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GASEOUS SULFIDATION OF PURE
MOLYBDENUM AT 700° - 950°C

DISSERTATION

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

By

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1980

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ACKNOWLEDGEMENTS

First of all, I would like to thank my adviser, Prof. R. A. Rapp for his helpful discussions, encouragements and guidance throughout all phases of this research program. I feel deeply indebted to him for his personal concern during my studies at Ohio State.

Appreciation is extended to the reading committee, Prof. J. P. Hirth and Prof. C. B. Shumaker, for serious discussions.

This research was performed under the sponsorship of the Department of Energy of the United States, and their financial support is greatly appreciated.

I have benefited from numerous discussions with fellow graduate students, Rax Chou, Wei Chu Fang and Bruce Miglin.

I would like to express my appreciation to Dr. Hagel of Climax Molybdenum Co. for sending me a Molybdenum sheet.

Finally, I would like to thank my wife, Kyung-hee, for her pushing husband through (Ph.T) effort, and my parents for their patience and financial support.
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I. INTRODUCTION

The practical importance of the sulfidation of metals and alloys has become apparent because of the ever increasing utilization of high temperature alloys in industrial atmospheres containing sulfur and its compounds. Furthermore, the increased use of low grade fuels makes the high temperature sulfidation problems even more important.

Environments containing sulfur or its compounds are in general more aggressive than oxygen environments. Near the temperature of 400°C, corrosion rate of iron-group metals in sulfur environments is so high that their applications are limited to 200 - 300°C. The degree of disorder of the crystal lattices of sulfides is far higher than those of oxides, and this causes a higher migration rate of sulfur anions or metal cations in sulfides, and results in much higher rates of sulfidation than oxidation. For example, the parabolic sulfidation rate constant of Cr is about one million times higher than parabolic oxidation rate constant of Cr in an oxygen environment. Also, the eutectic points of metal-sulfide systems are far lower than those of metal-oxide systems,
which very often leads to catastrophic failure.

While noble metals or oxidation-resistant metals like silver, copper, nickel and chromium show very poor sulfidation resistance, refractory metals like molybdenum, tungsten and niobium that show poor oxidation resistance have very high sulfidation resistance.

Pure Mo is known to be very resistant to sulfur environments. However, a small amount of oxygen causes the formation of MoO$_3$ which has a low melting point (795°C) and is very volatile. For this reason, pure Mo does not get attention for high temperature applications in oxygen.

The principal practical environments requiring sulfidation resistance are threefold: gasified coal gases of high sulfur activities and very low oxygen activities; combusted coal gases (high SO$_2$) of high oxygen activity, and the high S$_2$ gas pressure associated with the sodium-sulfur (beta-alumina or alkali chloride electrolyte) battery. In the first environment, pure Mo can be considered because of the relatively low oxygen activity. In current sodium-sulfur battery technology, a molybdenum wire is used as the cathode current collector and lead wire.

An alternate means to achieve acceptable corrosion resistance in a given environment is to coat or clad a cheaper or mechanically more acceptable base-metal or
alloy by a metal exhibiting the maximum in scaling resistance, possibly Mo. In this case, the corrosion behavior of this metal should be known. Many investigators have studied the sulfidation resistance of the base-metals iron, nickel, cobalt and copper, as well as their alloys with chromium. In each case, the high concentrations and mobilities of point defects in the sulfide scales yield unacceptably high scaling rates.

However, some previous studies of molybdenum sulfidation have reported slow scaling rates. These previous studies of Mo sulfidation in either $S_2$ or $H_2S$ have been limited to special ranges of temperatures and sulfur or hydrogen sulfide activities.

The purpose of this research is to determine kinetic information for the sulfidation of pure Mo over a wide range of sulfur activities and temperatures and to understand the mechanisms of sulfidation. Kinetic studies can be utilized to predict the life of a component made of Mo in the above mentioned environments. This information can also be used to establish optimum conditions for synthesizing $MoS_2$ which is a good lubricant. Better understanding of the mechanisms of sulfidation of pure molybdenum can increase the sulfidation resistance of this metal even more.
II. LITERATURE SURVEY

A. Gas Corrosion of Metals

1. Thermodynamic Driving Force

The oxidation of a pure divalent metal can be expressed by the equation

\[ \text{Me} + \frac{1}{2} \text{X}_2 = \text{MeX} \]  

where Me represents the metal, and X the oxidant.

The free energy change, \( \Delta G \), for the above reaction is

\[ \Delta G = \mu^{\text{o}}_{\text{MeX}} - \mu^{\text{o}}_{\text{Me}} - \frac{1}{2} \mu^{\text{o}}_{\text{X}_2} \]  

The relation between the chemical potential and the activity of a given component of a system is

\[ \mu_i = \mu^{\text{o}}_i + RT \ln a_i \]  

The activities of pure solid substances Me and MeX are equal to unity, and, therefore, \( \mu_{\text{Me}} = \mu^{\text{o}}_{\text{Me}} \) and \( \mu_{\text{MeX}} = \mu^{\text{o}}_{\text{MeX}} \).

\[ \mu_{\text{X}_2} = \mu^{\text{o}}_{\text{X}_2} + RT \ln P_{\text{X}_2} \]
Then, equation (2) becomes,

\[ \Delta G = \mu_{\text{MeX}}^o - \mu_{\text{Me}}^o - 1/2 \mu_{\text{X}_2}^o - 1/2 RT \ln P_{\text{X}_2} \]  

(2')

For a given temperature T,

\[ \Delta G_T = \Delta G_T^o - 1/2 RT \ln P_{\text{X}_2} \]  

(5)

In a state of thermodynamic equilibrium,

\[ \Delta G_T = 0 . \]

Thus \( \Delta G_T^o \) can be expressed as

\[ \Delta G_T^o = 1/2 RT \ln P_{\text{X}_2}^e \]

where \( P_{\text{X}_2}^e \) is the dissociation pressure of MeX compound.

The Eq. (5) may be presented as

\[ \Delta G_T = 1/2 RT \ln P_{\text{X}_2}^e - 1/2 RT \ln P_{\text{X}_2} \]  

(6)

When \( P_{\text{X}_2} > P_{\text{X}_2}^e \), \( \Delta G_T < 0 \), then the reaction (1) will proceed spontaneously to the right. On the other hand, when \( P_{\text{X}_2} < P_{\text{X}_2}^e \), then \( \Delta G_T > 0 \), and the MeX compound cannot be formed. The free energy difference is the driving force for the reaction.
2. Idealized Modes of Scale Growth

The growth of a single-phase corrosion product scale upon the reaction of a single oxidant with a pure metal or alloy involves the series and parallel combination of several reaction steps.

The diffusional growth of a corrosion product scale is an electrochemical process with spatial separation of oxidation and reduction reactions. The scales are mixed ionic and electronic conductors, and the galvanic cell of the oxidation reaction is internally short-circuited. The diffusional growth of scales may be limited either by the diffusion of ions or by electrons. The two fluxes are absolutely equated through the electrochemistry.

Diffusional growth of an electronically conducting scale can be limited either by outward cation migration or by inward anion migration. Figure 1 shows the diagrams for each case.

