WESTINGHOUSE ELECTRIC CORPORATION
Research Laboratories
Pittsburgh, Pennsylvania 15235

Project Number: ARO-D-196

Final Report

STUDIES ON THE HIGH TEMPERATURE OXIDATION OF
MOLYBDENUM, TUNGSTEN, NIOBium, TANTALUM,
TITANIUM, AND ZIRCONIUM

Contract Number: DA-31-124-ARO-D-196

April 18, 1967

E. A. Gulbransen
K. F. Andrew
F. A. Brassart

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STUDIES ON THE HIGH TEMPERATURE OXIDATION OF
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General Introduction and Purpose

   1.1 Introduction
   1.2 Static and Flow Reaction Systems

2. Oxidation of Rhenium and a Rhenium-8% Titanium Alloy at Oxygen Pressure of 1 to 10 Torr and at 800\degree to 1400\degree C in Flow Environments
   2.1 Introduction
   2.2 Literature
   2.3 Experimental
   2.4 Results
   2.5 Discussion of the Mechanism of Oxidation
      2.5.1 Absolute Reaction Rate Theory
      2.5.2 Flow and Kinetic Theory Efficiencies

3. Oxidation of Molybdenum in Flow Environments at Temperatures of 900\degree to 1600\degree C and at Oxygen Pressures of 9 \times 10^{-3} to 49 Torr
   3.1 Introduction
   3.2 Experimental
   3.3 Method
   3.4 Results
   3.5 Discussion of Mechanisms
      3.5.1 Efficiency Calculations
      3.5.2 Absolute Reaction Rate Theory
4. Thermochemical Analyses on the Oxidation of Molybdenum

5. High Voltage Electron Diffraction Apparatus for Studying Oxidation Reactions at Pressure, at Temperature and under Flow Conditions

5.1 Introduction
5.2 Electron Diffraction Camera
5.3 Strip Heater Furnace and Reaction Chamber
5.4 Test of Gas Handling System
5.5 Determination of Instrument Constant
5.6 Results
   5.6.1 Test Study on Rhombohedral α-Fe₂O₃
   5.6.2 Study of Molybdenum Oxidation

6. Summaries of Recent Scientific Papers

6.1 The Graphite-Hydrogen Reactions and Their Implications in Geochemistry
6.2 Nature of the Reaction Products Formed in the Graphite-Hydrogen Reaction at 1300°-1400°C
6.3 Oxidation of Silicon at High Temperatures and Low Pressures under Flow Conditions and the Vapor Pressure of Silicon
6.4 Oxidation of Silicon Carbide at 1150° to 1400°C and at 9 x 10⁻³ to 5 x 10⁻¹ torr Oxygen Pressure

7. List of Publications and Technical Reports

8. List of Participating Scientific Personnel
GENERAL INTRODUCTION AND PURPOSE

The purpose of these studies was twofold: (1) to extend and develop vacuum microbalance and electron diffraction methods for studying fast oxidation reactions of high temperature metals and solids under carefully controlled conditions of temperature, pressure, and gas flow; and (2) to determine the kinetic and mechanisms of oxidation of a number of high temperature metals and solids.

The oxidation resistance of the highest melting point and lowest volatility elements, tungsten, molybdenum, rhenium, and carbon, is not controlled by the transport of reacting species through an oxide scale or film since volatile oxides are formed at high temperatures. Other materials, such as silicon, silicon carbide, and molybdenum disilicide can take on passive or active properties depending on the reaction conditions.

For some reaction conditions adsorption of oxygen, desorption of the oxide, or chemical reaction of the adsorbed species limits the kinetics of oxidation. For other conditions the diffusion of oxygen molecules through a barrier layer of volatilized oxide vapors limits the rate of oxidation of these elements. The transition between chemical controlled reaction mechanisms and gas diffusion of oxygen through the volatilized gases must be studied.

High temperature materials for many energy producing and space devices are under severe flow conditions. Flow can accelerate gas-solid reactions by removing the reaction products so that normal equilibrium conditions are not achieved and by removing the barrier layers of oxide vapors which may limit access of oxidizing gases to the surface.
The nature of the reaction interface between the metal and the oxidizing gas, under reaction conditions, is very important in determining the mechanism of the reaction. Similarly, the nature of the reacting gases whether molecular or atomic is important. The equilibrium between atomic and molecular oxygen can be calculated from free energy data.

The work performed under the present contract will be given under the following headings:

1. Vacuum microbalance apparatus and methods
2. Kinetic studies on the oxidation of rhenium
3. Kinetic studies on the oxidation of molybdenum
4. Thermochanical studies on the oxidation of molybdenum
5. Summaries of other kinetic studies
6. Electron diffraction apparatus and method
7. Electron diffraction studies on the oxidation of molybdenum
1. VACUUM MICROBALANCE METHODS FOR STUDYING FAST GAS-METAL REACTIONS

1.1 Introduction

Both static and dynamic or flow type of reaction systems can be used to measure the wide variety of chemical reactions occurring on metal surfaces. Both systems can be incorporated in a single apparatus. A static reaction system is one where no external flow is imposed on the system. Some gas circulation occurs as a result of thermal gradients along the furnace tube. If such a system is operated at constant pressure, the make-up gas as well as the weight change can be used to evaluate the kinetics of complex oxidation reactions.

A flow reaction system is one in which external gas flow is imposed on the system which is usually at atmospheric pressure. Flow systems operating at pressures below atmospheric require careful control of the gas source and the exhaust pump in order to maintain a constant pressure in the system.

Weight change methods using various types of microbalances have been used in both static and dynamic reaction systems. These methods have been developed extensively during the past six years. Oxygen consumption methods should become more useful in the future with the recent development of sensitive quartz type of Bourdon gauges and the sensitive types of constant temperature capacity manometers. Capacity manometers sensitive to $1 \times 10^5$ are now available. Thermal conductivity and gas analysis methods have also been developed extensively.
1.2 Static and Flow Type Reaction Systems

In a static reaction system operating at constant pressure, both weight change and oxygen consumption methods are used to follow the course of a gas-solid reaction. Where both oxide films and volatile oxides are formed, these methods make possible the determination of both oxide film formation and oxide volatility. (1)(2) When oxygen consumption is to be measured, it is necessary to keep the volume of the reaction and measuring systems to 1 liter or less so as to improve the precision of pressure control.

Figure 1 shows the balance housing, furnace tube and associated reaction system. Various types of balances having an overall beam length of 14.5 cm and sensitivities as low as 1 μg/0.001 cm deflection at 7.25 cm can be used. Some of these balances have been described in earlier papers. (3)(4)

Figure 2 shows a gold plated Invar beam balance (5) designed for the study of fast reactions and occupying a small volume. The sensitivity and period can be varied by positioning movable beam weights which are not shown in Figure 2. The beam weighs 46 g, has a period of about 2 seconds and in one modification a sensitivity of 75 μg/0.001 cm at 7.25 cm distance and for a weight of 1.4 g.

Fig. 1 - Reaction System
Fig. 2—Invar Balance
Specimens were suspended from the balance using platinum wire in the hot zone and 2 mil nickel-chromium wire in the cold zone. Above 1500°C platinum wire was unsatisfactory for supporting many materials. Silica or alumina fibers can be used above 1500°C for the support of some materials. Reactions between oxides and metals can occur. Special care must be used in choice of the support system.

The furnace tube shown in Figure 1 was a one inch diameter high density mullite or zircon tube. These materials can be sealed directly to glass. (6) Alumina tubes were used for temperatures above 1200°C. One of the critical problems in the design of practical reaction systems is the furnace design. Figure 3 shows a special high temperature furnace using molybdenum disilicide furnace elements. The high temperature properties of molybdenum disilicide and a high temperature furnace design has been described. (7) Using 2 six inch S-306 Kanthal elements having an available power of 880 watts each, furnaces can be readily built to operate at temperatures up to 1650°C. One set of furnace elements was in use every day for 3 years at temperatures between 1000° and 1650°C. Calibrated Pt-Pt + 10% Rh thermocouples were used within the furnace tube or attached externally to the furnace tube. The temperature of the furnace could be established by adjusting the current in the heater elements.

Figure 4 shows a schematic diagram of the vacuum system, gas preparation trains, and the system for measuring oxygen consumption. The vacuum system was not bakeable. The residual pressure obtainable at room temperature was $10^{-6}$ torr. The pressure in the system was automatically controlled by a Granville-Phillips pressure control system. For pressures above 0.1 torr, a capacity manometer was used as a pressure sensor, and for pressures below $10^{-4}$ an ion gauge was used as a pressure sensor. For intermediate pressures of $10^{-4}$ to $10^{-1}$ torr the ion gauge

Fig. 3—Kanthal furnace
Fig. 4—Schematic diagram of vacuum microbalance system
can be used as a Pirani gauge type pressure sensor. The Pirani gauge function has not been successfully used as of this date. The several pressure sensors were used to control the opening of a sensitive leak valve to adjust the pressure in the system to the desired value. The amount of gas used was measured by reading the pressure on a calibrated reservoir. Two sensitive Wallace-Tiernan pressure gauges were used to measure the pressure in the reservoir. Using a 2.6 liter reaction system and controlling the pressure to $10^{-1}$ torr, oxygen consumption could be measured to $\pm 4 \times 10^{-4}$ g. This sensitivity could be improved by using a more accurate capacity manometer, by reducing the volume of the reaction system and by improving the pressure readout on the calibrated reservoir.

