5$
- $t = 0.5, V = 6.5$
- $t = 20, V = 6.3$
FIGURE 20. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_b = 1200^\circ\text{C}$,
$P_{O_2} = 5 \times 10^{-7}$ TORR  90,000 X

$t = 0, V = 5.3$  
$t = 2.5, V = 6.3$

$t = 1, V = 6.5$  
$t = 7.5, V = 6.3$
FIGURE 21. TUNGSTEN-OXYGEN REACTION SEQUENCE FOR $T_s = 1200^\circ$ C, $P_{O_2} = 1 \times 10^{-5}$ TORR  90,000 X

$t = 0, V = 5.2$

$t = 2, V = 6.4$

$t = 1, V = 6.4$

$t = 6, V = 6.2$
C. Tantalum-Oxygen Reactions

In contrast to the tungsten reactions with substrates near room temperature, oxygen on tantalum at these temperatures exhibited shadowing effects due to preferential oxygen adsorption on the side of the emitter closest to the oxygen source. An example is given in Figure 22 for the substrate at 200°C with the beam source at a 6 o'clock position. The second photograph in this sequence, corresponding to a 10-minute exposure to oxygen at $1 \times 10^{-7}$ torr, is without enhancement effects. The remaining patterns were obtained after heating this tip for 1 and 3 minutes, respectively, to 400°C in the absence of gas phase oxygen. The heterogeneous nature of the surface diffusion process is clearly evident. Note the relatively rapid emission deactivation in the $\{211\}$ regions due to more rapid diffusion (and hence adsorption) through these paths.

The beam effect continues to be noticeable (although to a lesser degree) until substrate temperatures in the range of 450°C are reached. Although mottling is pronounced in the patterns obtained for reactions with substrates below 500°C, oxidation effects cannot be detected. Such a reaction sequence for the substrate at 450°C is given in Figure 23 (excluding the last photograph). Mottling is noticeable throughout the entire reaction (of which the two-minute and ten-minute patterns are shown). In this instance the average work function of the emitter became so large that the available applied voltage was not sufficient to maintain the emission current level.
FIGURE 22. TANTALUM-OXYGEN REACTION SEQUENCE FOR $T_s = 200^\circ C$, $P_{O_2} = 1 \times 10^{-7}$ TORR; AND EFFECTS OF SUBSEQUENT HEATING TO $T_s = 400^\circ C$ IN ABSENCE OF GASEOUS OXYGEN 60,000 X

$t = 0, V = 7.9$

$t = 10 (T_s = 200^\circ C)$
$V = 8.5$

plus 1 min. at $T_s = 400^\circ C$
$V = 8.3$

plus 2 min. at $T_s = 400^\circ C$
$V = 11.7$
FIGURE 23. TANTALUM-OXYGEN REACTION SEQUENCE FOR $T_s = 450^\circ \text{C}$, $P_{O_2} = 1 \times 10^{-7}$ TORR; AND EFFECT OF HEATING TO $T_s = 700^\circ \text{C}$ IN ABSENCE OF GASEOUS OXYGEN 40,000 X

$t = 0, V = 10.4$

$t = 10, V = 21.1$

$t = 2, V = 18.0$

plus 3 additional minutes at $700^\circ \text{C}$,
$V = 9.6$
corresponding to the clean pattern (i.e., constant current is not maintained throughout the sequence of photographs given). Since reaction times up to 30 minutes do not produce detectable changes in emission from that resulting after a ten-minute reaction, the pattern obtained after a ten-minute exposure corresponds to a saturated state.

Curiously enough, however, if such a stable configuration is heated for several minutes into the 600° to 800° C temperature range in the absence of appreciable gas-phase oxygen, great numbers of oxide microcrystals appear (primarily in \{\text{\text{\{111\}}}\} region). This is shown in the last pattern of Figure 23. Note the highly localized enhancement in the \{\text{\text{\{111\}}}\} regions. The microcrystallites are apparently quite refractory and stable, as their appearance and distribution remains essentially unaltered upon continued heating at 700° C for 10 to 20 minutes. Furthermore, this reaction is not reversible with respect to re-exposure to gas-phase oxygen at the initial pressure and substrate temperature. And as we will see, the distribution of oxide microcrystals resembles that resulting from completely isothermal oxidation in the presence of gas-phase oxygen at substrate temperatures of 700° to 800° C.

The interesting feature of this set of events involves an apparent inability to form oxide at lower substrate temperatures in the presence of gaseous oxygen, and the subsequent oxidation if the substrate temperature is raised in the absence of additional oxygen. Note that this same behavior was observed in the tungsten reactions.
Typical gas-substrate reactions at more elevated temperatures are given in Figures 24 and 25 (for \(T_s = 600^\circ C\)), Figures 26 and 27 (for \(T_s = 800^\circ C\)), Figure 28 (for \(T_s = 900^\circ C\)), Figures 29 and 30 (for \(T_s = 1000^\circ C\)), and Figure 31 (for \(T_s = 1200^\circ C\)).

An unfortunate operating difficulty presented itself, however, with most tantalum emitters which had been exposed to oxygen. Emission current stability was very poor during the first minutes of emission—even at liquid nitrogen temperature. It was therefore necessary (in order that contamination by residual gases be held to a reasonable low level during viewing) to photograph the emission patterns and proceed with the reaction rather than wait for stability. Since the nature of the instability seemed to depend on the extent of tip exposure, reliable characterization of the instability was not achieved. The above difficulty rendered futile all attempts to obtain reproducible fractional voltage-time curves.

The general characteristics of the oxidation reaction on tungsten are also apparent on tantalum. At low pressures oxide microcrystals are not observed (Figure 24) even after reaction times of the order of one hour. At increased pressure the surface apparently passes through the adsorbed stages of the lower pressure reactions and eventually forms stable microcrystallites (Figure 25, \(t = 10\) and \(t = 20\)). The most noticeable field enhancement appears in the extensive regions surrounding \{111\}.