3. Wagner's Parabolic Scaling Theory

Wagner's parabolic scaling rate theory has the following assumptions.

a. Single phase layer of the compound $M_{Z_X}^X_{Z_M}^M$, a morphologically perfect, compact, and adherent scale grown on a pure metal,
Fig. 1 a) Diffusional growth of MeX scale by outward cation migration

\[
\text{Gas phase} \quad \text{Reduction reaction} \\
\text{Site of scale growth } X_2(g) \quad X(ads) + Me^{+X} \rightarrow \\
\frac{1}{2} X_2(g) \rightarrow X(ads) \quad Me^{+X} + V''_M + 2h^+ + X^X
\]

\[
\begin{array}{c}
\text{Scale MeX} \\
\text{Me}^{2+} \quad V''_M \quad 2h^+
\end{array}
\]

\[
\text{Metal} \quad Me^0 + V''_M + 2h^+ \rightarrow Me^{+X}
\]

\[
\text{Total reaction} \\
Me^0 + \frac{1}{2} X_2(g) \rightarrow MX
\]

Fig. 1 b) Diffusional growth of MeX scale by inward anion migration

\[
\text{Reduction reaction} \\
X(ads) + V'' + 2e^- \rightarrow X^X
\]

\[
\begin{array}{c}
\text{Scale MeX} \\
X^{2-} \quad V''_X \quad 2e^-
\end{array}
\]

\[
\text{Me} \quad X^X + Me^0 \rightarrow Me^{+X} + X^X + V''_X + 2e^-
\]

\[
\text{Total reaction} \quad Me^0 + \frac{1}{2} X_2(g) \rightarrow MX
\]
b. Scaling rate limited by the independent migration of ions and electrons (or positive holes) through the scale of constant cross-sectional area,

c. Local equilibrium between non-metal and scale at gas/scale interface and between metal and scale at the metal/scale interface,

d. Local equilibrium between neutral species, ions, ionic defects, and electrons throughout the scale,

e. Local electrical neutrality in the scale,

f. Quasi-steady-state flux, i.e., trivial accumulation of species within the scale, so that the flux is essentially independent of the distance.

The derivation of the theory can be found elsewhere. The final equation for the rate is,

\[
\frac{dn}{dt} = \frac{A}{\xi} \left\{ \frac{1}{96,460 N_0 e} \int \left( \frac{\mu_x^{(o)}}{\mu_x^{(i)}} \right) (t_1 + t_2) t_3 \sigma \frac{d\mu_X}{z_2} \right\}
\]

where \( \tilde{n} \) : number of equivalents
\( \xi \) : scale thickness
\( A \) : surface area
\( t_1, t_2, t_3 \) : transference number of the cations, anions and electrons, respectively
\( \mu_x^{(i)}, \mu_x^{(o)} \) : chemical potentials of non-metal at the metal/scale and gas/scale interface, respectively
\( e \) : electronic charge
\( \sigma \) : electrical conductivity of the film.
Equation (7) can be shortened as
\[
\frac{dn}{Adt} = \frac{\tilde{k}}{\tilde{\xi}}
\]  
(8)

where \( \tilde{k} \) is Wagner's rational rate constant with units of equivalents/cm.sec.

The limiting cases of this theory are:

i) when the scale is a predominant ionic conductor, \((t_1 + t_2) \approx 1, \ t_3 \ll 1 \) :
\[
\text{rate} \gg \int_{\mu_{x}}^{(i)} (t_1 + t_2) \sigma d \mu_x \gg \sigma \Delta G_{\text{rex}'} n
\]

ii) when the scale is a predominant electronic conductor, \( t_3 \approx 1, \ (t_1 + t_2) \ll 1 \) :
\[
\text{rate} \gg \int_{\mu_{x}}^{(i)} (t_1 + t_2) \sigma d \mu_x \gg \sigma_{\text{ion}} \Delta G_{\text{rex}'} n
\]

Equivalents of scale per unit area can be converted to scale scale thickness:

\[
\xi = \frac{\tilde{n}}{Ac} \quad \text{and} \quad \frac{d\xi}{dt} = \frac{1}{A\tilde{c}} \frac{dn}{dt}
\]  
(9)

where \( \tilde{c} \) is the number of equivalents per unit volume of scale. Substitution of Eq. (9) into Eq. (8) gives
\[
\frac{d\xi}{dt} = \frac{\tilde{k}}{\tilde{c} \xi}
\]

Upon integration,
\[
\xi^2 = 2 \frac{\tilde{k}}{\tilde{c}} = 2k_p't; \quad \xi = (2k_p')^{\frac{1}{2}}
\]
where \( k' \) is called the "practical" reaction rate constant with units of \( \text{cm}^2/\text{sec} \). In terms of thermogravimetric units
\[
\left( \frac{\Delta m}{A} \right)^2 = 2k' \rho_{ox} t = k_g t
\]
where \( (\Delta m/A) \) is the weight gain per unit area, \( \rho_{ox} \) the density of the scale and \( k_g \) the gravimetric rate constant with units of \( g^2/\text{cm}^4 \cdot \text{sec} \). For this work, instead of \( k_g \), \( k_p \) will be used indicating parabolic rate constant.

4. Scaling Kinetics

The most important parameter of metal scaling from an engineering viewpoint is the reaction rate. Methods of investigating the growth of scale layers include determinations of the changes in thickness of the scale, in weight of the specimen, or in volume of the surrounding gas in a closed system. Most quantitative data have been obtained as changes in weight(\( \Delta m \)) per unit surface area.

Kinetic theory is concerned primarily with the progress of a reaction with time. Thus, the first task is to find relationships between weight change and time.

a. Linear Kinetics

Linear scaling is characteristic of metals for which a porous or cracked scale is formed so that the scale does not represent a diffusion barrier between the
reactants. Linear kinetics can be expressed as

\[ \Delta m = k_1 t. \]

b. Parabolic Kinetics

The ideal conditions and theory for parabolic kinetics have already been discussed. In general, rate laws of a nearly parabolic nature are quite common and are usually associated with thick, coherent scales. However, the failure of experimental data to satisfy exactly a parabolic rate dependence for a thick, coherent scale probably only indicates that morphological complications are preventing the retention of ideal parabolic conditions; ionic diffusion in the scale may still principally control or limit the scaling rate.

The parabolic kinetics can be expressed as

\[ (\Delta m)^2 = k_p t \quad \text{or} \quad \Delta m = (k_p t)^{1/2}. \]

This represents a straight line when \((\Delta m)^2\) is plotted against time, or when \(\Delta m\) is plotted against \(t^{1/2}\).

c. Logarithmic Kinetics

This can be expressed as

\[ \Delta m = k_e \log (a \cdot t + b) \]

Logarithmic scaling behavior is generally observed with thin scale layers (e.g., less than 1000 A) at low temperatures. It is generally believed that logarithmic scaling
results from the effect of electric fields within very thin scale layers in assisting ionic transport across the scale.

d. Other Kinetics

Many systems do not follow simple kinetics mentioned above except over a limited ranges of temperature, and a number of mechanisms have been suggested to account for these deviations from simple kinetics. Especially, when the scale has more than one phase and/or one layer, the kinetics become complicated and different mechanisms should be applied to explain them.