For the flow type reaction system a fore pump is activated and the pumping speed varied by an adjustable orifice. By control of the fore pump speed and the servo leak, the flow rate of gas over the specimen can be regulated and measured.
2. OXIDATION OF RHENIUM AND A RHENIUM-8% TITANIUM ALLOY
AT OXYGEN PRESSURES OF 1 TO 10 TORR AND AT
800° TO 1400°C IN FLOW ENVIRONMENTS

2.1 Introduction

Carbon, rhenium, molybdenum, and tungsten are some of the
best high temperature elements. Each forms a volatile oxide when
oxidized above a certain critical temperature. Above the temperature
for formation of volatile oxides, thick oxide films are absent from the
metal surface and fast chemical reactions occur. For these conditions
chemical reaction of oxygen molecules or atoms occurs with the metal
interface or with a thin layer of non-volatile lower oxide. At some
temperature diffusion of oxygen gas through a barrier layer of
volatilized oxide occurs.

Experimentally, rhenium is one of the best metals for studying
high temperature oxidation processes. Although rhenium has a melting
point of 3967 ± 60°C and a boiling point of about 5900°C (est.), the
oxide Re₂O₇ melts at 296°C and boils at 362°C. The metal can be
obtained in a dense form and in a relatively pure state.

Rhenium forms the volatile oxide Re₂O₇ during oxidation.
Thick oxide films are absent on the metal and fast oxidation reactions
can occur. These fast oxidation reactions may be controlled by chemical
processes such as adsorption and desorption and by gas diffusion of
oxygen through a barrier layer of volatilized Re₂O₇. The chemical
processes can be distinguished from gas diffusion controlled processes
by a careful study of the temperature and pressure coefficients of the
rates of reaction and the effect of sample size or flow on the rates
of reaction.
2.2 Literature

The oxidation of rhenium has not been studied extensively. Lavrenko (8) studied the oxidation of 99.94% Re over the temperature range of 350°-750°C. Linear oxidation rates were observed. Phillips (9) has reviewed recent work and has extended the oxidation studies to 1300°C. Linear oxidation rates were observed for air oxidation. The oxide formed was Re2O7.

2.3 Experimental

A flow reaction system (10) was used for all of the kinetic measurements. The pure rhenium specimens were right cylinders having surface areas of about 0.75 cm² whereas the rhenium-8% titanium specimens were rectangular plates having surface areas of about 0.6 cm². The specimens were suspended from one end of a sensitive microbalance that was enclosed in the vacuum and reaction system. The balance was a recording type electrobalance having a sensitivity of 10⁻⁷ g/mm change on the recorder chart, a period of less than 0.1 sec, a load capacity of 1 g and a range of 1 g. The oxygen gas was preheated, led to the bottom of the furnace and exhausted at the top of the furnace tube. The gas handling system was automated to control the pressure and gas flow rate by using a servo-operated leak valve. Pressures of 1 to 10 torr were used. Gas was added manually and after the desired pressure was achieved the reaction system was switched to automatic control. Reliable readings on the recorder chart were obtained after 10-30 seconds of elapsed time.

To minimize the formation of films of non-volatile impurities on the surface, high purity metal and high purity oxygen must be used. Reagent grade oxygen having 8.4 ppm N₂, 20 ppm CH₄ and 15.2 ppm Kr was used. The rhenium was obtained from Materials Research Corp. and had a purity of 99.999%.

2.4 Results

Figure 5 shows a typical weight loss vs. time curve for the oxidation of the Re-8% Ti alloy at 1400°C and 5 torr oxygen pressure. Figure 5 shows the weight loss to be a linear function of time. An initial buoyancy correction of 2.5 mg was found for the gas flow of 72 cm/sec. The gas flow rate was calculated from pressure readings on a standard volume of gas. An oxidation rate of 3.37 x 10⁻⁴ g of Re/cm²-sec was found. This is 1.09 x 10¹⁸ atoms of Re reacting/cm²-sec.

The flow rate calculated as O₂ molecules was 1.84 x 10¹⁹ molecules/sec.

The oxidation of high purity rhenium was studied at 1, 2, 5, and 10 torr for the temperature range of 600°-1400°C. The oxidation of the alloy was studied at 2 and 5 torr for the temperature range of 600°-1507°C.

Figure 6 shows a log weight change versus 1/T plot for the kinetic data on the oxidation of pure rhenium. Parallel straight lines were obtained for 2, 5, and 10 torr pressures below 1000° or 1100°C. For this region an enthalpy of activation of 16.8 kcal/mole was obtained. Above 1100°C a break occurs in the plot for 2, 5, and 10 torr oxygen pressures. The kinetic data below 1100°C can be considered as under control of chemical factors such as adsorption, desorption or chemical reaction. At about 1100°C a transition occurs to gas diffusion controlled rate processes. This was probably the diffusion of oxygen molecules through the volatilized oxide to the reaction interface. The temperature coefficient for this region is small. A summary of the kinetic data is given in Table 1.
Fig. 5—Weight loss vs time. Oxidation Re-8% Ti, 1400°C, 5 torr, flow $1.84 \times 10^{19}$ O$_2$ molecules/sec
Fig. 6 - $\log \frac{dn}{dt} vs \frac{1}{T}$, oxidation of Rhenium, $600^\circ$-$1400^\circ$C, flow $0.42-1.95 \times 10^{19}$ $O_2$ molecules/sec.
**Table 1**