As substrate temperatures increase the oxide distribution changes somewhat as shown in Figures 27, 28 and 30, but exhibits an
FIGURE 24. TANTALUM-OXYGEN REACTION SEQUENCE FOR \( T_b = 600^\circ\) C, 
\( P_{O_2} = 1 \times 10^{-6}\) TORR  60,000 X

\[ \begin{align*}
  t = 0, \ V = 8.0 & \quad t = 1, \ V = 8.3 \\
  t = 7.5, \ V = 9.1 & \quad t = 12.5, \ V = 9.5
\end{align*} \]
FIGURE 25. TANTALUM-OXYGEN REACTION SEQUENCE FOR $T = 600^\circ$ C, $P_{O_2} = 1 \times 10^{-5}$ TORR 60,000 X

$t = 0, V = 8.0$
$t = 10, V = 10.8$
$t = 1.5, V = 9.7$
$t = 20, V = 12.4$
FIGURE 26. TANTALUM-OXYGEN REACTION SEQUENCE FOR $T_s = 800^\circ C$, $P_{O_2} = 1 \times 10^{-7}$ TORR 60,000 X

$t = 0, V = 8.4$

$t = 7.5, V = 8.9$

$t = 17.5, V = 9.5$

$t = 27.5, V = 9.5$
Figure 27. Tantalum-oxygen reaction sequence for $T_s = 800^\circ C$, $P_{O_2} = 1 \times 10^{-7}$ Torr, 60,000 x

$t = 0, V = 9.1$  \hspace{1cm} $t = 5, V = 11.0$

$t = 10, V = 11.1$  \hspace{1cm} $t = 60, V = 11.0$
FIGURE 28. TANTALUM-OXYGEN REACTION SEQUENCE FOR $T_s = 900^\circ C$, $P_{O_2} = 2 \times 10^{-5}$ TORR  60,000 X

$t = 0, V = 7.9$  \quad  $t = 0.5, V = 9.8$

$t = 2.5, V = 11.3$  \quad  $t = 20, V = 13.9$
FIGURE 29. TANTALUM-OXYGEN REACTION SEQUENCE FOR T = 1000°C,
P_{O_2} = 9 \times 10^{-7} \text{ TORR} \quad 60,000 \times

\begin{align*}
t = 0, & \quad V = 8.7 \\
t = 15, & \quad V = 9.3 \\
t = 5, & \quad V = 9.4 \\
t = 20, & \quad V = 9.3
\end{align*}
FIGURE 30. TANTALUM-OXYGEN REACTION SEQUENCE FOR $T_s = 1000^\circ$ C, $P_{O_2} = 6 \times 10^{-5}$ TORR  60,000 X

$t = 0, V = 8.3$
$t = 5.5, V = 9.6$
$t = 1.5, V = 9.1$
$t = 7.5, V = 10.9$
FIGURE 31. TANTALUM-OXYGEN REACTION SEQUENCE FOR $T_b = 1200^\circ C$,
$P_{O_2} = 1 \times 10^{-5}$ TORR 60,000 X

$t = 0, V = 8.2$
$t = 10, V = 11.3$
$t = 1, V = 10.3$
$t = 29, V = 9.9$
apparent preference for certain high index regions of the substrate. At highest pressures, needle-like growth may result, an indication of which is given in Figure 28 after five minutes. The apparent extent of the oxidized regions decrease as substrate temperature exceeds 1000°C. And for substrates at 1200°C and above, even pressures in the $10^{-5}$ range do not produce apparent oxidation (Figure 31) during the reaction times employed in this work (i.e., up to two hours).

D. Effect of Gases Other Than Oxygen

A number of experiments were carried out in which appreciable quantities of gases other than oxygen were either introduced purposely or accidentally (at the beginning of the experimental program).

In several experiments ambient air (presumably at $N_2/O_2 \approx 4$ and including ambient $H_2O$) was leaked onto the tip through the G. P. valve. The reaction sequence on W (with $T_s = 800°C$) is given in Figure 32. While the incubation times appear to be nearly independent of the gases other than oxygen (see Figures 12 and 13), the microcrystallite distribution in the $\{100\}$ region is apparently altered.

In another set of experiments on W at 750°C, a tungsten filament ionization gauge was used in relatively high pressures of oxygen. The reaction of oxygen with the hot tungsten filament in these gauges is capable of producing large quantities of CO and CO$_2$ (48, 49). This results from a reaction between oxygen and the carbon in tungsten. Some typical results are given in Figures 33
FIGURE 32. TUNGSTEN-AIR REACTION SEQUENCE FOR $T_a = 800^\circ C$,
$P_{total} = 10^{-6}$ TORR  90,000 X

$t = 0, V = 5.8$  
$t = 1, V = 7.0$  
$t = 3, V = 9.6$  
$t = 20, V = 10.11$
FIGURE 33. TUNGSTEN-OXYGEN REACTION SEQUENCE WITH HOT ION GAUGE FOR $T_b = 750^\circ$ C,
P_{total} = 10^{-7}$ TORR  100,000 X

$t = 0, V = 5.1$  
$t = 0.5, V = 5.3$  
$t = 1.0, V = 5.6$

$t = 1.5, V = 6.3$  
$t = 2.5, V = 6.5$  
$t = 3.5, V = 6.9$
and 34 for total pressures of $10^{-7}$ and $10^{-5}$ torr, respectively. In this instance incubation times for nucleation appear to have increased. At $10^{-5}$ torr, the presence of these gases (primarily CO and CO$_2$) apparently catalyzed nucleation in the $\{110\}$ region and whisker-like growth resulted.

Whisker-like growth also resulted on Ta when oxygen was admitted into the system through the diffusion pump, zeolite trap, and liquid nitrogen traps. Figure 35 shows the reaction sequence on tantalum containing a grain boundary at 830°C. The whisker-like growths resulting from this type of reaction were subsequently identified as $\beta$-Ta$_2$O$_5$ (see Appendix). Note the lack of oxidation in the vicinity of the grain boundary (undoubtedly a high diffusivity path for oxygen), the lack of crystallographic dependence of the nucleation sites (randomly located in this case), and the apparent inability of most $\{111\}$ sites (usually the most favorable if contaminating gases are not present in large quantities) to act as nucleation catalysts.

E. Summary of Results

The foregoing has demonstrated a great number of similarities between the initial stages in the oxidation of tungsten and tantalum. Differences appear to be in degree rather than kind.