One of the most often mentioned mechanisms is called a Loriers mechanism. Studying of the oxidation of cerium, Loriers suggested that the observed paralinear kinetics could be explained by the formation of a porous CeO$_2$ layer on top of a nonporous Ce$_2$O$_3$ barrier layer. The outer scale layer was observed to grow at the expense of the barrier layer at a constant rate while the consumption of metal was controlled by a diffusion process in the thin inner barrier layer. The barrier layer approached a constant thickness as the rate of its formation became equal to the rate of formation of the outer porous layer. Similar mechanisms are used to explain the oxidation of tungsten$^3$, uranium$^4$ and thorium$^5$. 
Yurek, Hirth and Rapp developed a quantitative theory for the diffusion-limited growth of double-layered scales on pure metals. Their theory is similar to that of Jost, but they took into account the differences in the molar volumes of the two product phases.

e. Filling-Bedworth Ratio

Pilling and Bedworth proposed that oxidation resistance should be related to the volume ratio of the oxide product to the metal. Mathematically, this can be expressed as:

$$R = \frac{W}{D} \frac{d}{w}$$

where $W$ is the molecular weight of the oxide, $w$ is the atomic weight of the metal, $D$ and $d$ are the specific densities of the oxide and metal, respectively. The ratio $R$ indicates the volume of oxide formed from a unit volume of metal.

When this ratio $R$ is much greater than 1, large compressive stresses are supposed to be introduced into the oxide to cause poor oxidation resistance with cracking and spalling. So, in this case, good high temperature plasticity to resist fracture is needed for the scale to be protective.
B. Molybdenum - Sulfur System

1. Sulfides of Molybdenum

In the chemical literature, the existence of Mo$_2$S$_3$, MoS$_2$, Mo$_2$S$_5$, MoS$_3$ and MoS$_4$ has been reported$^9$. However, work by Ehrlich$^{10}$ has shown that, by synthesis, preparations are obtained which contain only the phases Mo and MoS$_2$. MoS$_3$ can be prepared only by decomposition of complex thiomolybdates$^{11}$. By thermal decomposition of MoS$_2$ at temperatures around 1100°C, McCabe$^{12}$ obtained a sulfide which was identified by X-ray and chemical analysis as Mo$_2$S$_3$. McCabe stated that "it is certain that the molybdenum sulfide in equilibrium with sulfur vapor and molybdenum metal from 1025 to 1150°C is molybdenum sesquisulfide, Mo$_2$S$_3$".

The compound MoS$_3$, formed chemically, has a variable composition. When heated, it loses excess S until, at 350°C, it transforms to rhombohedral MoS$_2$, also of variable composition. With further temperature rise, the rhombohedral form changes to hexagonal MoS$_2$.$^{13}$ X-ray investigation of MoS$_3$ shows that it is amorphous; on heating above 200°C(in vacuum), it yields hexagonal Mo$_{0.83}$S$_2$.

Richardson$^{14}$ attempted to index the powder pattern of Mo$_2$S$_3$, and proposed a tetragonal unit cell. Later,
Jellinek\textsuperscript{15} using a Phillips diffractometer concluded that the true symmetry of the phase is monoclinic. The unit-cell dimensions are $a = 8.633 \, \text{Å}$, $b = 3.208 \, \text{Å}$, $c = 6.092 \, \text{Å}$ and $\beta = 102^\circ$.

According to Cannon\textsuperscript{16}, high-purity MoS$_2$ melts at some temperature in excess of $1800^\circ \text{C}$. This contradicts the work of Zelikman\textsuperscript{17}, who reported $1185^\circ \text{C}$. On the basis of sintering behavior, Cannon speculates a melting temperature of $2375^\circ \text{C}$.

2. The Structure and Properties of MoS$_2$

MoS$_2$ has a layer structure in which each layer consists of a sheet of Mo ions sandwiched between two sheets of S ions. The coordination about the Mo ions is not octahedral, but the six neighbors are arranged at the corners of a trigonal prism. The layers are superposed in such a way that alternate layers are identical, and are held together only by weak Van der Waals bonds. Figure 2 shows the layered structure and the unit cell of MoS$_2$.

Evans and Young\textsuperscript{18} measured the electrical conductivity of a MoS$_2$ single crystal with the dimension of $0.8 \times 0.4 \times 0.1 \, \text{cm}$. The results are shown in Figure 3 as a function of temperature ($230 - 500 \, \text{K}$). Electrical conductivity of single crystals at $290 \, \text{K}$ is $\sigma_{\parallel} = 4.6 \times 10^{-4} \, \text{cm}^{-1}$ and $\sigma_{\perp} = 7.8 \times 10^{-2} \, \text{cm}^{-1}$. 
Fig. 2. (a) Layered structure of MoS$_2$

(b) Clinographic projection of the unit cell of MoS$_2$. The four S atoms represented by heavy circles are those within the unit cell; the others lie outside the cell but have been added to show the co-ordination about the Mo atoms.
Fig. 3. The electrical conductivity in a single crystal of MoS$_2$ plotted as a function of temperature. $\bullet$, $\sigma \perp c$; $\circ$, $\sigma \parallel c$. After Evans and Young(19).
where $\sigma_{||}$ is in the direction parallel to c-axis, and $\sigma_\perp$ is in the direction perpendicular to c-axis.

Although the electrical conductivity is the sum of electronic and ionic conductivities, MoS$_2$ is clearly a predominant n-type electronic semi-conductor$^{19}$. It is clear that electrons can migrate readily in the direction perpendicular to the c-axis.

C. Oxides of Molybdenum

The compounds of molybdenum and oxygen reported are Mo$_3$O, MoO$_2$, Mo$_4$O$_{11}$, Mo$_8$O$_{23}$, Mo$_9$O$_{26}$, Mo$_{10}$O$_{29}$, Mo$_{11}$O$_{32}$, MoO$_3$ and Mo$_x$O$_{3-x}$. Research workers$^{20,21}$ investigating the nature and composition of the oxide scales and films forming on molybdenum at moderate and elevated temperatures have reported only MoO$_2$, MoO$_3$ and several oxides whose compositions lie between MoO$_2$ and MoO$_3$ and which may be part of the series Mo$_x$O$_{3x-1}$.

Molybdenum dioxide powder has colors of brownish-black, or violet or bluish violet. The crystal structure is monoclinic with two molecules in the unit cell.

Molybdenum trioxide is a white powder with a melting point of 795°C. MoO$_3$ is very volatile, fuming visibly at 700°C. MoO$_3$ is tetragonal.
D. Thermodynamics of Mo-S-O system

Thermodynamic data needed for this research exist. Larson and Elliott\textsuperscript{22} measured the $\Delta G^\circ_f(\text{MoS}_2)$ for the reaction

$$\text{Mo} + \text{S}_2 = \text{MoS}_2$$

to obtain $\Delta G^\circ_f(\text{MoS}_2) = -88,100 + 37.33T$ cal/mole $\text{S}_2$ ($\pm$ 300 cal) for the temperature range 1123-1373K.

Two different values of $\Delta G^\circ_f(\text{Mo}_2\text{S}_3)$ for the reaction

$$\frac{4}{3}\text{Mo} + \text{S}_2 = \frac{2}{3}\text{Mo}_2\text{S}_3$$

exist. Hager and Elliott\textsuperscript{23} reported $2/3 \Delta G^\circ_f(\text{Mo}_2\text{S}_3) = -83,400 + 34.6T$ cal/mol $\text{S}_2$ ($\pm$ 300 cal) for the temperature range 1365-1610K.

Stubbles and Richardson\textsuperscript{14} reported

$$\frac{2}{3} \Delta G^\circ_f(\text{Mo}_2\text{S}_3) = -85,700 + 36.41T$$

cal.