Kinetic Data Oxidation of Rhenium 600° to 1400°C

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Temp. °C</th>
<th>Area cm²</th>
<th>Gas Flow O atoms/sec</th>
<th>dw'/dt g/cm²·sec</th>
<th>dn'/dt atoms Re/cm²·sec</th>
<th>log dn'/dt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>800</td>
<td>0.674</td>
<td>2.57 x 10¹⁹</td>
<td>3.64 x 10⁻⁵</td>
<td>1.17 x 10¹⁷</td>
<td>17.068</td>
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<td>1</td>
<td>1000</td>
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<td>2.65 x 10¹⁹</td>
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<td>1100</td>
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<td>2.74 x 10¹⁹</td>
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<td>2.74 x 10¹⁷</td>
<td>17.456</td>
</tr>
<tr>
<td>1</td>
<td>1200</td>
<td>0.715</td>
<td>2.69 x 10¹⁹</td>
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<td>1</td>
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<tr>
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<td>0.743</td>
<td>2.79 x 10¹⁹</td>
<td>2.52 x 10⁻⁴</td>
<td>8.15 x 10¹⁷</td>
<td>17.911</td>
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<tr>
<td>2</td>
<td>600</td>
<td>0.640</td>
<td>8.39 x 10¹⁸</td>
<td>5.34 x 10⁻⁵</td>
<td>1.73 x 10¹⁶</td>
<td>16.238</td>
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<tr>
<td>2</td>
<td>800</td>
<td>0.640</td>
<td>8.70 x 10¹⁸</td>
<td>2.93 x 10⁻⁵</td>
<td>9.46 x 10¹⁶</td>
<td>16.976</td>
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<tr>
<td>2</td>
<td>1000</td>
<td>0.730</td>
<td>9.66 x 10¹⁸</td>
<td>9.55 x 10⁻⁵</td>
<td>3.08 x 10¹⁷</td>
<td>17.489</td>
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<td>1100</td>
<td>0.645</td>
<td>9.56 x 10¹⁸</td>
<td>1.67 x 10⁻⁴</td>
<td>5.40 x 10¹⁷</td>
<td>17.730</td>
</tr>
<tr>
<td>2</td>
<td>1200</td>
<td>0.707</td>
<td>9.96 x 10¹⁸</td>
<td>1.71 x 10⁻⁴</td>
<td>5.53 x 10¹⁷</td>
<td>17.745</td>
</tr>
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<td>2</td>
<td>1300</td>
<td>0.665</td>
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<td>17.894</td>
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<td>7.40 x 10¹⁷</td>
<td>17.964</td>
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<td>16.444</td>
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<td>800</td>
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<td>1.64 x 10¹⁷</td>
<td>17.215</td>
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<td>0.625</td>
<td>3.68 x 10¹⁹</td>
<td>1.96 x 10⁻⁴</td>
<td>5.53 x 10¹⁷</td>
<td>17.745</td>
</tr>
<tr>
<td>5</td>
<td>1100</td>
<td>0.575</td>
<td>3.75 x 10¹⁹</td>
<td>2.63 x 10⁻⁴</td>
<td>8.50 x 10¹⁷</td>
<td>17.976</td>
</tr>
<tr>
<td>5</td>
<td>1200</td>
<td>0.615</td>
<td>3.79 x 10¹⁹</td>
<td>2.83 x 10⁻⁴</td>
<td>9.15 x 10¹⁷</td>
<td>17.969</td>
</tr>
<tr>
<td>5</td>
<td>1400</td>
<td>0.600</td>
<td>3.69 x 10¹⁹</td>
<td>3.57 x 10⁻⁴</td>
<td>1.09 x 10¹⁸</td>
<td>18.057</td>
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<td>0.785</td>
<td>1.37 x 10¹⁹</td>
<td>1.16 x 10⁻⁶</td>
<td>3.74 x 10¹⁶</td>
<td>16.573</td>
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<tr>
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<td>800</td>
<td>0.730</td>
<td>1.66 x 10¹⁹</td>
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<td>2.53 x 10¹⁷</td>
<td>17.405</td>
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<td>7.70 x 10¹⁷</td>
<td>17.986</td>
</tr>
<tr>
<td>10</td>
<td>1100</td>
<td>0.607</td>
<td>3.55 x 10¹⁹</td>
<td>2.95 x 10⁻⁴</td>
<td>9.46 x 10¹⁷</td>
<td>17.973</td>
</tr>
<tr>
<td>10</td>
<td>1200</td>
<td>0.580</td>
<td>3.90 x 10¹⁹</td>
<td>3.44 x 10⁻⁴</td>
<td>1.11 x 10¹⁸</td>
<td>16.845</td>
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<tr>
<td>10</td>
<td>1300</td>
<td>0.560</td>
<td>3.81 x 10¹⁹</td>
<td>3.71 x 10⁻⁴</td>
<td>1.20 x 10¹⁸</td>
<td>18.072</td>
</tr>
<tr>
<td>10</td>
<td>1400</td>
<td>0.540</td>
<td>3.81 x 10¹⁹</td>
<td>4.00 x 10⁻⁴</td>
<td>1.29 x 10¹⁸</td>
<td>18.111</td>
</tr>
</tbody>
</table>
Figure 7 shows a similar plot for the Re-8% Ti alloy for 2 and 5 torr oxygen pressure. The log dn'/dt vs. 1/T plots in Figure 7 were similar to those for rhenium except in the low temperature region 600°-1000°C which shows a steeper slope, i.e. greater enthalpy of activation. 21 kcal/mole. The transition between chemical controlled oxidation and gas diffusion controlled oxidation occurs at or about 1100°C. The rates of oxidation at high temperatures were similar to those obtained with the pure metal. Figure 8 shows a comparison of the rate data for high purity rhenium and the Re-8% Ti alloy at 5 torr oxygen pressure.

2.5 Discussion of the Mechanism of Oxidation

2.5.1 Absolute Reaction Rate Theory

Eyring and coworkers\(^{(11)}\) have developed rate equations for the several types of surface reactions including mobile adsorption, chemical reaction, and desorption. The Eyring and coworkers' expression for mobile adsorption is

\[
dn'/dt = \frac{s}{i} C g kT \times (2mkT)^{-1/2} \times \exp \left(-\frac{\Delta H_1}{RT}\right) \tag{1}\]

Where dn'/dt is the rate of reaction in atoms of Re/cm\(^2\)-sec, \(i\) is the stoichiometric factor, \(S\) is the surface area/cm\(^2\), \(C_g\) is the concentration of \(O_2\) molecules per cubic centimeter in the gas phase, \(k\), Boltzmann's constant, \(T\), absolute temperature, and \(\Delta H_1\), enthalpy of activation. Work in our laboratory has shown that mobile adsorption is probably the rate controlling step in the oxidation of carbon\(^{(1)}\) and of molybdenum.\(^{(2)}\)

Another probable chemical mechanism is desorption of the oxide. The activated state theory expression for desorption is

\[ \frac{dn'}{dt} + \frac{S}{k} \times C_a \times \frac{kT}{h} \times e^{-\frac{\Delta H_2}{RT}} \]

where \( C_a \) is the number of reaction sites per \( \text{cm}^2 \) and \( \Delta H_2 \) is enthalpy of activation of desorption.

According to the activated state theory of surface reactions, zero order chemical surface reaction would give the same equation as that given for desorption. To apply these equations it is necessary to determine \( \frac{dn'}{dt} \), \( \Delta H \), and the pressure dependence of \( \frac{dn'}{dt} \).

Equation 1 for mobile adsorption of oxygen molecules can be fitted to the data of Figure 6 for 2, 5, and 10 torr oxygen pressures using \( \Delta H = 16.8 \text{ cal/mole} \). Table 2 shows a comparison of the experimental rates of oxidation at 1000°C with values calculated from the mobile adsorption model and the desorption model of chemical processes. The agreement with the mobile adsorption model is good if a surface area of 1 or 2 for each \( \text{cm}^2 \) of geometrical area is used. The pressure dependence at 1000°C is \( P^{0.57} \). Although the mobile adsorption equation fits the experimental data, a closer analysis of the pressure dependence indicates additional factors are affecting the rates of oxidation in addition to an adsorption process.

In Table 2 we assumed all of the gas was involved in mobile adsorption with an activation energy of 16.8 kcal for pure rhenium. Actually we postulate a monolayer of oxygen is preliminarily absorbed with a lower activation energy and that mobile adsorption of oxygen occurs on this surface. This adsorption complex undergoes chemical reaction and desorption to form \( \text{Re}_2\text{O}_7 \).

Table 2
Comparison Theoretical and Experimental Rates of Oxidation at 1000°C
2 and 5 Torr Oxygen Pressure

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Rates of Oxidation (atoms/cm²·sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure</td>
</tr>
<tr>
<td>A. Rhenium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Torr</td>
</tr>
<tr>
<td>2</td>
<td>4.81 x 10¹⁸</td>
</tr>
<tr>
<td>5</td>
<td>1.84 x 10¹⁹</td>
</tr>
<tr>
<td>B. Re-8% Ti</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Torr</td>
</tr>
<tr>
<td>2</td>
<td>3.1 x 10¹⁸</td>
</tr>
<tr>
<td>5</td>
<td>1.77 x 10¹⁹</td>
</tr>
</tbody>
</table>

*Stoichiometric factor used = 1.75
We conclude that the mechanism of oxidation of rhenium for the region AB of Figure 6 is probably mobile adsorption of oxygen modified by thickness or structural changes at the reaction interface. Studies of the reaction interface would be necessary to establish a complete mechanism.

2.5.2 Flow and Kinetic Theory Efficiencies

The flow efficiency, $E$, is given by the equation

$$E = \frac{dn}{dt} \times \kappa \times \frac{1}{F} \times 100$$

(3)

where $F$ is the flow in oxygen molecules per second and $dn/dt$ is the rate of reaction in atoms of Re/sec. The percent of oxygen molecules passing over the sample which react is given by $E$.

The kinetic theory efficiency, $\epsilon$, is given by

$$\epsilon = \frac{dn'}{dt} \times \kappa \times \frac{1}{n} \times 100$$

(4)

where $n$ is the number of oxygen molecule collisions with a $\text{cm}^2$ of surface. $n$ is given by the equation

$$n = 3.5 \times 10^{22} \times \frac{P}{MT}^{1/2}$$

(5)

where $P$ is the pressure in torr, $T$ is the temperature and $M$ the molecular weight. The kinetic theory efficiency gives the fraction of total collisions which react.

Table 3 gives both the flow and kinetic theory efficiencies in the gas diffusion region of reaction.
Table 3
Flow and Kinetic Theory Efficiency Calculations

<table>
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<tr>
<th>Temp. °C</th>
<th>Pressure Torr</th>
<th>Flow $O_2$ molecules/sec.</th>
<th>Flow E %</th>
<th>Kinetic Theory $\epsilon$ %</th>
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3. OXIDATION OF MOLYBDENUM IN FLOW ENVIRONMENTS
AT TEMPERATURES OF 900° TO 1600°C AND AT
OXYGEN PRESSURES OF 9 x 10⁻³ TO 49 TORR

3.1 Introduction

The oxidation of molybdenum from room temperature to 1700°C
involves a number of different oxidation processes. Below 600°C a
compact oxide film is formed which acts to prevent further reaction.
The oxide film begins to volatilize at 600°C. At 795°C the oxide melts.
Above 800°C oxidation occurs without appreciable oxide film formation.
The volatile oxides consist of polymers of MoO₃. Chemical processes on
the metal interface are rate controlling. Above a certain transition
temperature, the primary chemical reactions are masked by gas diffusion
of oxygen through a barrier layer of reaction products to the gas-metal
interface for reaction. This transition temperature depends on the
pressure, specimen size, gas flow, and the reaction system.