It is convenient to summarize the results as a function of substrate temperature.
FIGURE 34. TUNGSTEN-OXYGEN REACTION SEQUENCE WITH HOT ION GAUGE FOR $T_g = 750^\circ$ C,
$P_{\text{total}} = 10^{-5}$ TORR 100,000 X

$t = 0, V = 5.2$
$t = 2.5, V = 7.6$
$t = 5.0, V = 8.4$

$t = 11, V = 8.3$
$t = 31, V = 8.2$
$t = 36, V = 7.7$
FIGURE 35. TANTALUM-OXYGEN REACTION SEQUENCE WITH OXYGEN ADMITTED THROUGH DIFFUSION PUMP FOR $T_s = 830^\circ$ C, $P_{total} = 10^{-5}$ TORR 40,000 X

$t = 0, V = 19.8$  
$t = 6, V = 23.0$  
$t = 2, V = 22.2$  
$t = 21, V = 23.0$
Substrate Temperatures under 500° C. The reaction on both tungsten and tantalum involves initially preferential adsorption on high-index regions. The extent to which the reaction proceeds depends upon substrate crystallography, substrate temperature, and oxygen pressure (i.e., the equilibrium between adsorption, desorption, and diffusion into the bulk). No indications of oxidation are apparent even at the highest pressures employed (≈10^{-5} torr).

Substrate Temperatures between 500° C and 1000° C. Three distinct stages in the reaction are apparent: adsorption, nucleation of oxide, and oxide growth.

a) Adsorption. The time extent of this stage has been seen to be acutely dependent upon crystallography. This is apparent from Table 4, in which the "incubation time" for oxide nucleation is listed as a function of substrate temperature, crystallography, and oxygen pressure. For those crystallographic regions listed in Table 4 for which no time is listed, oxide microcrystals were not observed during the total reaction time. Note that under high pressure conditions the total reaction time was sometimes quite short due to tip failure as mentioned earlier. The uncertainty in incubation times corresponds in some cases to the time period between consecutive observations, but more frequently to the difficulty in analyzing emission patterns.

Over the range of experimental conditions employed, the incubation time lasts for only a fraction of a minute for the most reactive planes and crystallographic regions to possibly longer than the duration of the experiments (over 60 minutes in some cases) for
<table>
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<th>Substrate Temp. (°C)</th>
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<th>Total Reaction Time (min.)</th>
<th>Incubation Times (Minutes) on Various Crystallographic Regions</th>
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<td>Incubation Times (Minutes) on Various Crystallographic Regions</td>
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<td>1200</td>
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<td>10</td>
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<td></td>
<td>1 x 10^{-5}</td>
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<td>(TANTALUM)</td>
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### TABLE 4. INCUBATION TIMES FOR OXIDATION NUCLEATION (CONTINUED)

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<tr>
<th>Substrate Temp. (°C)</th>
<th>Oxygen Pressure (torr)</th>
<th>Total Reaction Time, (min.)</th>
<th>Incubation Times (Minutes) on Various Crystallographic Regions</th>
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<td>-</td>
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<td>$6 \times 10^{-5}$</td>
<td>7.5</td>
<td>5.5 to 7.5</td>
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<td>1200</td>
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<td>29</td>
<td>-</td>
</tr>
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<td>-</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>$8 \times 10^{-5}$</td>
<td>16</td>
<td>-</td>
</tr>
</tbody>
</table>
the least reactive. The equilibrium state, of course, is determined by the relative rates of arrival, diffusion into the lattice, desorption, and whether or not the next stage of the reaction (nucleation) can occur.

b) Nucleation. Oxide nucleation on both W and Ta is observed to be quite rapid and to occur at preferential high-index sites on the substrate if the applied oxygen pressure is sufficiently high (i.e., a minimum pressure for oxidation within the time period of these experiments is necessary). The pressures required to initiate oxidation are much greater than the equilibrium dissociation pressures of the oxide and decrease as substrate temperature increases. Despite the observed importance of the applied oxygen pressure, the mechanistic role of this variable is curious since oxide can also be nucleated on an "oxygenated" substrate in the absence of gas-phase oxygen. Although the field enhancement effect prevents a direct measure of the size of nuclei, distances between nucleating centers on the approximately hemispherical substrate appear to fall in the range of 50 to several hundred angstrom units depending upon crystallography. The nuclei density on the surface seems not to be strongly dependent upon substrate temperature.

c) Growth. Two general modes of growth are observed: (1) a growth largely restricted to rather localized areas of the substrate, and initially, at least, predominately lateral, and (2) needle-like growth. After the relatively rapid nucleation of oxide occurs in a particular region of the substrate, the surface growth
morphology is seen to be very well fixed or predetermined in nearly all of the observations involving the former mode of growth.

As substrate temperature is increased between 1000° and 1300° C, it becomes more and more difficult to maintain oxide micro-crystals on the surface, i.e., higher and higher pressures are required. This is undoubtedly the result of increased rates of the thermally activated processes of oxide evaporation, and oxygen desorption and diffusion into the bulk.

At substrate temperatures greater than 1300° C oxide micro-crystals have not been observed even after reaction with the highest oxygen pressures obtainable (\( \sim 5 \times 10^{-5} \) torr).

In the presence of appreciable amounts of gases other than oxygen, the entire mechanism outlined above may be drastically altered. Although only a limited number of experiments have been carried out, two types of effects are noticed.

a) A temporary "poisoning" effect has been noted in some cases in which the incubation time for oxidation may be increased but the morphology of the end product appears to be relatively unaltered.

b) A permanent "poisoning" effect has probably been observed in the experiments in which hydrocarbons from the diffusion pump could have entered the reaction chamber. In this case whisker-like growth resulted.
IV. IMPLICATIONS

A. Nucleation

Despite the highly specific nature of many of the results and the numerous questions which remain unanswered, a number of potentially important observations and tendencies need to be brought into sharper focus in order to elucidate the mechanism of initial oxidation.

In the first place, relatively high supersaturations have been required (i.e., oxygen pressures much greater than the equilibrium pressures) in order to initiate oxidation within the period of observation. At least in the temperature range below which appreciable oxide evaporation is expected (say below 900° C), the critical supersaturation* has decreased with increasing substrate temperature.