Using Hager and Elliott's data, $\text{Mo}_2\text{S}_3$ is not stable at temperatures below 1400°C. However, Young and Smeltzer\textsuperscript{24} reported the formation of $\text{Mo}_2\text{S}_3$ on a Ni-Mo alloy at 700°C. Stubbles and Richardson's data show the existence of $\text{Mo}_2\text{S}_3$ at lower temperatures as shown in Ellingham-type stability diagram, Figure 4. For this reason, the data of Stubbles and Richardson\textsuperscript{14} were used to draw the Ellingham-type diagrams for the Mo-S system shown in Figure 4 and for the Mo-S-O system shown in Figure 5.
Thermodynamic data for MoO$_2$ and MoO$_3$ are the following:

$$\text{Mo} + \text{O}_2 \rightarrow \text{MoO}_2 \quad \Delta G^0_T = -140,500 - 4.6T\log T + 55.8 \ T$$

$$\text{MoO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{MoO}_3 \quad \Delta G^0_T = -38,700 + 19.5 \ T$$

These data are taken from Kubaschewski and Catterall$^{25}$.

E. Kinetics of Sulfidation of Mo

Dutrizac$^{26}$ investigated the thermogravimetric kinetics of the sulfidation of Mo in pure sulfur vapor for sulfur pressures ranging from 0.03 to 300 torr. Dutrizac obtained linear kinetic curves for the temperature range 415 - 550°C for $P_{S_2} > 20$ torr. For lower $P_{S_2}$, parabolic kinetics were obtained for approximately half the experiments. He concluded that the linear sulfidation kinetics of Mo are controlled by some reaction occurring at either the MoS$_2$ or Mo surface. The mechanism of scale growth was not studied, and hexagonal MoS$_2$ was reported as the only reaction product formed under all conditions. He also reported that the kinetic rate was insensitive to changes in sulfur pressures at pressures in excess of 20 torr, but lower sulfur pressures decrease the sulfidation rate. The activation energy was 103.3 ± 13.4 KJ/mol.
Fig. 4. Ellingham-type stability diagram for Mo – S system.
Fig. 5. Ellingham-type stability diagram for Mo-S-O system at 800°C.
Gerlach and Hamel\textsuperscript{27} obtained parabolic sulfidation curves for gas mixtures of $\text{H}_2$ and $\text{H}_2\text{S}$ at $900 - 1050^\circ\text{C}$. Gold markers were used, and it was concluded that the diffusion rate of the sulfur ion is higher than that of the Mo ion (inward diffusion). They used a constant gas mixture ratio for each temperature, and reported the activation energy for sulfidation as 198.7 KJ/mol. They reported MoS$_2$ to be the only corrosion product. They also observed slope changes in $(\Delta m)^2$ vs $t$ plots, but did not elaborate.

Fueki, Ishibashi and Mukaiba\textsuperscript{28} studied the sulfidation of Mo in $\text{H}_2/\text{H}_2\text{S}$ gas mixtures at $800 - 950^\circ\text{C}$. They obtained parabolic kinetic curves, but the rate constants differed from those of Gerlach and Hamel. From the description of their experiments, the work was probably done in a static system; hence, the problems of thermal gas segregation preclude an accurate calculation of the sulfur partial pressure. The effect of sulfur pressure variation on the rate was not determined by these authors.

Table I summarizes the existing kinetic data for Mo sulfidation. No systematic mechanism study has been conducted yet.
Table 1. Literature on Sulfidation of Mo

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Temp. range</th>
<th>Sulfur Press.</th>
<th>Kinetics</th>
<th>Sensitivity of Spring</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dutrizc (1970)</td>
<td>415-550°C</td>
<td>( P_t = 0.03 - 300 \text{ torr} )</td>
<td>linear</td>
<td>500 ( \mu \text{g}/0.01\text{mm} )</td>
</tr>
<tr>
<td>Gerlach and Hamel (1970)</td>
<td>900-1050°C</td>
<td>( \frac{P_{H_2S}}{P_{H_2}} = 0.1 - 0.5 )</td>
<td>parabolic</td>
<td>unknown</td>
</tr>
<tr>
<td>Fueki et al (1962)</td>
<td>800-950°C</td>
<td>( \frac{P_{H_2S}}{P_{H_2}} = 1 ) ( P_{H_2S} = P_{H_2} = 20\text{torr} )</td>
<td>parabolic</td>
<td>66.5 ( \mu \text{g}/0.01\text{mm} )</td>
</tr>
</tbody>
</table>
III. EXPERIMENT

A. Experimental Apparatus

1. Elemental Sulfur Experiments

A quartz-spring TGA balance system was designed and constructed. There are two major problems in designing a TGA system for sulfidation experiments which are not encountered in oxidation studies. First, most metals including platinum and gold react with sulfur readily in the experimental temperature ranges. Therefore, no metallic materials can be used inside the reaction chamber. Even thermocouples have to be sealed in Vycor glass, and a quartz spring was the only choice. Secondly, sulfur deposits on cold surfaces, and to prevent this, all parts of the system must be heated.

Conventional design is shown in Figure 6. There are two big disadvantages in this kind of design. First, the size (length) of a furnace has a limitation, and only a short length spring with low sensitivity can be used. And this cannot measure very small weight gains that are
Fig. 6. Conventional design of TGA system for sulfidation experiments, after Dutrizac(26)
observed in the sulfidation of molybdenum. Secondly, after every run, the end of the chamber has to be cut to remove the sample, and has to be rejoined for the next run.

Figure 7 shows the present design. Total length of the reaction tube(1) is about 150 cm, and the top of the tube is connected to the flange. The lower part of the tube is connected to the sulfur reservoir from which the intended sulfur vapor pressure is generated by heating liquid sulfur. At this connection, high temperature vacuum grease* that can stand temperatures up to 280°C was used, because this connection part is heated to a temperature about 30°C higher than that of the sulfur reservoir.

To monitor the temperature of this connection between the main column and the sulfur reservoir, a quartz cylinder(15) was introduced and a heating tape was wound around it, with a thermometer placed inside the cylinder. Thus, the temperature of this connection was maintained about 30°C above that of the sulfur reservoir.

A cathetometer(5) was used to monitor the weight gain of the specimen by measuring the elongation of the spring(2). A limiter(4) was used to lower or to raise the sample instead of a winch, because this gives a better vacuum seal and a metallic chain could not be used inside the reaction chamber.

* General Electric Company, Silicone Products Dep't.
Fig. 7. Schematic drawing of experimental setup for molybdenum sulfidation study.
In the first couple of experimental runs, the total length of the quartz spring was found to be inversely proportional to the temperature, i.e., when the temperature of the column was lowered, the length of the spring increased, which can be misread as a weight gain. A temperature fluctuation of the spring column by 2-3°C made accurate specimen weight gain measurements difficult. To resolve this problem, glass fiber insulation was added around the spring column and the temperature of the column was continuously monitored. Only after the column temperature remained constant, were weight-gain measurements initiated.

Figure 8 shows the shape and the dimensions of the quartz spring that has been used. The spring was purchased from Worden Quartz*, and had a sensitivity of 40 \( \mu \text{g} / 0.01 \text{ mm} \).