This paper will present new studies on the high temperature
oxidation of molybdenum using a flow reaction system for a number of
pressures over the temperature range of 900° to 1600°C. The purpose of
the study is to investigate the reaction conditions under which chemical
processes are rate controlling. The influence of gas flow and of
pressure are of special interest.

3.2 Experimental

The reaction system differs in some details from that used in
earlier studies. Larger diameter stainless steel tubing was used
to connect the furnace tube and balance housing. This arrangement
facilitated the measurement of the pressure at low pressure when large fractions of the oxygen gas were consumed by the reaction. The molybdenum specimen was suspended from one end of a Cahn electrobalance enclosed in the reaction system. Oxygen was preheated and passed over the specimen. An auxiliary fore pump was used to pump the oxygen gas through the system. For the low pressure runs, the mercury vapor diffusion pumps were used to pump the oxygen gas over the sample.

The flow rate and gas pressure were maintained constant by a sensitive leak valve. The volume and flow rate of the oxygen used were calculated from measurements of the pressure change of a calibrated gas-reservoir. The system pressure and flow rate were changed by controlling the exit pumping speed and the volume of gas added through the leak valve.

The Cahn balance had a capacity of about 1 g, a sensitivity of better than $10^{-6}$ g for a 1 g sample and a period of less than 0.1 sec. To support the sample, a section of 8 mil Pt wire was used in the hot zone and a section of 2 mil nickel-chromium wire was used in the cold zone.

The furnace tube, balance housing and associated apparatus were attached to a series of mercury diffusion pumps and a fore pump. A liquid-nitrogen trap was used to condense the mercury vapor. At 1200°C a vacuum of lower than $2 \times 10^{-6}$ torr could readily be achieved.

A Kanthal-Super furnace was used. Its construction and operation has been described. The temperature of the specimen was determined by a Pt-Pt + 10% Rh thermocouple mounted adjacent to the specimen inside the furnace tube. The thermocouple was calibrated to 1200°C. Maximum temperature variation of the furnace was ± 5°C.

Precision Wallace-Tiernan pressure gauges were used to measure pressures above 1 torr. Calibrated thermocouple gauges were used to

measure pressures from \(5 \times 10^{-3}\) to 0.5 torr. The thermocouple gauges were attached directly to the furnace tube to measure the pressure in the reaction zone.

Specimens were machined from high purity molybdenum rod and polished through 4/0 polishing paper. Samples were then cleaned in petroleum ether and alcohol. The standard specimen was a cylinder with hemispherical ends, 0.16 cm in diameter, 1.2 cm long, 0.6 cm\(^2\) surface area and weighing 0.24 g.

Spectroscopic analysis showed the following impurities in parts per million: Cu 10, Cr 45, Mn 5, Al 40, Fe 200, Ca 10, Ni 70, Sn 10, Mg 5, Si 50, and B 1. The elements Ba, Sr, Pb, Co, Ag, Cd, V, Nb and Ti were not detected.

Commercial grade oxygen and air were used. The gases were dried before using.

### 3.3 Method

The specimens were suspended from the balance, the system closed and then evacuated to a pressure of \(2 \times 10^{-6}\) torr. The furnace was raised about the furnace tube and the vacuum read on an ion gauge or a McLeod gauge. After the desired reaction temperature was reached, oxygen was added directly from the reservoir to avoid having the gas come in contact with mercury. The auxiliary pump or mercury pumping system was used to exhaust the gases. A liquid-nitrogen trap was placed between the reaction system and mercury pumps to minimize mercury contamination.

Weight changes of the molybdenum specimen and pressure changes of the oxygen reservoir were read and recorded as a function of time. The oxygen pressure in the reaction system was maintained constant. Readings were made at 15 sec intervals. Continuous adjustment of the leak valve was necessary to maintain constant pressure and reproducible balance readings.
3.4 Results

The oxidation of molybdenum was studied at temperatures from 900°C to 1600°C in oxygen at 9 x 10^{-3}, 4 x 10^{-2}, 1 x 10^{-1}, 2, 19, and 49 torr. The oxygen flow rates were 0.7 x 10^{-7} to 8.5 x 10^{19} molecules oxygen per second.

The flow rate of oxygen through the furnace tube is calculated from the pressure change of the calibrated gas-reservoir in units of molecules of oxygen per sec. This value is then converted to atoms of oxygen per second, which permits a direct calculation of the efficiency of the oxidation processes.

The rates of oxidation were determined from the nearly linear weight-loss versus time plots of the data. The rate, dw/dt, in g/sec was determined at time t = 0 before surface area changes occur. Avogadro's number is used to convert the oxidation rate, dw/dt, to atoms of Mo reacting per sec, dn/dt. To compare the oxidation rates with theoretical predictions, the oxidation rate is given in units of atoms of molybdenum reacting per cm², dn'/dt. The velocity of the gases over the specimen can be calculated from the flow rate and the cross sectional area, 3.14 cm², of the tube.

Table 4 summarizes the kinetic studies. The reaction conditions are given at the left and the rates of oxidation at the right. The kinetic data are given in both weight units and in atoms of molybdenum reacting per cm²-sec. Surface temperatures were estimated as described in an earlier paper.  

Figure 9 shows a summary of the kinetic data. The logarithm of the rate of oxidation in atoms of Mo per cm²-sec is plotted against 1/T. The data are compared to results on molybdenum oxidation at 76 torr obtained using a static reaction system and specimens of

### Table 4

**Summary: Kinetic Data Oxidation of Molybdenum 900°-1600°C in Flow Environments at Oxygen Pressures of 9 x 10^{-3} to 49 Torr**

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Furnace Temp. °C</th>
<th>Surface Temp. °C Estimated</th>
<th>Flow (atoms O/sec)</th>
<th>( \frac{dw}{dt} ) (( \gamma )/sec)</th>
<th>( \frac{dn}{dt} ) (atoms/sec)</th>
<th>( \frac{dn'}{dt} ) (atoms/cm²/sec)</th>
<th>log ( \frac{dn'}{dt} )</th>
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<th>Pressure (torr)</th>
<th>Furnace Temp. °C</th>
<th>Surface Temp. °C Estimated</th>
<th>Flow (atoms O/sec)</th>
<th>dw/dt (g/sec)</th>
<th>dn/dt (atoms/sec)</th>
<th>dn'/dt (atoms/cm²·sec)</th>
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Fig. 9—Log dn'/dt vs 1/T, oxidation of molybdenum AB chemical control 76 torr O₂ pressure. ACD experimental results static system 0.6 cm² samples; E, F, G, H, I, J, K results flow system; E - 49 torr, F - 19 torr, G - 5 torr, H - 2 torr, I = 1 × 10⁻¹ torr, J - 4 × 10⁻² torr, K - 9 × 10⁻³ torr
0.6 cm² area. For the chemical controlled oxidation region, these results are in good agreement with results obtained using the flow reaction system. The data fall on straight lines. A heat of activation of 41 kcal/mole was calculated for the $9 \times 10^{-3}$ and $4 \times 10^{-2}$ torr series of experiments while a heat of activation of 29 kcal/mole was found for the $1 \times 10^{-1}$ torr series of experiments. A heat of activation of 19.7 kcal was found in an earlier work for a pressure of 76 torr. The heats of activation for the 2, 5, 19 and 49 torr series are in agreement with that found for the 76 torr series of experiments.

Figure 10 shows the effect of pressure on the rate of oxidation at four temperatures, 1000°, 1100°, 1200° and 1400°C. The pressure dependence varies from $P^{0.77}$ to $P^{0.7}$. This pressure dependence suggests that the reaction mechanism is complex.

3.5 Discussion of Mechanisms
3.5.1 Efficiency of Calculations

Two types of efficiencies are used to compare the experimental oxidation rates with kinetic theory and with the actual flow rate of oxygen molecules and atoms over the sample. The kinetic theory expression for the collision number $n$, is given by

$$n = 3.5 \times 10^{22} \times P/(MT)^{1/2}$$

Here $P$ is the pressure in torr, $M$ is the molecular weight and $T$ is the temperature. The kinetic theory efficiency $\varepsilon$, is given by

$$\varepsilon = \Delta n'/dt \times \frac{k \times 1/n \times 100}{1}$$

Here $k$ is the stoichiometric factor, $k = 2/3$ for the formation of MoO₃.
Fig. 10—Log rate vs log pressure, oxidation of molybdenum
○ - 1000°C, ◊ - 1100°C, □ - 1200°C, △ - 1400°C
The second efficiency compares the experimental rate of reaction with the rate of gas flowing over the sample. Flow efficiencies, \( E \), are calculated from the equation

\[
E = \frac{3 \, \text{dn}'/dt \times A \times 1/F \times 100}{100}
\]  

(8)

Here \( A \) is the surface area, \( F \) is the flow rate in atoms of \( \text{O} \) per sec, \( \text{dn}'/dt \) is the rate of reaction in terms of atoms of Mo per \( \text{cm}^2 \)-sec and \( 3 \) is the stoichiometric ratio of \( \text{O/Mo} \) in \( \text{MoO}_3 \).