Secondly, most high-index regions of both W and Ta substrates which gave no indication of oxidation after relatively long reaction times with gas-phase oxygen at a particular temperature were frequently observed to suddenly oxidize after heating to slightly higher temperatures in the absence of gas-phase oxygen (e.g., Figures 8 and 23). These observations are, of course, consistent with the concept of a thermally activated barrier to oxidation, and suggest that the gas supply function is not rate controlling. Two alternatives become immediately apparent. On the one hand, rate control may be governed

*The critical supersaturation will be discussed more fully in the following section on comparison with experiment. It will suffice for the moment to define it as that supersaturation which produces an observable nucleation rate.
by the frequency factor of a surface event such as surface diffusion. And on the other hand, the reaction may be controlled by the rate at which a subcritical region of the substrate becomes supercritical. The former possibility becomes a bit suspect, however, in view of the relatively rapid rates of surface diffusion at substrate temperatures above several hundred degrees centigrade (as demonstrated by the lack of oxygen beam effects in the present experiments), and the observed rapid rearrangement of adsorbate and substrate atoms even at room temperature(29).

The possibility of rate control by the transformation of a subcritical to a supercritical configuration depends somewhat upon the obtainable level of oxygen-metal concentration in the transformation region. Despite the low bulk solubility of oxygen in W and Ta, the surface concentration may be much greater. For example, the solubility of oxygen in Ta close to the oxide-metal interface has been observed to be higher by at least a factor of three over the bulk solubility(65). Furthermore, the low energy electron diffraction work mentioned above(29) indicates that the surface concentration of oxygen in (or on) the substrate may be of the order of 50% on even the most densely packed \{110\} planes of tungsten. Thus, the possibility of a mechanism involving precipitation of oxide micro-crystals from a supersaturated surface phase is not only compatible with the present observations, but also with experimental evidence obtained by other techniques.
If indeed the precipitation mechanism prevails, then, subject to the usual reservations regarding the assignment of macroscopic thermodynamic properties to small clusters of atoms (66, 67, 68, 69, 70), one can treat gaseous oxidation in the initial stages as a modification of classical nucleation as proposed by Volmer and Weber (71) and Becker and Doring (72) for the homogeneous case, Volmer (73) for the heterogeneous case, and modified by others.*

For the present, let us restrict our attention to oxidation in the temperature range of 500 to 800° C—a range over which oxide evaporation may be neglected.

Under these conditions it is possible to envision the nucleation process as consisting of the formation of clusters by "bimolecular" reactions consisting of the following sequences:

\[
\begin{align*}
(mM + nO) & \rightarrow (M_mO_n)_1 \\
(M_mO_n)_1 + (mM + nO) & \rightarrow (M_mO_n)_2 \\
(M_mO_n)_2 + (mM + nO) & \rightarrow (M_mO_n)_3 \\
& \vdots \\
(M_mO_n)_{i-1} + (mM + nO) & \rightarrow (M_mO_n)_i
\end{align*}
\]

(7)

where \((mM + nO)\) is an adsorbed cluster, and \((M_mO_n)_i\) is an oxide cluster containing \(i\) "unit cells" each of which contains \(m\) metal atoms or ions \((M)\) and \(n\) oxygen atoms or ions \((O)\). The above model does not, of course, imply that a particular \((mM + nO)\) cluster, necessarily retains its identity with respect to long range diffusion. The model permits differing rates of diffusion for both species, but simply defines the growth in terms of integral multiples of \(O\) and \(M\) atoms or ions.

*See (67) and (69) for excellent reviews.
The Gibbs free energy of a cluster containing \( i \) unit cells, \( \Delta G_i \), will be comprised of a negative volume free energy (or chemical free energy) \( \Delta G_V \), and a positive surface free energy, \( \Delta G_S \). In this first approximation a possible stress contribution will be neglected due to the proximity of the "free" surface. \( \Delta G_i \) as a function of \( i \) will initially increase through a critical size \( i^* \), and then decrease for larger \( i \). The nucleation rate may then be approximated by the rate at which single clusters join the critical-sized clusters, i.e.,

\[
J = c_{i^*} \omega
\]

where \( J \) is the nucleation rate for a particular crystallographic region (number of nuclei per unit area per unit time), \( c_{i^*} \) the concentration of critical-sized clusters (number of clusters per unit area), and \( \omega \) the frequency with which a critical-sized cluster becomes supercritical. Equation 8 neglects the Zeldovich correction for departure from the idealized steady state equilibrium distribution of clusters due to finite rates of formation and decomposition of critical-sized clusters. Also neglected, is a possible correction for thermal nonaccommodation(74).

The concentration \( c_{i^*} \) is usually obtained from its relation to \( \Delta G_{i^*} \) through the van't Hoff isotherm applied to the sum of the "bimolecular" reactions given in Equations 7. Accordingly, the equilibrium constant \( K \) for the sum of these reactions is given by
\[ K = \frac{a(M_mO_n)_{i^*}}{a^{(mM+nO)}} \approx \frac{N(M_mO_n)_{i^*}}{N^{(mM+nO)}} = \frac{\sum_{i=1}^{i^*} C_i}{\sum_{i=1}^{i^*} \left( \frac{C^{(mM+nO)}}{C_i} \right)^{i^*}} \]  

where \( a, c, \) and \( N \) represent the activity, surface concentration, and surface mole fraction of the various clusters, respectively, and \( c_i \) is an abbreviation for \( C^{(mM+nO)}_i \). Furthermore,

\[ K = \exp \left( -\frac{\Delta G_{i^*}}{kT} \right) \]  

with \( k \) and \( T \) being Boltzmann's constant and absolute temperature respectively. Invoking the usual assumption that

\[ C_1 = C^{(mM+nO)}_1 \gg \sum_{i=2}^{i^*} C_i \]  

for heterogeneous nucleation on substrates, Equation 10 becomes

\[ \frac{C_{i^*}}{C_1} = \exp \left( -\frac{\Delta G_{i^*}}{kT} \right) \]  

with \( c_1 \) being the abbreviation for \( C^{(mM+nO)}_1 \).