Figure 9 shows the upper part of the reaction tube. The quartz beam(7) that holds the quartz spring, two thermocouples(3), and a limiter(6) were all attached to the top flange with o-ring fitting, so that they could be raised or lowered. The flange was cooled to room temperature by a blower, while the spring column below the pyrex cylinder(8) was heated to 200°C. Thus, there was a

* A division of Ruska Instrument Corporation
6121 Hillcroft, Houston, TX. 77036
Fig. 8. Dimensions of the quartz spring.
Fig. 9. Upper part of the reaction tube.
temperature gradient as shown in this figure. As a result, two bands were formed, where solid and liquid sulfur were stable, respectively. Due to the glass wool inside the cylinder, a suspended liquid sulfur band can exist which prevents continuous sulfur deposition after it reaches an equilibrium with the gas phase.

2. Sulfidation Experiments in H₂/H₂S gas Mixtures

As a preliminary step, 1 atm Ar gas was introduced to the TGA system, and a quartz dummy specimen was heated to 800°C. Because of the large temperature gradient between the spring column(200°C) and the main furnace(800-950°C), convection becomes apparent, and this caused severe fluctuation of the spring. Accurate measurement of the weight change was impossible, and major modification of the system was necessary. It was believed that the use of high sensitivity spring worsened this problem( the maximum load of this spring is 2 g).

This fluctuation problem can be reduced by inducing one way flow of gas around the specimen, and by increasing the resistance to the gas flow.

As shown in Fig.10, the reaction tube was redesigned. The gas close to the outer tube will become hot, and the gas will move upward in direction(1). This will create the flow (2), which in turn will induce the flow (3).
Fig. 10. Modified reaction tube for H₂/H₂S experiments.
Inlet gas will follow the route (4). All the components of this tube were made of quartz. A quartz plate(a) was used to block the gas flow into the spring column.

This design indeed reduced the fluctuation significantly, and the weight gain measurement was possible.

Two flowmeter purchased from Matheson* were used for H₂S and H₂, and they were calibrated using a soap bubble technique. The calibration curves are in the Appendix C.

Prepurified H₂ gas was purchased from NCG Industrial Gas Company, and H₂S gas was purchased from Matheson.

*Matheson, P.O.Box 85, East Rutherford, N.J. 07073
B. Specimen Preparation

Thin (0.25mm) cold-rolled sheet of pure Mo (99.97%) was purchased from Alfa Chemical Co.*, and this was cut into specimen sizes of 2cm X 3cm X 0.025cm for elemental sulfur experiments and of 1cm X 5cm X 0.025cm for H₂/H₂S gas mixture experiments. A small hole (1 mm diameter) was drilled at the top of a specimen.

The surface of the as-received sheet was shiny. When the as-rolled surface was used, the specimen was degreased with a strong detergent and warm water, and was stored in acetone. When a ground and polished surface was used, the specimen was ground to 600 grit sand paper, polished with 3μalumina, and washed with a strong detergent and warm water.

Molybdenum sheet with a much larger grain size of equiaxed grains was received from Climax Molybdenum Co.**, and the specimen preparation procedure was the same as before.

The purity of the molybdenum sheet was about 99.97%, and in addition to molybdenum, the sheet contains:

---

* Alfa Products, 152 Andover St. Danvers, Ma. 01923

** Climax Molybdenum Co. of Michigan, 1600 Huron Parkway Ann Arbor, MI. 48106
70 ppm C  
80 ppm O  
48 ppm Si  
23 ppm Al  
17 ppm Ca  
11 ppm K  
4 ppm Mg  
2 ppm Na

It was believed that the molybdenum sheet from Alfa Chemical Co. had about the same amount of impurities.

Sublimed sulfur was purchased from Mallinckrodt, Inc.* and was used to generate sulfur vapor.

** Paris, Kentucky 40361
C. Experimental Procedures

Although the thermal expansion coefficient of quartz is very low and positive, the length of the quartz spring was found to decrease as the column temperature was raised and vice versa. Then, during kinetic runs the spring column was thermally insulated, and the column temperature was maintained constant and monitored. The spring constant at 25°C was measured to be 39.9 μg/0.01 mm.

To measure the spring constant at the column temperature used, first a quartz sample of M + Δm was weighed. Then Δm was removed from the sample, and the spring constant was calculated. This procedure was followed in vacuum and also at realistic experimental conditions with the actual furnace temperature. Table II shows the spring constants for the sample temperature used.

<table>
<thead>
<tr>
<th>Sample Temperature</th>
<th>Inert Sample</th>
<th>Sulfidation Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>42.1 μg/0.01mm</td>
<td>41.7 μg/0.01mm</td>
</tr>
<tr>
<td></td>
<td>41.3 μg/0.01mm</td>
<td></td>
</tr>
<tr>
<td>850°C</td>
<td></td>
<td>42.6 μg/0.01mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>43.5 μg/0.01mm</td>
</tr>
<tr>
<td>900°C</td>
<td></td>
<td>43.8 μg/0.01mm</td>
</tr>
</tbody>
</table>
To avoid the formation of any oxides on the specimen during residence in the column (at ~200°C) prior to the experiment, the sulfur reservoir was brought to temperature before the specimen was lowered into the hot zone. After 10 to 20 minutes, the weight change was recorded. To insure that only the sulfidation weight gain was measured, a quartz specimen was submitted to the same procedure. The quartz specimen did not gain any weight in 2 hours. In addition to continuous measurement, before and after each experimental run, the weight of the specimen was measured and the spring constant was recalculated. Table II lists the values of the spring constant.

For the experimental run, the specimen was hung with a quartz fiber onto the hook at the end of the quartz spring which was limited by the limiter (Item 4, Fig. 7). Then the system was evacuated to $10^{-5}$ torr with a mechanical pump.

The main furnace for the specimen was turned on, and the system was evacuated approximately once every hour. When the furnace reached the intended temperature, the sulfur reservoir furnace was turned on. It took about 5 minutes to get the intended sulfur temperature, but the specimen was lowered only after one or two hours to make sure that the inside of the chamber had achieved an equilibrium.
For a dummy specimen (quartz) experiment, it took at least 10 minutes for the spring to adjust to the new condition (spring elongated, changed column temperature) after the specimen was lowered. This was the reason that kinetic measurements were not recorded until after 10 or 20 minutes.

D. Calculation of the Sulfur Activities

For the elemental sulfur experiments, at the experimental temperatures (700 - 950°C), gaseous sulfur is consisted mainly of $S_2$. Further, the reaction chamber was in the viscous pressure regime and the pressure inside the chamber is uniform everywhere.

The total vapor pressure above the liquid sulfur was calculated using the formula described in the Appendix A.

For the experiments in $H_2/H_2S$ gas mixture, the gas mixture ratio was adjusted to have 1 torr sulfur activity of $P_{S_2}$ for all the temperatures used according to the graph in Figure 78 in Appendix B.
IV. RESULTS AND DISCUSSION

A. Elemental Sulfur Experiments at Lower Temperatures (700 - 800°C)

1. Kinetics

Figure 11 shows the general kinetic behavior for sulfidation of pure Mo at lower temperatures. The curve is initially linear, but after about 0.15 mg/cm² weight gain, Period II, the kinetics become similar to parabolic (sometimes they look linear) exhibiting a far slower rate than in Period I. The next Period III shows continuous sequences of parabolic weight gains and interruptions. During this period, a vibration of the spring was detected occasionally, which may indicate some sudden releases of stress by scale fracture. This kind of behavior was common for studies in the temperature range of 700 to 800°C, as shown in Figures 12 through 21.