Table 5 shows a summary of the two efficiency calculations. The kinetic theory efficiencies reach a value of 0.166 at 1600°C and \( 9 \times 10^{-3} \) torr pressure. Flow efficiencies up to 0.89 were calculated. Nearly all of the oxygen leaked into the reaction system is consumed by the molybdenum sample.

Table 5 shows the kinetic theory and flow efficiencies to be a function of temperature and of pressure. The two efficiencies increase with temperature and decrease with pressure.

Rosner and Allendorf\(^{(15)}\) have also observed high efficiencies for the molybdenum-oxygen reaction. They found a heat of activation of 26 kcal per mole for the reaction of molecular oxygen with molybdenum. Complex departures from first order kinetics were observed. Oxygen atoms were found to be more reactive than \( \text{O}_2 \) molecules. At 1200°K the efficiencies of reaction for \( \text{O} \) atoms was 100 times higher than for \( \text{O}_2 \) molecules. One Mo atom was reacted for every ten \( \text{O} \) atoms striking a 1200°K surface.

We have not studied the \( \text{O} \) atom reaction directly; however at low pressure appreciable concentrations of \( \text{O} \) atoms exist in equilibrium with oxygen molecules. At 1600°C and \( 9 \times 10^{-3} \) torr oxygen pressure an

<table>
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<tr>
<th>Temp. °C</th>
<th>Pressure Torr</th>
<th>Flow Atoms O/sec</th>
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<tr>
<td>1000</td>
<td>$4 \times 10^{-2}$</td>
<td>$1.4 \times 10^{17}$</td>
<td>$8.93 \times 10^{15}$</td>
<td>0.19 11.0</td>
</tr>
<tr>
<td>1100</td>
<td>$4 \times 10^{-2}$</td>
<td>$1.4 \times 10^{17}$</td>
<td>$1.29 \times 10^{16}$</td>
<td>0.31 16.1</td>
</tr>
<tr>
<td>1200</td>
<td>$4 \times 10^{-2}$</td>
<td>$1.4 \times 10^{17}$</td>
<td>$2.34 \times 10^{16}$</td>
<td>0.55 29.2</td>
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<tr>
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<td>$2.9 \times 10^{17}$</td>
<td>$6.71 \times 10^{16}$</td>
<td>1.40 41.7</td>
</tr>
<tr>
<td>1500</td>
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<td>$5.8 \times 10^{17}$</td>
<td>$2.60 \times 10^{17}$</td>
<td>6.60 80.6</td>
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<td>$1 \times 10^{-1}$</td>
<td>$6.7 \times 10^{17}$</td>
<td>$1.79 \times 10^{16}$</td>
<td>0.15 4.6</td>
</tr>
<tr>
<td>1200</td>
<td>$1 \times 10^{-1}$</td>
<td>$6.7 \times 10^{17}$</td>
<td>$4.1 \times 10^{16}$</td>
<td>0.37 11.0</td>
</tr>
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<td>1400</td>
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<td>0.80 23.0</td>
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<td>$1 \times 10^{-1}$</td>
<td>$2.2 \times 10^{18}$</td>
<td>$3.5 \times 10^{17}$</td>
<td>3.5 45.0</td>
</tr>
<tr>
<td>1600</td>
<td>$1 \times 10^{-1}$</td>
<td>$2.2 \times 10^{18}$</td>
<td>$8.4 \times 10^{17}$</td>
<td>8.8 69.0</td>
</tr>
<tr>
<td>1400</td>
<td>2</td>
<td>$5.4 \times 10^{18}$</td>
<td>$5.7 \times 10^{17}$</td>
<td>0.28 19.1</td>
</tr>
<tr>
<td>1400</td>
<td>5</td>
<td>$8.1 \times 10^{18}$</td>
<td>$9.64 \times 10^{17}$</td>
<td>0.19 21.5</td>
</tr>
</tbody>
</table>
0 atom pressure of $6.3 \times 10^{-4}$ torr was calculated. The ratio of $P_0$ to $P_{O_2}$ is 7 percent. Assuming three $O$ atoms are required to remove one $Mo$ atom, the collision rate of the $O$ atoms is not sufficient to account for more than 30% of the observed reaction. Similar calculations at 1300°C show that 8 percent of the rate of oxidation can be due to $O$ atoms. At 1000°C only 1.9 percent of the experimental rate of oxidation can be due to $O$ atoms.

Although $O$ atoms due to thermal dissociation were present in the reacting gas, the calculated collision rates were not sufficient to account for the high rates of reaction that were observed experimentally.

3.5.2 Absolute Reaction Rate Theory

In an earlier paper we applied the predictions of the absolute reaction rate theory with the experimental rate of oxidation of molybdenum at 900°C and 76 torr oxygen pressure. The calculations were based on an experimental heat of activation 19.7 kcal/mole. Mobile adsorption of oxygen molecules was shown to be the most feasible mechanism for the oxidation of molybdenum. The molybdenum surface was assumed to be covered with a surface layer of oxygen. The equations for the mobile adsorption and desorption mechanisms of reaction were given in an earlier section of this report.

Table 6 shows the results obtained in this study together with those of the earlier study using the static type of reaction system and a pressure of 76 torr. The comparison is made for the chemical controlled region of oxidation. Again the mobile adsorption mechanism gives the best fit to the experimental data.

Correlation of Absolute Reaction Rate Theory with Experimental Rates of Oxidation of Molybdenum 900° and 1000°C

$\Delta H = 19.7$ kcal/g mole

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Pressure Torr</th>
<th>Flow Molecules $O_2$/sec</th>
<th>Experimental $dn'/dt$ (atoms/cm$^2$-sec)</th>
<th>Theory Adsorption</th>
<th>Theory Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>76</td>
<td>--</td>
<td>$1.08 \times 10^{18}$</td>
<td>$3.6 \times 10^{17}$</td>
<td>$1.29 \times 10^{24}$</td>
</tr>
<tr>
<td>1000</td>
<td>49</td>
<td>$8.5 \times 10^{19}$</td>
<td>$2.74 \times 10^{18}$</td>
<td>$5.3 \times 10^{18}$</td>
<td>$2.2 \times 10^{25}$</td>
</tr>
<tr>
<td>1000</td>
<td>5</td>
<td>$2.7 \times 10^{18}$</td>
<td>$1.63 \times 10^{17}$</td>
<td>$5.5 \times 10^{18}$</td>
<td>$2.2 \times 10^{25}$</td>
</tr>
<tr>
<td>1000</td>
<td>2</td>
<td>$2.7 \times 10^{18}$</td>
<td>$9.1 \times 10^{16}$</td>
<td>$2.2 \times 10^{17}$</td>
<td>$2.2 \times 10^{25}$</td>
</tr>
<tr>
<td>1000</td>
<td>$9 \times 10^{-3}$</td>
<td>$1.45 \times 10^{17}$</td>
<td>$1.09 \times 10^{15}$</td>
<td>$2.1 \times 10^{11}$</td>
<td>$4.83 \times 10^{20}$</td>
</tr>
</tbody>
</table>

*Calculated on basis of $\Delta H = 41$ kcal/g mole.
Calculations for the results at $9 \times 10^{-3}$ torr and $4 \times 10^{-2}$ torr, where a heat of activation of 41 kcal/mole was obtained, cannot be interpreted by either an adsorption or desorption mechanism for reaction. These calculations are also shown in Table 6. Mobile adsorption gives a rate too slow to explain the rate of reaction, while the desorption calculation is too fast. This region of reaction will require further experimentation.
4. THERMOCHEMICAL ANALYSES ON THE OXIDATION OF MOLYBDENUM

The thermochemical conditions during the oxidation of molybdenum are complex since several oxides are formed. In addition, the oxides can exist as solids, liquids and gases.

Table 7 shows the several oxidation and volatilization reactions which occur in the oxidation of molybdenum. The expressions for the equilibrium constant and the values of the logarithm of the equilibrium constants for temperatures between 1000° and 2000°K are tabulated for each of the reactions.