Before an expression can be obtained for \( \Delta G_{i^*} \), the shape of the nucleus must be considered. The field emission evidence alone is of limited use in this regard. However, a detailed analysis of the oxidized surface of W with the field ion microscope(75) revealed pits
of about 20 Å in depth with a diminishing diameter as a function of depth. In view of this direct evidence of the geometry of the substrate side of the nucleus, and the field enhancement effects from the vapor side, we shall take the shape of the nucleus to be that of a double convex lens in a first approximation. Such a nucleus is shown in Figure 36, and implies isotropic surface energies.

The geometry of the nucleus is characterized by two contact angles \( \Theta \) and \( \Phi \), and two radii of curvature \( r_\Theta \) and \( r_\Phi \). If the same configuration is maintained as the cluster grows, it has been shown\(^{76}\) that

\[
r_\Phi = br_\Theta
\]

and

\[
b = \frac{\gamma_{n-s}}{\gamma_{g-n}} = \frac{\sin \Theta}{\sin \Phi}
\]

where \( \gamma_{g-n} \) and \( \gamma_{n-s} \) are the interfacial free energies of the gas-nucleus and nucleus-substrate interfaces, respectively. Furthermore, the volume, \( V \), and total surface area, \( A \), of the nucleus are given by

\[
V = \frac{4}{3} \pi r_\Theta^3 \left[ f(\Theta) + b^3 f(\Phi) \right]
\]

\[
A = A_\Theta + A_\Phi = 2\pi r_\Theta^2 (1 - \cos \Theta) + 2\pi r_\Phi^2 (1 - \cos \Phi)
\]

where

\[
f(\Theta) = \frac{2 - 3 \cos \Theta + \cos^3 \Theta}{4}
\]

and

\[
f(\Phi) = \frac{2 - 3 \cos \Phi + \cos^3 \Phi}{4}
\]
FIGURE 36. DOUBLE CONVEX LENS MODEL OF OXIDE NUCLEUS
If the Gibbs free energy of formation of clusters is now expressed in terms of the two radii of curvature instead of one obtains

\[ \Delta G_r = \frac{4\pi x}{3} r_0^3 \frac{\Delta G_v}{\pi} + \pi r_0^2 \left[ 2 (1 - \cos \Theta) \gamma_{3-n} \right. \\
+ \left. 2 b^2 (1 - \cos \Phi) \gamma_{n-s} - (\sin^2 \Theta) \gamma_{g-s} \right] \] (16)

where the first term on the right side is the volume or chemical contribution (\( \Delta G_v \)) with \( \Delta G_v \) and \( \gamma \) being the molar free energy change and molar volume respectively, the second term is \( \Delta G_s \), and

\[ X = \left[ f(\Theta) + b^3 f(\Phi) \right]. \]

Further simplification is possible through use of the relationships for the balance of horizontal and vertical components of interfacial energies and Equation 14, yielding

\[ \Delta G_r = \frac{4\pi x}{3} r_0^3 \left( \frac{\Delta G_v}{\gamma} \right) + 4\pi r_0^2 \gamma_{3-n} X. \] (17)

\( \Delta G_r \) is now obtained by maximizing Equation 17 with respect to \( r_0 \). The result is

\[ \Delta G_r = \frac{16 \pi \gamma_{3-n} X}{3 \left( \frac{\Delta G_v}{\gamma} \right)^2}. \] (18)

The change in volume free energy, \( \Delta G_v \), refers to the sum of the reactions given by Equations 7, i.e., the transformation from the adsorbed to the oxidized state. Being a state property, \( \Delta G_v \) is, of course, independent of the path taken for calculation. Since the primary aim of the present work is to experimentally determine the mechanism of oxidation, we shall choose a path involving experimentally known (or determinable) parameters and neglect recent statistical mechanical considerations(77,78).
The direct application of the van't Hoff isotherm to the sum of Equations 7 is of limited use, inasmuch as the adsorbed cluster (metal and oxygen) is difficult to work with thermodynamically. A useful alternative is to consider the adsorbed cluster as being composed of adsorbed oxygen atoms and metal atoms which are saturated with oxygen.

In this case $\Delta G_{v}$ is given by

$$
\Delta G_{v} = \Delta G_{v}^{0} + RT \ln Q = \Delta G_{v}^{0} + RT \ln \frac{\partial_{\text{oxide}}}{(\partial_{\text{ads. oxygen}})(\partial_{\text{sat. metal}})}. \tag{19}
$$

Consider now the following standard states: for adsorbed oxygen, that concentration which is in equilibrium with oxygen gas at unit fugacity and the given temperature; for the metal atoms, pure metal atoms saturated with oxygen at unit fugacity at the given temperature; and for the oxide, pure oxide saturated with oxygen at unit fugacity at the given temperature. $\Delta G_{v}^{0}$ then becomes

$$
\Delta G_{v}^{0} = RT \ln p^{0}
$$

(where $p^{0}$ is the equilibrium oxygen pressure). In view of the observed increasingly rapid rate of approach to equilibrium on the surface as oxidizing conditions are approached (this was shown for W, see Figures 10 and 11) an assumption of equilibrium between gaseous and adsorbed oxygen for conditions giving rise to oxidation is surely
reasonable. Furthermore, if the activities of the oxide and of the metal atoms saturated with oxygen are not appreciably affected, then the change in the volume free energy for the isothermal reaction will be given by

\[ \Delta G_v = -RT \ln \frac{p}{p^0} \]  

(20)

where \( p \) is the actual oxygen pressure existing, and \( p/p^0 \) is the supersaturation for oxidation.