To investigate the effects of the molybdenum surface finish and of grain size on the kinetics of sulfidation, four different surfaces were used. Molybdenum sheets purchased from Alfa Products were used in the as-received
Figure 11. Representative kinetic curve for lower temperatures (700 - 800°C).
condition or with a ground and polished surface as described previously. Climax specimens with larger grain sizes were also used in the as-received condition or with a ground and polished surface. Average grain sizes for Alfa and Climax specimens were 3\(\mu\)m and 6\(\mu\)m, respectively.

TGA kinetic curves from Alfa as-received surfaces are shown for different temperatures in Figures 12 - 14, and those from Climax as-received surfaces are shown in Figures 15 - 18. Figures 19 - 21 report the kinetics for ground and polished surfaces of Alfa and Climax specimens. Sulfur pressures for all these curves were 0.03 torr.

Figure 22 is an Arrhenius plot for the initial linear sulfidation rates of these four different specimens for different temperatures. The slopes, which provide the activation energies for the rate limiting step, are about the same for different sets of specimens. The activation energy for the linear sulfidation calculated from this plot was 103.4 ± 21.2 KJ/mol, which is in good agreement with 103.3 ± 13.4 KJ/mol from Dutrizac who established linear scaling rates at 415 - 550°C.

As can be seen in Figure 22, the as-rolled Alfa specimens have the highest linear kinetic rates, and the as-rolled Climax specimens are next highest. The polished Alfa and Climax specimens were the lowest, and showed the same rates.
Fig. 12. Molybdenum sulfidation kinetics for as-rolled Alfa specimen at 706°C, $P_{S_2} = 0.03$ torr.
Fig. 13. Molybdenum sulfidation kinetics for as-rolled Alfa specimen at 750°C and sulfur pressure of 0.03 torr.
Fig. 14. Sulfidation kinetics for as-rolled Alfa specimen at 800°C, $P_{S_2} = 0.03$ torr.
Fig. 15. Sulfidation kinetics for as-rolled Climax specimen at 700°C, $P_{S_2} = 0.03$ torr.
Fig. 16. Sulfidation kinetics for as-rolled Climax specimen at 750°C, $P_{S_2} = 0.03$ torr.
Fig. 17. Sulfidation kinetics for as-rolled Climax specimen at 800°C, \( P_{S_2} = 0.03 \) torr.
Fig. 18. Sulfidation kinetics for as-rolled Climax specimen at 850°C, $P_{S_2} = 0.03$ torr.
Fig. 19. Sulfdation kinetics for polished Climax specimen at $800^\circ$C, $P_{S_2} = 0.03$ torr.
Fig. 20. Sulfidation kinetics for polished Alfa specimen at 800°C, $p_{S_2} = 0.03$ torr.
Fig. 21. Sulfidation kinetics for polished Climax specimen at 750°C, $p_{S_2} = 0.03$ torr.
Fig. 22. Arrhenius plot for the linear sulfidation of molybdenum specimens with four different surfaces.
X-ray diffraction patterns were made from these unreacted Mo surfaces to understand the possible relations between the molybdenum grain orientations and the kinetic rates. Figure 23 shows the X-ray diffraction patterns made from the as-rolled surface of an Alfa Mo specimen, the as-rolled surface of a Climax molybdenum specimen and the ground surface of an Alfa Mo specimen. In the diffraction pattern from the as-rolled Alfa specimen, the \{110\} peak at 2θ equal to 40.54°, which is expected to exhibit the highest intensity, is very small. Instead, the peaks from \{200\} and \{211\} were very strong. This means that the surface of the as-rolled Alfa Mo specimen was predominantly comprised of \{100\} planes so that \{110\} planes were normal to the surface.

The as-rolled surface of Climax Mo showed a high \{110\} peak, which indicated a lesser degree of preferred orientation. A ground and polished Alfa specimen showed the highest peak from \{110\} planes.

From this information and the kinetic results of Fig. 11, it was concluded that the surface orientation of the Mo metal grains affected the rates of sulfidation. This will be discussed more in the Mechanisms Discussion section.

Dutrizac\textsuperscript{26} reported that the rate of molybdenum sulfidation was only slightly dependent on the surface roughness. He sulfidized three Mo specimens having
Fig. 23. X-ray diffraction patterns from
a. as-rolled surface of Alfa molybdenum
b. as-rolled surface of Climax molybdenum
c. ground surface of Alfa molybdenum.
different surface conditions at $523^\circ$C in 42 torr sulfur pressure. His linear rate constant for an electropolished specimen was $1 \times 10^{-8} \text{ g/cm}^2 \text{sec}$; that for a specimen abraded with emery paper was $1.22 \times 10^{-8} \text{ g/cm}^2 \text{sec}$. The rate constant for the as-received metal, which had been rolled to a smooth finish, was $1.25 \times 10^{-8} \text{ g/cm}^2 \text{sec}$. Although he claimed this was a slight dependence, the tendency is the same as the one observed in this investigation, i.e., the increased rate probably resulted for those orientations of the metal grains at the surface.

It was also concluded, from this work, that the grain size of the metal does not affect the sulfidation rate. As shown in Figure 22, polished Alfa and Climax specimens of different grain sizes showed the same sulfidation rate. Figure 24 shows a cross-section of a sulfidized specimen. The thickness of the scale is uniform, and the grain boundaries of the metal do not show any preferential attack, which supports the above conclusions.

2. Structure of Scale

From the X-ray diffraction pattern of the scale formed at the lower temperatures, $\text{MoS}_2$ is the only corrosion product phase.
Fig. 24. MoS$_2$ scale on ground and polished Mo surface of fractured Climax specimen. $T = 800^\circ C$, $P_{S_2} = 0.03$ torr 5,000X.
3. Scale Morphology

The morphology of the scale changed as the reaction temperature was changed. But the scale always exhibited a uniform thickness and columnar aggregate grains as shown in Figure 25. In the first photomicrograph, the scale was fractured intentionally to show the cross-section of the scale.

As shown in Figure 25, the outer surface of the scales formed at lower temperatures is quite porous, which explains the linear behavior of the Period I. The MoS$_2$ corrosion product was always tightly adherent, and there was no spalling of the scale.

The original surface condition affects the morphology of the scale somewhat, and scratches on the metal surface remain evident at the surface after the sulfidation. This feature represents evidence that sulfur is the mobile species in the scale (inward diffusion), so that new scale forms at the metal/scale interface. Further evidence for inward diffusion of sulfur is shown in Figure 26. This kind of edge (or corner) morphology is characteristic of inward diffusion of anions and scale formation at the metal/scale interface.

A marker experiment was also conducted by sputtering gold onto the surface of the molybdenum specimen before reaction. After the sulfidation, the gold markers
Fig. 25. a. MoS<sub>2</sub> scale on as-rolled Mo specimen sulfidized at T=800°C, P<sub>S2</sub> = 0.03 torr.

b. Top view of sulfidized Mo specimen in a.
Fig. 2.  a. Edge of the sulfidized Alfa specimen $T=800^\circ$C, $P_{S_2}=0.03$ torr. 14 hrs. 5,000X.
b. Edge of the same specimen. 5,000X.
remained on the surface as shown in Figure 27. This is further evidence for the inward diffusion of sulfur.