The thermochemical data for MoO(g), MoO₂(s), MoO₂(g), MoO₃(s), MoO₃(g), and Mo(g) are taken from the JANAF Tables. The thermochemical data for (MoO₃)ₙ(g) where n is about 3 was taken from a paper by Gulbransen, Andrew and Brassart. Figures 11 to 14 show a graphical interpretation. In these figures the logarithm of the volatile oxide pressure in atmospheres is plotted against the logarithm of the oxygen pressure in atmospheres. Vertical lines represent dissociation pressures of the solid and liquid oxide phases. Horizontal lines represent volatility curves which are independent of oxygen pressure. The remaining curves represent the effect of oxygen pressure on the volatile oxide pressure for the given reaction. Lines to the left of MoO₂(s) in the figures relate to equilibria of the type

\[ \text{Mo(s)} + \text{O}_2(g) \rightleftharpoons \text{MoO}_2(g) \]  

(9)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Expression</th>
<th>log $K_P$ at °K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>1. $\text{Mo} (s) + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{MoO} (g)$</td>
<td>$K = \frac{P_{\text{MoO}}}{(P_{\text{O}_2})^{1/2}}$</td>
<td>-14.21</td>
</tr>
<tr>
<td>2. $\text{Mo} (s) + \text{O}_2 \rightleftharpoons \text{MoO}_2 (s)$</td>
<td>$K = \frac{1}{P_{\text{O}_2}}$</td>
<td>21.24</td>
</tr>
<tr>
<td>3. $\text{Mo} (s) + \text{O}_2 \rightleftharpoons \text{MoO}_2 (g)$</td>
<td>$K = \frac{P_{\text{MoO}<em>2}}{P</em>{\text{O}_2}}$</td>
<td>1.63</td>
</tr>
<tr>
<td>4. $\text{Mo} (s) + \frac{3}{2} \text{O}_2 \rightleftharpoons \text{MoO}_3 (s,1)$</td>
<td>$K = \frac{1}{(P_{\text{O}_2})^{3/2}}$</td>
<td>25.81</td>
</tr>
<tr>
<td>5. $\text{Mo} (s) + \frac{3}{2} \text{O}_2 \rightleftharpoons \text{MoO}_3 (g)$</td>
<td>$K = \frac{P_{\text{MoO}<em>3}}{(P</em>{\text{O}_2})^{3/2}}$</td>
<td>14.65</td>
</tr>
<tr>
<td>6. $\text{MoO}_2 (s) + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{MoO}_3 (s)$</td>
<td>$K = \frac{1}{(P_{\text{O}_2})^{1/2}}$</td>
<td>4.57</td>
</tr>
<tr>
<td>7. $\text{MoO}_2 (s) + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{MoO}_3 (g)$</td>
<td>$K = \frac{P_{\text{MoO}<em>3}}{(P</em>{\text{O}_2})^{1/2}}$</td>
<td>-6.59</td>
</tr>
<tr>
<td>8. $\text{MoO}_2 (s) \rightleftharpoons \text{MoO}_2 (g)$</td>
<td>$K = P_{\text{MoO}_2}$</td>
<td>-19.61</td>
</tr>
<tr>
<td>9. $\text{MoO}_3 (s) \rightleftharpoons \text{MoO}_3 (g)$</td>
<td>$K = P_{\text{MoO}_3}$</td>
<td>-11.16</td>
</tr>
<tr>
<td>10. $\text{Mo} (s) \rightleftharpoons \text{Mo} (g)$</td>
<td>$K = P_{\text{Mo}}$</td>
<td>-26.69</td>
</tr>
<tr>
<td>11. $\text{Mo} (s) + \frac{3}{2} \text{O}_2 \rightleftharpoons \frac{1}{3} \text{(MoO}_3)_3 (g)$</td>
<td>$K = \left(\frac{P_{\text{MoO}<em>3}}{3}\right)^{1/3}/(P</em>{\text{O}_2})^{3/2}$</td>
<td>24.85</td>
</tr>
<tr>
<td>12. $\text{MoO}_3 (s,1) \rightleftharpoons \frac{1}{3} \text{(MoO}_3)_3 (g)$</td>
<td>$K = \frac{P_{\text{MoO}_3}}{3}$</td>
<td>-0.955</td>
</tr>
</tbody>
</table>

*Extrapolated
The equilibrium constant involves both $\text{MoO}_2(g)$ and $O_2(g)$. The $p_{\text{MoO}_2(g)}$ decreases as the $p_{O_2}$ decreases. Lines to the right of $\text{MoO}_3(s,l)$ represent reactions of the type

$$\text{MoO}_3(s,l) \rightarrow \text{MoO}_2(g) + \frac{1}{2} O_2 \quad (10)$$

Here the $p_{\text{MoO}_2(g)}$ remains constant or decreases as log $p_{O_2}$ increases. The lines in the chart between $\text{MoO}_2(s)$ and $\text{MoO}_3(s,l)$ represent equilibria of the type

$$\text{MoO}_2(s) \rightarrow \text{MoO}_3(g) \quad (11)$$

Figures 11 to 14 can be used to predict the surface oxides formed on molybdenum during oxidation and the nature of the volatile species for a wide variety of oxidation conditions. At 1000°K, Figure 11, $\text{MoO}_2(s)$ and $\text{MoO}_3(s)$ should form with $\text{MoO}_3(s)$ next to the metal and $\text{MoO}_3(s)$ adjacent to the gas phase for oxygen pressures $> \log p_{O_2} = 9.4$, i.e. $p_{O_2} = 3.98 \times 10^{-10}$ atm. Between log $p_{O_2} = -21.2$ and $-9.4$, $\text{MoO}_2(s)$ would be found on the metal surface. ($\text{MoO}_3)_3(g)$ and $\text{MoO}_3(g)$ would be the volatile gases formed. The equilibrium pressures can be taken from Figure 11. For log $p_{O_2} = -9.4$, log $p_{\text{MoO}_3(g)} = -2.9$.

Figure 12 shows the data at 1200°K. Above log $p_{O_2} = -7.0$, $\text{MoO}_3(l)$ and $\text{MoO}_2(s)$ are formed. Between log $p_{O_2} = -16.2$ and $-7.0$, $\text{MoO}_2(s)$ is formed. ($\text{MoO}_3)_3(g)$ and $\text{MoO}_3(g)$ are the volatile species. Below log $p_{O_2} = -16.2$ molybdenum oxidizes without oxide film formation to form $\text{MoO}_3(g)$ and $\text{MoO}_3(g)$ depending on log $p_{O_2}$. For log $p_{O_2} < -22.6$ molybdenum vaporizes.

Figure 13 shows the data at 1400°K. Above log $p_{O_2} = -5.8$ $\text{MoO}_3(l)$ and $\text{MoO}_2(s)$ are formed and ($\text{MoO}_3)_3$ is the volatile species. Between log $p_{O_2} = -12.6$ and $-5.8$, $\text{MoO}_2(s)$ is formed. ($\text{MoO}_3)_3(g)$ and $\text{MoO}_3(g)$ are the volatile species. Below log $p_{O_2} = -12.6$ molybdenum oxidizes directly to $\text{MoO}_3(g)$ and $\text{MoO}_3(g)$ depending on log $p_{O_2}$. At log $p_{O_2} < -18.4$ Mo(g) is formed.
Fig. 11 - Thermochemical data - oxidation of molydenum, 1000°K
Fig. 12 - Thermochromical data: oxidation of molybdenum. 1200°K
Fig. 13—Thermochemical data - oxidation of molybdenum, 1400°K
Fig. 14—Thermochemical data - oxidation of molybdenum, 1600°K
Since gas flow and quenching conditions are present in many reaction systems, the equilibrium conditions indicated in Table 7 and in Figures 11-14 may not be reached. Electron diffraction studies on the oxidation of molybdenum show that MoO₂(s) is the major oxide in the surface layer. MoO₃(s,l) is removed leaving MoO₂(s) on the surface layer. At 1600°K MoO₂(s) will remain on the surface at an oxygen pressure of log p₀₂ > -15.4. The oxide pressure log p_{MoO₂(g)} = -14.8.
5. HIGH VOLTAGE ELECTRON DIFFRACTION APPARATUS FOR
STUDYING OXIDATION REACTIONS AT PRESSURE,
AT TEMPERATURE AND UNDER FLOW CONDITIONS

5.1 Introduction

One of the important problems in the chemical behavior of
high temperature materials is the chemical composition and crystal
structure of the surface undergoing reaction. This is especially true
for the study of refractory metals where volatile oxides are formed.
Models for the oxidation of refractory metals have been proposed without
adequate information on the crystal structure of the reaction interface.
High voltage electron diffraction is the only method for the evaluation
of the surface crystal structure.

Recent studies at our laboratories and elsewhere have shown
that high voltage electron diffraction using 250 kV energized electrons
greatly improves the resolution of the diffraction patterns and the
possibilities of extending the method.

This report will briefly describe the chief components of the
250 kV electron diffraction camera and a new special reaction chamber
in the camera for studying reaction interfaces at temperature, in the
presence of a gas atmosphere and under flow conditions. Preliminary
studies have been made on the oxidation of molybdenum at temperatures
of 900° to 1300°C and at pressures of 10⁻¹ torr under flow conditions.