If \( c_1 \) is now redefined as the concentration per unit area of atomic oxygen, its value may be estimated by considering the various surface reactions other than (or prior to) nucleation, i.e., impingement, desorption, and bulk diffusion. Equating the rate of accumulation to the rate of condensation less the rates of desorption and bulk diffusion,

\[ \frac{dc_1}{dt} = \frac{2 \alpha p}{(2\pi m kT)^{1/2}} - \frac{c_1}{\tau_d} - \frac{c_1}{\tau_{BD}}. \]  

(21)

Here \( \alpha \) is the sticking coefficient for oxygen, \( t \) the time, \( m \) the mass of oxygen atoms, \( p \) the oxygen pressure in dynes per \( cm^2 \), \( \tau_d \) the stay time for desorption, \( \tau_{BD} \) the stay time for bulk diffusion, and the other symbols have their usual meaning. The stay time for bulk diffusion is constant only under steady state conditions, and will,
therefore, be considered in more detail in the next section on comparison with experiment. The rates of the thermally activated processes can also be given in terms of activational energies, $\Delta G'$, and vibrational frequencies, $\nu$. Thus, Equation 21 becomes

$$\frac{dc_1}{dt} = \frac{2\alpha p}{(2\pi mkT)^{1/2}} - c_1 \left[ \nu_d \exp \left( -\Delta G'_d / kT \right) - \nu_{BD} \exp \left( -\Delta G'_{BD} / kT \right) \right].$$

If the term in brackets is denoted by $Y$, the expression for $c_1$ is

$$c_1 = \frac{2\alpha p}{(2\pi mkT)^{1/2}} (Y)^{-1} \left( 1 - e^{-Yt} \right).$$

Equation 23 shows the exponential build-up of $c_1$ to the equilibrium value of $2 \alpha p(2\pi mkT)^{1/2} Y^{-1}$.

While the frequency factor $\omega$ in Equation 8 refers to the frequency with which a $(mM + nO)$ cluster joins the $(MmOn)_n$ nucleus, this need not imply that the cluster moves as a physical entity. In fact $\omega$ may be related to the frequency at which the least mobile specie $(M$ or $O$) joins the critical nucleus. In this event, $\omega$ can be evaluated in terms of $f$, the diffusion frequency of the least mobile specie by

$$\omega = A \left( \frac{f}{B} \right)$$

(24)

where $f$ is either $f_M$ or $f_O$, $B$ is the number of anions or cations respectively in the $(mM + nO)$ cluster, and $A$ is a geometrical factor giving the surface area of the nucleus which is exposed to the diffusive
flux. The expression for $f$ of an atom or ion moving across an internal interface has been derived according to absolute reaction rate theory (80) to be

$$f = \frac{kT}{h} \exp \left( -\frac{\Delta G^*_D}{kT} \right)$$

(25)

with $\Delta G^*_D$ being the activational free energy for diffusion (and in the present case, not necessarily equal to $\Delta G^*_B$).

The nucleation rate expression, Equation 8, can now be written in terms of Equations 12, 23, 24, and 25.

$$J = \frac{2\alpha P}{(2\pi n m kT)^{1/2}} \left( \frac{A}{B} \right) \frac{kT}{h} \left( 1 - e^{-\gamma t} \right) \exp \left( \frac{-\Delta G^*_D - \Delta G^*_X}{kT} \right).$$

(26)

B. Comparison With Experiment

Equation 26 may now be adapted to the particular systems studied and the experimental conditions prevailing. The primary alteration necessary involves the expression for $\gamma$.

In the case of W oxidation, the bulk solubility of oxygen is extremely low in the temperature range of primary interest here (below which appreciable oxide evaporation takes place), so that the drain off of oxygen at the surface due to bulk diffusion can probably be neglected in Equation 21. Accordingly,

$$\gamma_w = \nu_d \exp \left( -\frac{\Delta G^*_d}{kT} \right).$$

(27)
The situation regarding $\gamma_{\text{Ta}}$ is considerably more complex. In the first place, the bulk solubility of oxygen in Ta, being of the order of one atomic per cent in the temperature range of primary interest, may lead to a significant drain of oxygen from the surface. In the second place, the geometry of the system in the present experiment should not be expected to give rise to a constant stay time, $\tau^*_{\text{BD}}$.

In the first approximation, let us simplify the geometry of the present system so that an estimation of the drain-off may be made. Accordingly, we shall examine the diffusion from the surface into the bulk of a sphere of 1000 Å radius. The appropriate non-steady diffusion equation has been solved(81) for the boundary conditions: $c_1 = 0$ at $t = 0$, and $c_1 = c_0 (1-e^{-\beta t})$ at $t = t$ (where $c_0$ is the equilibrium concentration, and $\beta$ refers to the desorption loss alone. The graphical solutions of the diffusion equation permit one to determine the time necessary to reach a given level of bulk saturation if the diffusion coefficient and $\beta$ are known. For the given geometry, solubility, and taking the average saturated surface concentration as $10^{15}$ atoms per cm$^2$, the transfer of one monolayer from the surface to the bulk would correspond to an average bulk concentration of one-half the saturated condition.

If the diffusion coefficients at $500^\circ$ C and $800^\circ$ C, respectively are $1.5 \times 10^{-10}$ and $2.3 \times 10^{-8}$(82), and a reasonable estimate can be made for $\beta$, the time required for the loss of one monolayer from
the surface can be determined for the two temperature limits given above. Unfortunately, $\beta$ for Ta, i.e., $\nu_d \exp(-\Delta G_d^\prime/kT)$ is not well known. If one assumes the desorption activational energies for oxygen on Ta and W to be about the same, a reasonable value of $\Delta G_d^\prime$ might be the median of 60 and 120 kcal (see page 48) or 90 kcal per mole. In this event, the times required for the loss of a monolayer of oxygen from the surface (i.e., one half saturation of the bulk) due to bulk diffusion at 500°C and 800°C, respectively are $10^{13}$ and $10^6$ seconds. This relatively slow reaction permits one to neglect its contribution to $\gamma_{Ta}$ in the present experiment (at least in this first approximation) and yields

$$\gamma_{Ta} = \nu_d \exp\left(-\Delta G_d^\prime/kT\right).$$

(28)

It must be emphasized, however, that Equation 28 is only applicable to tantalum substrates of high surface-to-volume ratio, and then only if $\Delta G_d^\prime$ lies outside the range of about 50 to 70 kcal per mole for the present range of substrate temperatures.