4. Orientations of the Sulfide Crystals in Scales

Figure 28 shows the X-ray diffraction pattern from the Mo specimen (Mo + MoS₂) after sulfidation at 800°C in Pₘₒ₂ = 0.03 torr for 66 hours. In this pattern, MoS₂ should exhibit the highest peak for {001} at 14.75°(2θ), but this peak is missing. Instead, the planes {101} MoS₂ and {100} MoS₂, from the pyramidal and prism planes, respectively, show strong peaks. By comparing the patterns from Mo and Mo+MoS₂, all Mo peaks have decreased in relative intensity except the one at 58.65°(2θ), which results because the peak from {110} MoS₂ at 58.24(2θ) is overlapping. Missing peaks in diffraction patterns are caused by the preferred orientation of crystals. Based on the absence of peaks from the basal planes({001} MoS₂), the predominant arrangement of the sulfide crystals formed on the Mo grains of {100} preferred orientation is the one drawn schematically in Figure 29.

The epitaxial relations are described by {100} MoS₂ || {100} Mo and {001} MoS₂ ⊥ {100} Mo. This arrangement is favored, because the lattice parameter "a" of the MoS₂ is a good match with that of Mo, and the lattice parameter "c" of MoS₂ is about four times that of "a"
Fig. 27. Gold markers on the surface of the MoS$_2$ scale after sulfidation at 900°C, P$_{S_2} = 0.03$ torr for 1 hr.
Fig. 28. X-ray diffraction patterns from
a. Mo as-rolled surface (Alfa)
b. Mo + MoS\textsubscript{2} scale formed at 800° C, P\textsubscript{S\textsubscript{2}} = 0.03 torr.
c. MoS\textsubscript{2} powder scraped from the scale.
Fig. 29. Schematic diagram of the MoS$_2$ growing epitaxially on the surface of Mo \{100\}. 
for Mo.

An X-ray diffraction pattern was made from the backside of the scale (metal/scale interface) by removing the scale using adhesive tape, and the peak from the basal planes of MoS$_2$( 001)$_{MoS_2}$ was again missing.

The scale was scraped from the specimen, and an X-ray diffraction pattern was made from the scraped MoS$_2$ which was in powder form. As shown in Figure 28, the peak from the basal planes for MoS$_2$ appeared.

The sizes of the individual sulfide crystalline aggregates of the low-temperature MoS$_2$ scale ranged from 0.1 to 0.2 \( \mu \text{m} \) as shown in Figure 30. Thus, the more obvious columnar surface features were not individual grains, but were comprised of thousands of small crystallites as shown in the schematic diagram, Figure 31.

At higher temperatures, the scale morphology was different, revealing a layered MoS$_2$ structure as will be described later.

At the beginning of the sulfidation, perhaps a porous or microcrystalline scale is formed. Somehow the crystallites do not grow larger than some critical size, probably because of the particular structure and epitaxy of the MoS$_2$ crystals. Such an epitaxial layered structure would permit the (relatively rapid) anisotropic diffusion of sulfur between the basal planes or along grain boundaries.
Figure 30. MoS$_2$ scale formed on as-rolled Alfa specimen reacted at T=800°C, and $P_{S_2}$ =0.03 torr for 14 hours. 10KX.

Figure 31. Schematic diagram of the columnar MoS$_2$ scale.
When one \{100\} grain of Mo reacts with \(S_2\), as shown in Fig. 32, it can produce MoS\(_2\) grains of only two different equivalent epitaxial orientations. Because of the mismatch between adjoining MoS\(_2\) crystals of differing equivalent epitaxial orientation on the same Mo grain, they stop growing when they impinge on one another.

For lower temperatures, the nucleation rate must be relatively fast and the crystal growth rate relatively slow, and blocked. Thus, a large number of MoS\(_2\) crystals with the two differing orientations will form on one Mo grain, but their growth is prevented upon impingement.

On the other hand, at higher temperatures, the nucleation rate much slower and the crystal growth rate is relatively fast so that fewer sulfide crystals are able to grow much larger before impingement.

The second photomicrograph in Fig. 25 shows that the size of one aggregate of MoS\(_2\) crystallites is about the same as the grain size of the Mo specimen. So, one grain of Mo reacts to form one aggregate of crystallites. This picture shows that the gaps between aggregates are quite large which makes the scale porous.

Figure 33 shows a schematic drawing of crystallites formed at a former Mo grain boundary; this drawing suggests the reason for the large gap between two aggregates of MoS\(_2\) grains.
Fig. 32. Schematic diagram of the two possible epitaxial modes of MoS₂ formation on Mo of \{100\} orientation.
Fig. 33. Top view of the MoS$_2$ crystallites formed at the former grain boundary of Mo.
5. The Dependence of Kinetics on $P_{S_2}$

At 750°C, Alfa specimens were chosen for experiments at different sulfur activities in order to establish the effect of $P_{S_2}$ on the linear sulfidation rate constant. The 750°C temperature was chosen because 800°C was a transitional temperature between linear and parabolic kinetics, and at 700°C, the sulfidation rate was too low.

Three different sulfur pressures of 0.03, 0.6 and 1 torr were used at 750°C, and the kinetic curves for sulfidation are shown in Figures 13, 34 and 35.

Figure 36 shows the plot of log $k_1$ vs log $P_{S_2}$, and the slope from two points that represent $P_{S_2}$ of 0.03 and 0.6 torr is 0.08. For 1 torr of $P_{S_2}$, the kinetics were not linear, but parabolic; however, a $k_1$ derived from the first 5 points of Figure 36 is included as a square in Figure 37. This $k_1$ from the parabolic plot is not consistent with the other data, and was not used to estimate the slope. The significance of the slope of 0.08 will be discussed later.

In Figure 35, for the sulfidation of Mo at $P_{S_2}=1$ torr, initially the kinetics were parabolic, but after about 1.6 mg/cm² weight gain, clearly the scale fractured and a new parabola began. After about 5 hours, the sulfidation kinetics are described by a sequence of interruptions and parabolic continuations.
Fig. 34. Sulfidation kinetics for Alfa molybdenum specimen at 750°C, $P_{S_2} = 0.6$ torr.
Fig. 35. Sulfidation kinetics for Alfa molybdenum specimen at $750^\circ$C, $P_{S_2} = 1$ torr.
Fig. 36. $P_{S_2}$ dependence of the linear kinetic rate at 750°C.
At 750°C, the Mo sulfidation kinetics were linear for low sulfur activity and parabolic for high sulfur activity. To establish this behavior further and to test the reproducibility of the experiments, another experimental run was conducted at 750°C in $P_{S_2}$ of 1 torr. Figure 37 shows the parabolic plots of $\Delta m$ vs $t^{\frac{1}{2}}$ for the two sets of data represented as crosses and circles. Both plots are linear, indicating parabolic behavior, and the slopes of the two straight lines are quite close indicating good reproducibility.

6. Proposed Mechanism

From the kinetic information and the epitaxial morphology of the sulfide scales, a mechanism for low-temperature molybdenum sulfidation can be suggested.

As demonstrated by the Au markers and the retention of surface markings, sulfur is obviously transported through the MoS$_2$ scale to form new crystals at the Mo/MoS$_2$ interface. With this in mind, the rate limiting step(s) for each period in Figure 11 will be discussed.
Fig. 37. Sulfidation kinetics for Alfa specimen at 750°C from two independent experimental runs represented as o and x, respectively.
a. Period I, Initial Kinetics

The Pilling-Bedworth ratio $(\frac{V_{MoS_2}}{V_{Mo}})$ is about 3.5. Then, for a MoS$_2$ crystal to form or for the already existing crystals to grow, the previously formed sulfide crystallites must be pushed out or extruded toward the surface, and this would introduce microcracks. These microcracks are presumably generated almost continuously so that even the innermost scale can be considered to be porous. As mentioned before, the large mismatch between two adjoining crystallite can also help create porous scale above previous Mo grain boundaries.