Commercial electron microscopes and electron diffraction
cameras operate with accelerating voltages of 50-150 kV. A number of
higher voltage instruments have been built in England, France and Japan.
The relative advantages of higher voltage electron beams have been discussed by Finch, Lewis and Webb\(^{(18)}\) in 1953 and by several Japanese workers.\(^{(19)}(20)\)

The advantages of increasing the beam potential are:

1. greater transmission of electrons through thick specimens,
2. smaller adsorption of energy from the beam,
3. larger ratio of elastically to inelastically scattered electrons,
4. smaller disturbances occur in the diffraction patterns due to electrical charging of the specimen and
5. decrease in depth of penetration of the specimen by the electrons.

These factors improve
1. the contrast of the diffraction pattern,
2. the conditions for taking meaningful diffraction patterns and
3. the design considerations for the construction of internal reaction chambers for studying chemical reactions "in situ".

5.2 Electron Diffraction Camera

A brief description of the apparatus will be given. The instrument was designed for electron beam voltages up to 250 kV. Many parts of an older 50 kV camera were used in the new instrument. This limited the vacuum in the system and the basic electron optics. One of the major tasks was the development of a maintenance free electron gun. A 300 kV "Sames" D.C. voltage source and controlled D.C. power sources for the electron lenses, deflecting plates, and tilt coils were purchased. The electron gun, main column, condenser lens system, and x-ray shielding system were built in our laboratories. To minimize

contamination and high voltage breakdown problems, a new high vacuum pumping system was built.

Continuing our program, we recently built a reaction chamber furnace assembly and auxiliary gas handling apparatus for the study of high temperature gas-metal reactions "in situ".

Figure 15 shows a simplified schematic drawing of the several sections of the instrument. The 3-stage electron gun, voltage divider, and battery operated filament source are shown at the top of Figure 15. The two stage condensing lens system, electron beam tilt system and beam deflection system are shown in the center. The reaction chamber, furnace system and specimen support system, and the fluorescent screen and film chamber are shown at the bottom of Figure 15. Two liquid nitrogen cold traps are incorporated in the apparatus, the first is in the section below the specimen while the second is located adjacent to the condenser lenses and in the pumping line.

The three stage gun is enclosed in an acrylic plastic box surrounded by a uni-potential hemisphere. The air within the box is dried to prevent electrical breakdowns under moist atmospheric conditions. Voltage breakdowns have been minimized by equalizing the high voltage fields along the ceramic tube through the use of corona rings and by eliminating electrical stress points in the gun and in the voltage divider.

Below the electron gun four electromagnetic tilt coils are mounted at 90° intervals. The coils are used to align the beam in the column.

A double condenser lens system is used for controlling the beam size and beam intensity. Below the lower condenser or focusing lens is a system of deflection plates for manipulation of the beam in the X-Y plane on the fluorescent screen.

A "Sames" 300 kV D.C. 1 m.a. high voltage source is used. This unit has a ripple of 1% root mean square and a drift of 0.5% for
ELECTRON DIFFRACTION APPARATUS

FIG 18
a 5% change in line voltage. A 2 volt lead acid battery is enclosed in a polished aluminum corona dome to provide power for operating the tungsten filament electron source. All of the D.C. power sources for energizing the electron lenses, tilt controls, and deflection plates have stabilized solid state circuits.

3.3 Strip Heater Furnace and Reaction Chamber

Figure 16 shows details of the furnace and reaction chamber which was developed for electron diffraction study of chemical reactions "in situ" at temperature, pressure, and under flow. The metal specimen in the form of a strip .6 cm wide, 0.01 cm thick and 3.5 cm long is mounted under tension. Current is supplied to the strip by means of water cooled insulated leads. The strip can be moved in and out of the beam and tilted so as to vary the proper grazing angle. The specimen and specimen holder can be isolated from the camera by closing the two sections. Two apertures in the chamber are used to allow the electron beam to impinge on the specimen and to allow the diffracted electrons to pass out of the reaction chamber and on to the fluorescent screen and photographic plate.

Figure 17 shows a schematic diagram of the gas handling system. The furnace chamber at the right is shown in the closed position. Oxygen or other gases can be directed through a tube to the center of the heated sample. The gases can be removed by using an auxiliary pump or by pumping through the aperture into the main column of the diffraction camera. Using the apertures alone it is possible, by controlling the leak valve, to operate the furnace chamber at $10^{-1}$ torr and the column at $10^{-4}$ torr. The flow rate is determined by observations of the pressure on a calibrated reservoir. The pressure in the gas inlet line is read by sensitive capacity manometer. Pressure at the inlet line can be controlled from $10^{-6}$ torr to $10^{-1}$ torr.
5.4 Test of Gas Handling System

Tests were made on the flow rate of oxygen molecules in the reaction system using the apertures system for pumping into the column. Table 8 shows the calculated flow rates and an estimate on the rate of reaction of molybdenum based on a 100% flow efficiency and a 1 cm² reaction area. At a pressure of 10⁻¹ torr at the inlet line, a flow rate of 5.8 x 10¹⁷ molecules of O₂/sec was observed. The flow velocity through the 2 mm diameter orifice was 6000 cm/sec.

5.5 Determination of Instrument Constant

Zinc oxide and magnesium oxide smokes were used as comparison standards to calibrate the electron diffraction camera since the accelerating voltage could vary from day to day. For most precise work the comparison standard diffraction pattern is taken at the same time as the unknown diffraction pattern.

The instrument constant for transmission patterns is given by the equation \( K_T = D_{hk1} \times d_{hk1} \). Here \( D_{hk1} \) is the diameter of the ring for a given lattice spacing, \( d_{hk1} \). The instrument constant for reflection patterns is given by the equation \( K_R = R_{hk1} \times d_{hk1} \). Here \( R_{hk1} \) is the radius of the half rings for a given lattice spacing, \( d_{hk1} \). This constant is calculated for each ring and an average value determined. The best calibrating materials should give 10 or more sharp diffraction rings. An accuracy of about 0.3 percent was obtained for reflection patterns and about 0.2 percent for transmission patterns. The instrument constant \( K_T \) for transmission determined from an MgO pattern was 1.920 cm⁻¹Å. The instrument constant for reflection also determined from MgO was 0.950 cm⁻¹Å. The specimen to plate distance was different for reflection and transmission. This accounts for the fact that \( K_T \) is not \( 2 \times K_R \).
Table 8
Flow Rates and Estimated Reaction Rates for
Electron Diffraction Reaction System

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>ΔP (torr/sec)</th>
<th>cc (torr)</th>
<th>Molecules $O_2$/sec</th>
<th>Estimated Rates of Reaction*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.5</td>
<td>18</td>
<td>$5.8 \times 10^{17}$</td>
<td>$3.9 \times 10^{17}$</td>
</tr>
<tr>
<td>0.01</td>
<td>0.05</td>
<td>1.8</td>
<td>$5.8 \times 10^{16}$</td>
<td>$3.9 \times 10^{16}$</td>
</tr>
</tbody>
</table>

*Based on 100% flow efficiency and 1 cm$^2$ area

**Pressure measured in gas inlet line
5.6 Results

5.6.1 Test Study on Rhombohedral $\alpha$-$Fe_2O_3$

To evaluate the electron diffraction camera an electron diffraction pattern was taken of high purity $\alpha$-$Fe_2O_3$ obtained from Dr. M. Bloom of the Naval Research Laboratories. A transmission pattern was taken of the powder dispersed on a thin Parlodion film. Table 9 shows the calculated $d_{hkl}$ values and intensities together with literature values obtained from an x-ray diffraction study. (21) The $d_{hkl}$ values are in excellent agreement. Many more reflections could be obtained from the pattern. However, the $d_{hkl}$ values were not tabulated from the literature source. $d_{hkl}$ values as low as 0.5 can be obtained with the high voltage electron diffraction camera. These values are of special use for lattice parameter studies.

5.6.2 Study of Molybdenum Oxidation

Table 10 shows the results of a study on the oxidation of molybdenum at various temperatures using a flow rate of $5.8 \times 10^{17}$ $O_2$ molecules/sec. The pressure in the gas inlet tube was 0.1 torr. Patterns were taken in the following sequence: in the vacuum of the camera before reaction, at reaction times of 1, 5, and 15 minutes, and in vacuum after oxidation. $MoO_2$ was the predominant oxide found. At $1300^\circ$C single crystal diffraction spots of 3 molybdenum crystals were observed and diffraction rings of an unidentified structure. The spot patterns were indexed as molybdenum.