In view of the observed rapid rates of nucleation and the inherent difficulty of observing and specifying accurately the number of nuclei existing at a particular instant in a reaction sequence, the applicability of Equation 26 can perhaps best be judged on the basis of a critical nucleation rate(16), $J_{crit}$. This rate is identified as the observable rate under the existing conditions of observation. Equation 26 can then be written as:
\[ J_{\text{crit}} = \frac{2\alpha P_{\text{crit}}}{(2\pi mkT)^{1/2}} \frac{(A)}{B} \frac{kT}{h} (1-e^{-Yt}) \exp \left( -\frac{\Delta G'_d - \Delta G'_{\text{crit}}}{kT} \right). \] (29)

Letting
\[ \mathcal{L} = \frac{2\alpha kTA}{(2\pi mkT)^{1/2} Bh} \] (30)
and substituting for \( Y \) from Equation 27 or Equation 28, one obtains:

\[ J_{\text{crit}} = \mathcal{L} P_{\text{crit}} \left[ \exp \left( \frac{\Delta G'_d - \Delta G'_D - \Delta G'_{\text{crit}}}{kT} \right) \right] (1-e^{-Yt}) \] (31)

and
\[ \ln J_{\text{crit}} = \ln \mathcal{L} + \ln P_{\text{crit}} \frac{1}{kT} \left( -\Delta G'_d + \Delta G'_D + \Delta G'_{\text{crit}} \right) + \ln (1-e^{-Yt}). \] (32)

Upon substituting Equation 18 for \( \Delta G_{\text{crit}} \) and rearranging, Equation 32 becomes

\[ \frac{1}{(\Delta G_y)_2} = \frac{3kT}{16\pi Y^3 g n X} \left[ \ln \mathcal{L} + \ln P_{\text{crit}} - \ln J_{\text{crit}} + \ln (1-e^{-Yt}) \right] - \frac{3}{16\pi g^3 n X} (-\Delta G'_d + \Delta G'_D). \] (33)

Thus, a plot of \( \frac{1}{(\Delta G_y)_2} \) versus \( kT \) times the terms in the square brackets should yield a straight line of slope, \( S = 3 \left( \frac{16\pi Y^3 g X}{n} \right)^{-1} \) and intercept involving \( \Delta G'_d - \Delta G'_D \). Since reasonably good estimates of \( \Delta G_y \) and the terms in the square brackets can be made from published data and the experimental results obtained in the work, the above plot can be made.
For example, consider the \{111\} regions of W and the \{211\} regions of Ta. The apparent minimum oxygen pressures for the oxidation of these crystallographic regions are listed in Table 4. In the first approximation, the critical pressures may be taken as the apparent minimum pressures producing oxidation. The density of nuclei in these crystallographic regions is approximately $5 \times 10^{10}$ per cm$^2$, so an observable nucleation rate would be of the order of $5 \times 10^8$ nuclei per cm$^2$ per second.

Compared to the variation of $\Delta G_v$ and $\ln p_{\text{crit}}$ with temperature in Equation 33, the uncertainty in other quantities appearing in this equation will have a relatively minor effect on the test of the equation. For example, in view of the increasingly rapid rate of approach to equilibrium surface coverage as oxidizing pressures are approached for W (see Figures 10 and 11), it is reasonable to expect the quantity $(1 - e^{-\gamma t})$ to take on values not far from unity. Even in the case of Ta oxidation in the 500° C to 800° C range of temperature, it is not expected that the quantity $(1 - e^{-\gamma t})$ should vary over the range of an order of magnitude. And thus, even though the absolute value of $(1 - e^{-\gamma t})$ for Ta is not known, the test of Equation 33 should not depend strongly upon it.

Proceeding under the above assumptions, then, one may omit the quantity $\ln (1 - e^{-\gamma t})$ from Equation 33 for testing purposes.

The oxygen pressures needed for the calculation of $\Delta G_v$ are given in Table 5 for the lowest stable oxide of tungsten, WO$_2$, and Ta$_2$O$_5$. For $\varphi$, the following data have been used, (a) $\varphi = 0.1$
### TABLE 5. OXYGEN PRESSURES USED IN TESTING EQUATION 33

#### Tungsten - W\text{O}_2

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<th>T (°C)</th>
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<th>$P_{\text{crit} {111}}$ \text{(Table 4)} (dynes/cm²)</th>
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<tr>
<td>750</td>
<td>$5 \times 10^{-15}$</td>
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</tr>
<tr>
<td>800</td>
<td>$2 \times 10^{-14}$</td>
<td>$1.3 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

#### Tantalum - Ta\text{O}_5

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$p^0$ \text{(84)} (dynes/cm²)</th>
<th>$P_{\text{crit} {211}}$ \text{(Table 4)} (dynes/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>$7 \times 10^{-41}$</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>600</td>
<td>$2 \times 10^{-34}$</td>
<td>$9.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>700</td>
<td>$1.4 \times 10^{-29}$</td>
<td>$6.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>800</td>
<td>$1.6 \times 10^{-25}$</td>
<td>$3.9 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
and is independent of substrate temperature, (b) anion-diffusion control prevails(2), i.e., \( B_w = 2 \) and \( B_{Ta} = 5 \), (c) \( \nu_d = 10^{12} \), (d) \( A = 2.5 \times 10^{-13} \text{ cm}^2 \), i.e., one-half the surface area of a sphere of 20 Å radius(75), and (e) the gas temperature is 300° K. This gives \( \Delta W = 4.6 \times 10^{27} \text{ kT} \), and \( \Delta_{Ta} = 1.85 \times 10^{27} \text{ kT} \), where the temperature variable is that of the substrate.

These data are plotted in Figure 37. The given least-squares lines should be interpreted primarily as an indication of tendencies in the data, in view of the numerous assumptions invoked. The intercepts give activational free energies for oxidation of \( 1.8 \times 10^{-20} \) joules per atom (2.6 kcal per mole) and \( 5.6 \times 10^{-20} \) joules per atom (8.1 kcal per mole), respectively, for W and Ta.
FIGURE 37. TEST OF NUCLEATION EQUATION 33
V. CONCLUSIONS

The present study (representing the first attempt to observe directly the initial oxidation kinetics of atomically clean metal surfaces at elevated temperatures and in highly oxidizing atmospheres) has produced both expected, and unexpected results. One of the most striking unexpected results is that although variation exists between the specific behavior of W and Ta, the general features are very similar as follows.

1) Three stages have been identified in the initial reaction: incubation, nucleation, and growth. Each stage is strongly dependent upon crystallography and on the preceding stage.

2) The incubation stage comprises the three part processes of adsorption, desorption, and diffusion.

3) Nucleation appears most pronounced in the high index regions and can be extremely sensitive to the presence of gases other than oxygen. It is not observed at substrate temperatures below 500° C.