The crystal structure studies suggest that $MoO_2$ and possibly $MoO_{2.75}$ exist on the surface during oxidation. Molybdenum does not oxidize to volatile oxides directly from bare metal surface. The $MoO_2$ or $MoO_{2.75}$ oxide film is sufficiently thick to give a good electron diffraction pattern.

<table>
<thead>
<tr>
<th>( \alpha-\text{Fe}_2\text{O}_3 ) Experimental</th>
<th>( \alpha-\text{Fe}_2\text{O}_3 ) Literature$^{(21)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{I}{I_0} )</td>
<td>( d_{hkl} )</td>
</tr>
<tr>
<td>5</td>
<td>3.651</td>
</tr>
<tr>
<td>10</td>
<td>2.698</td>
</tr>
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<td>10</td>
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<td>10</td>
<td>2.201</td>
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<td>7</td>
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<td>1.692</td>
</tr>
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<td>4</td>
<td>1.592</td>
</tr>
<tr>
<td>6 Diffuse</td>
<td>1.485</td>
</tr>
<tr>
<td>6 Diffuse</td>
<td>1.451</td>
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<tr>
<td>6</td>
<td>1.303</td>
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<td>-</td>
<td>1.310</td>
</tr>
<tr>
<td>-</td>
<td>1.258 v.w.</td>
</tr>
<tr>
<td>2 Diffuse</td>
<td>1.203</td>
</tr>
<tr>
<td>2 Diffuse</td>
<td>1.186</td>
</tr>
<tr>
<td>2 Diffuse</td>
<td>1.102</td>
</tr>
<tr>
<td>3 Diffuse</td>
<td>1.046</td>
</tr>
</tbody>
</table>

v.w. Very weak  
N.G. Not given
Table 10
Oxides formed on Molybdenum at Temperatures and in Gas Flow of $5.8 \times 10^{17}$ O<sub>2</sub> molecules/sec.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Pressure torr</th>
<th>Time min.</th>
<th>Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>vac</td>
<td>0</td>
<td>MoO&lt;sub&gt;2.75&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>5</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>15</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>vac</td>
<td>wait 10 min</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>1000</td>
<td>vac</td>
<td>0</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>5</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>15</td>
<td>MoO&lt;sub&gt;2.75&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>vac</td>
<td>wait 10 min</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>1100</td>
<td>vac</td>
<td>0</td>
<td>Mo + MoO</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>5</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>15</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>vac</td>
<td>wait 10 min</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>1200</td>
<td>vac</td>
<td>0</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
<td>MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>5</td>
<td>Mo + MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>vac</td>
<td>wait 10 min</td>
<td>Mo + MoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>1300</td>
<td>vac</td>
<td>0</td>
<td>Unidentified structure</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1</td>
<td>Mo + Unidentified structure</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>5</td>
<td>Mo + Unidentified structure</td>
</tr>
<tr>
<td></td>
<td>vac</td>
<td>wait 5 min</td>
<td>Mo + Unidentified structure</td>
</tr>
</tbody>
</table>
Two mechanisms of reaction can be suggested: (1) Molybdenum atoms diffuse through the oxide film of MoO$_2$ to the surface where reaction occurs with oxygen to form (MoO$_3$)$_3$. (2) Some of the oxygen diffuses through the oxide film to form MoO$_2$ at the metal oxide interface. The remainder of the oxygen reacts with MoO$_2$ solid to form MoO$_3$ which volatilizes.

The formation of unidentified structures on the surface is not unexpected if small quantities of impurities which form non-volatile oxides are in the metal. Consider the case of a 0.01 percent iron impurity and assume the maximum rate of reaction 600 \AA/sec. After 15 minutes or 900 seconds one would have 540,000 \AA of molybdenum reacted with 54 \AA of iron remaining on the surface to form an oxide film of iron.
6. SUMMARIES OF RECENT SCIENTIFIC PAPERS


The reaction of graphite with hydrogen at high temperature and low pressure under rapid quenching conditions was studied using levitation heating and mass spectrometric analyses of the reaction products. Small quantities of methane, ethylene, acetylene, benzene, and toluene were formed. Thermochemical analyses suggests that no appreciable reactions should occur. In one experiment at 1400°C and 10 torr hydrogen pressure, 0.34 mole percent methane, 0.11 ethane, 0.21 ethylene, and 0.17 benzene were formed in a two minute heat.

These results are of interest not only in high temperature chemistry of materials but also in geochemistry. Reactions of this type could have occurred at an early stage in the formation of the earth's atmosphere, hydrosphere, and lithosphere.


Graphite has been shown to react with hydrogen at elevated temperature, however the reaction products are unstable. A special system of small volume with levitation heating of the specimen and a mass spectrometer was used to study the nature of the reaction products. At 1300°-1400°C and at pressures of 5 x 10^{-2} to 400 torr, methane, ethylene, acetylene, benzene, and toluene were the major hydrocarbons...
formed. Calculations from kinetic data suggest that only a small fraction of the reaction products are observed due to inadequate quenching and to the inherent instability of the hydrocarbons. The graphite-hydrogen reaction is an example of a chemical reaction proceeding under conditions where the reaction products are unstable.


Wagner has predicted from thermochemical and diffusion theory analyses that silicon may react actively or passively with oxygen at high temperature depending on the oxygen pressure. To determine the characteristics of the oxidation reaction for these reaction conditions, a kinetic study was made at temperatures between 1100°C and 1300°C and pressures of $9 \times 10^{-3}$, $4 \times 10^{-2}$, and $1 \times 10^{-1}$ torr using a dynamic reaction system. Very fast reactions were found where predicted. At $10^{-1}$ torr and 1200°C, an oxidation rate of $3.7 \times 10^{18}$ silicon atoms per cm$^2$-second was observed. This was 7100 Å of silicon reacting per second. The rates of oxidation were nearly independent of temperature, but were a linear function of gas flow or pressure. Flow efficiencies of over 70% were found for the $9 \times 10^{-3}$ torr pressure runs.

Several conclusions were made from the kinetic studies.
(A) Gas diffusion processes were rate controlling for the conditions of the reaction; (B) Silicon reacted completely with oxygen under the conditions with only trace amounts of silica as resids; (C) Maximum oxygen pressure for maintaining oxide free surfaces were increased by the imposition of flow on the reaction; (D) Extreme care must be used to avoid contamination of the gas source or system with gases containing carbon; (E) The rate of oxidation was a direct function of flow or gas pressure.
6.4 Oxidation of Silicon Carbide at 1150° to 1400°C and at 9 \times 10^{-3} to 5 \times 10^{-1} torr Oxygen Pressure, E. A. Gubransen, K. F. Andrew and F. A. Brassart, J. Electrochem. Soc. 113, 12, 1311 (1966).

A kinetic study was made of the oxidation of high-purity silicon carbide using a dynamic-type reaction system. Two types of oxidation behavior were found. Passive oxidation occurred for conditions where silica films were formed on the surface. Active oxidation occurred for conditions where volatile silicon monoxide was formed. The transition conditions between the two types of oxidation were studied as a function of oxygen pressure and temperature. The transition temperatures and pressures were related to thermochanical conditions for the reaction of silicon carbide with silica to form silicon monoxide and carbon monoxide. Kinetic theory efficiencies up to 123% were calculated for the active region of oxidation.
7. PUBLICATIONS AND REPORTS

STUDIES ON THE HIGH TEMPERATURE OXIDATION OF MOYBDENUM, TUNGSTEN, NIOBium, TANTALUM, TITANIUM AND ZIRCONIUM

Project Number: ARO-D-196
Contract Number: DA-31-124-ARO-D-196


Progress Report No. 2 - Period covered: October 1, 1964 to March 31, 1965

Progress Report No. 3 - Period covered: April 1, 1965 to September 30, 1965

Progress Report No. 4 - Period covered: October 1, 1965 to March 31, 1966

Progress Report No. 5 - Period covered: April 1, 1966 to September 30, 1966

These reports were submitted to: Metallurgy and Ceramics Division, U.S. Army Research Office, Durham, North Carolina 27706.


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Approved: W. T. Lindsay, Jr., Manager
Physical Chemistry R&D
The purpose of these studies was twofold: (1) to extend and develop vacuum microbalance and electron diffraction methods for studying fast oxidation reactions of high temperature metals and solids under carefully controlled conditions of temperature, pressure, and gas flow; and (2) to determine the kinetics and mechanisms of oxidation of a number of high temperature metals and solids.

**Key Words:**
- oxidation resistance
- tungsten
- molybdenum
- niobium
- tantalum
- titanium
- zirconium
- volatized gases
- kinetics of oxidation

**Abstract**

The purpose of these studies was twofold: (1) to extend and develop vacuum microbalance and electron diffraction methods for studying fast oxidation reactions of high temperature metals and solids under carefully controlled conditions of temperature, pressure, and gas flow; and (2) to determine the kinetics and mechanisms of oxidation of a number of high temperature metals and solids.