4) Nucleation requires a relatively large supersaturation which decreases as the substrate temperature increases.

5) The predominant mechanism of initial oxidation (at substrate temperatures below which appreciable oxide evaporation is expected) consists of the precipitation of oxide microcrystallites from supersaturated chemisorbed regions of the substrate.

6) Nucleation kinetics may be described approximately in terms of classical macroscopic properties.
7) Growth appears to be largely restricted to the surface except under conditions of high oxygen pressure (\( \sim 5 \times 10^{-6} \) torr) or substrate contamination, in which cases needle-like growth is frequently observed.

8) For substrate temperatures above 1000° C the extent of the regions in which nucleation occurs decreases with increasing temperature up to about 1300° C. Above 1300° C, nucleation is not observed even at the highest oxygen pressures (\( \sim 5 \times 10^{-5} \) torr).
APPENDIX

The rather frequent appearance of individual highly intense spots in the patterns of tips oxidized at the higher pressures and temperatures between 700-1000° C (and also under contaminating conditions) offered the constant experimental challenge to attempt examination of the substrate by auxiliary techniques. While little doubt existed as to the needle-like shape of the surface product giving rise to such emission, the curious fact remained that structural features had never been observed in the spots themselves. Too, if needle-like crystals did indeed exist on the surface, the possibility of phase identification seemed reasonable.

After experiments had been carried out on tantalum tips containing a grain boundary within the field of view, and it was established that the grain boundary itself did not give rise to preferential oxidation or unusual growth, it was decided to attempt identification of reaction products on the shank of the tip by electron diffraction. The goal was to react tips in the field emission microscope with oxygen, transfer the tip to a conventional electron microscope, and analyze the resulting electron diffraction.

It soon became evident that the surfaces of revolution on the specimen would not present much diffractable surface to the incident electron beam. Accordingly, tips were etched from 10-mil diameter blanks containing a polished axial flat extending over the entire length of the specimen. This flat was then positioned (after transfer to the electron microscope) in the path of the electron beam.
The experimental procedure consisted of admitting oxygen into the emission tube through the diffusion pump (in the same manner as described earlier) and allowing tantalum tips (previously cleaned by high temperature flash) to react at $\sim 800^\circ$ C. The reaction was allowed to proceed until a number of highly intense spots were noticed in the emission pattern.

The specimen was then removed from the field emission microscope and placed in the electron microscope for diffraction. The extent of oxidation was comparable to that shown in Figure 35.

The resulting diffraction patterns, although faint, usually contain about a dozen spots and sometimes exhibit Kikuchi lines (commonly observed in foils of several hundred $\AA$ thickness). The diffracted spots are sometimes distributed in more than one array, indicating that more than one microcrystallite is diffracting. Figure 38 is such a diffraction pattern. Not only do the ratios of distances between spots in a particular array agree (usually within 1%) with the ratios of interplanar spacings of $\beta$-Ta$_2$O$_5$, but the spots index consistently with the low-index planes of $\beta$-Ta$_2$O$_5$. Since diffraction from tantalum is not observed, the oxide microcrystallites are apparently in a much more favorable position for diffraction, i.e., they protrude above the surface to such an extent that localized transmission can take place.

While this electron diffraction technique used in conjunction with field emission is potentially a powerful tool, the
FIGURE 38. ELECTRON DIFFRACTION PATTERN FROM SHANK OF TANTALUM Emitter AFTER OXIDATION
knowledge of several additional factors is essential if a relatively unambiguous interpretation of the diffraction pattern in terms of the field emission pattern is to be obtained. This is because diffraction occurs from an unknown position on the \(~4\) mm-long shank of the tip while field emission originates at the tip itself. The following factors (or relative characteristics of the shank region from which diffraction occurs and the tip) must be considered:

(a) relative topography, (b) relative reaction temperature, and (c) the effect of atmospheric exposure during transfer between microscopes.

In the present experiment the effect of the relative topography of the two regions can probably be neglected since the initial tantalum oxide nucleation appears to be independent of crystallography under these contaminated conditions and exhibits no preference for grain boundaries. The degree of imperfection may be assumed to be approximately equivalent since both the tip and the shank have been subjected to the same thermal cleaning treatment.

The relative reaction temperature of the tip and of any position on the shank may be estimated by the measured and calculated temperature gradient in the optical pyrometer temperature range. This range of temperature over the entire specimen represents an uncertainty in the reaction temperature at the position from which diffraction occurs on the shank, since this position is not known precisely. Fortunately, in the present experiment this temperature
range is estimated to be less than $100^\circ$ C, and throughout this range the general nature of the observed reaction on the tip was found to be the same.

In subsidiary experiments with chemically cleaned tantalum tips, which were exposed to the same atmospheric conditions before diffraction as were those transferred from the field emission microscope to the electron microscope, no diffraction patterns could be obtained. Therefore, the effect of the transfer in the atmosphere is probably not important.

One concludes that—

1) the electron diffraction spot patterns and Kikuchi lines verify the interpretation of the localized discontinuities in field emission intensity as being the result of protruding, needle-like, microcrystals;

2) the second-phase formed in the reaction of oxygen on a thermal surface of tantalum in the temperature and pressure range being considered in the present experiment is $\beta$ -Ta$_2$O$_5$ despite the presence of gases other than oxygen; and

3) suboxides of tantalum are not observed.
REFERENCES


76. Moazed, K., unpublished work.


84. Kubaschewski, O., and Evans, E., Metallurgical Thermochemistry, Pergamon (1958), 342.
I, Doyle W. Rausch, was born May 3, 1931, in Dover, Ohio, and graduated from Dover High School in 1949. After working some six years in tool design and process development related to fabrication of "Teflon" and epoxy resins, I entered The Ohio State University in 1956. Graduation, cum laude, with the B.Met.E. degree followed in 1961.

From 1959 to 1961, I worked summers and part time at Battelle Memorial Institute on high-temperature chemical metallurgy. As a Research Fellow at The Ohio State University Research Foundation, I conducted my graduate research during the period 1961 through 1964.

I married Lois A. Barker of Columbus, Ohio, in January, 1964.

I have accepted a position as Assistant Professor in the Department of Metallurgical Engineering at Illinois Institute of Technology.