To form new crystals at the Mo/MoS$_2$ interface, or to grow these sulfide crystals, the steps illustrated in Figure 38 should be involved. In this illustration, it is assumed that the MoS$_2$ scale is porous everywhere. Because the arrival flux of S$_2$ molecules in the gas phase is clearly adequate to support the observed kinetics, one of the steps 1 to 5 in Figure 38 should be the rate limiting step for Period I.

In Figure 38, step (1) is the transport of sulfur molecules, step (2) is the dissociation of diatomic sulfur molecules to form adsorbed atomic sulfur, and step (3) is the ionization(reduction) of the internally adsorbed atomic sulfur. Step (4) is the diffusion of S$^-$ through MoS$_2$ crystals for the crystal growth. And step
(5) is the nucleation step for new crystallites.

If the rate limiting step were the dissociation of the molecular gas\( (S_2) \), one would expect the sulfidation rate to increase with the square root of the gas pressure. As shown in Figure 36, the power dependence of the linear kinetic rate constant on \( P_{S_2} \) is 0.08. Although the plot of Figure 36 only provides two data points, it is clear that the slope is not 0.5. So the dissociation step of \( S_2 \) can be ruled out as a rate limiting step.

Now, one can say that the following conclusions are probably true.

(1) Dissociation of \( S_2 \) is not the r.l.s. (rate limiting step).

(2) The r.l.s. is affected by the Mo orientation (because \( k_1 \) is affected by the Mo grain orientation)

(3) Formation of small size crystallites indicates that nucleation of new crystallites is going on continuously.

(4) Because the size of the MoS\(_2\) crystallites is small, the growth rate by diffusion of \( S^2^- \) should be fast.

So, it is concluded that out of five steps listed in Figure 38, step (5), the nucleation step, should be the rate limiting step for the linear sulfidation. The epitaxial nucleation process should be affected by the Mo orientation.
(1) Sulfur molecules reach the reaction site
(2) Sulfur molecules dissociate to atomic sulfur
(3) \[ S + 2e = S^= \]
(4) Short distance diffusion of \( S^= \)
(5) Atomic sulfur nucleates a new crystallite

Fig. 38. Illustration of series reaction steps for the \( \text{MoS}_2 \) scale growth.
b. Period II

As mentioned before, after a weight gain of 0.13 - 0.16 mg/cm² (scale thickness: 0.5 - 0.7 μm), the sulfidation kinetics were not linear any longer but similar to parabolic, and showed far slower rates of sulfidation.

A high Pilling-Bedworth ratio indicates that as the scale gets thicker, the compressive stress in the scale becomes higher. Thus, after some critical thickness of the scale, it becomes difficult to make a porous scale, which means that diffusion process through the compact scale begins to become important and slows down the sulfidation rate.

However, this Period II often shows a behavior similar linear kinetics of which the rate is considerably lower than the one in Period I. So, it is believed that this Period II is the transition period from linear to parabolic kinetics.

A hold-up period was often observed between the Period I and II which lasted for about an hour at 700°C and about 20 minutes at 750°C. Although the reason is not clear, it is believed that cracking of the scale might be necessary for the Period II to initiate.
c. Period III

At the end of the Period II, cracking of the scale occurred, which was followed by a clearly parabolic kinetic behavior. In Period III, compact inner scale forms at the interface of Mo and MoS₂, and the diffusion of sulfur through the inner scale becomes the rate-limiting step. As a result, Period III shows parabolic behavior until the increased thickness and the decreased plasticity of the MoS₂ scale prevents further plastic deformation, so that scale fracturing is introduced.

Figure 39 shows the surface of the sulfidized Climax Mo specimen reacted at 750°C in P₈₂ of 0.03 torr for 9 hours. The granular aggregates of MoS₂ product were extruded outward as a result of the scale fracturing.

One further factor should be noted. The Climax specimens showed linear behavior up to 850°C, while Alfa specimens began to show parabolic features at 800°C, and exhibited excellent parabolic behavior at 850°C. Below 850°C, the sulfidation rates of Climax specimens (slightly rolled, with lesser [100] texturing) were lower than those of the Alfa specimens (heavily rolled, oriented). However, at 850°C, the sulfidation rates of Alfa specimens were lower than those of the Climax specimens.
Fig. 39. Surface of sulfidized Climax Mo specimen reacted at 750°C in $P_{S_2} = 0.03$ torr for 9 hrs. 10KX.
From the fact that Alfa specimen showed excellent parabolic behavior at 850°C, cracks apparently do not exist at this high temperature. Then, what caused porous scale for the Climax specimen? The only difference between these two specimens is the grain size and grain orientation. So it is concluded that it is not the microcracks but the microcrystalline scale caused by the two different epitaxial orientations of the MoS$_2$ grains that makes the scale porous.

Figure 40 shows the surface morphology of the scales formed on Climax specimens at 850°C. From the top picture in Figure 40, it is clear that the granular aggregates have random orientations, and probably this orientation mismatch between adjoining aggregates caused gaps between the aggregates through which gaseous sulfur could pass.
Fig. 40. MoS$_2$ scale formed on as-rolled Climax specimen. T=850°C, P$_{S_2}$=0.03 torr, 14 hrs. 2K.
A more detailed examination of the scales formed on Climax specimens shows that there are actually two kinds of grain morphologies; one shows texture (or orientation), which is marked as "B" in Figure 41, and the other shows only small sulfide crystals, which is marked as "A" in Figure 41. Presumably this latter group of grains (or crystals) was formed on \{100\} planes of Mo, because the sulfide grains formed on as-rolled Alfa specimens showed this morphology without showing the texture.

As shown in Figure 41, the part of the scale that has the textured grains is very porous, while the part that has small crystals is less porous.

Thus, the scale formed on planes other than \{100\}_Mo (e.g., \{110\}_Mo) is thought to be more porous than the one formed on \{100\}_Mo, and this may have caused linear behavior for Climax specimens even at high temperature (850°C).
Fig. 41. Sulfide scale formed on as-rolled Climax specimen at 850°C, $P_{S_2} = 0.03$ torr.
14 hrs.
a. 500X     b. 10,000X
B. Elemental Sulfur Experiments at Higher Temperatures (850 - 950°C)

1. General

For a plotting of linear kinetics, the origin of the plot is not too critical. For instance, if one starts recording the kinetics 10 minutes after the sample was lowered, the correct slope in a plot of \( \Delta m \) vs \( t \) is still obtained.

However, for a plotting of parabolic kinetics, the origin of the plot is very important. If a wrong origin is used, a wrong slope of the \( (\Delta m)^2 \) vs \( t \) plot will result. In this plot, because of the squared term of \( (m - m_o)^2 \), the uncertainty of the starting point \( m_o \) will be exaggerated.

As mentioned earlier, about 10 minutes were required for the spring to adjust to the new condition when the specimen was lowered, so that the position of the marker immediately after the specimen was lowered was not used as the origin.

On the other hand, the time for sulfidation can be always measured accurately, and if a plot of \( \Delta m \) vs \( t^{\frac{1}{2}} \) is used, the slope of the curve in this plot is always accurate. For this investigation, plots of \( \Delta m \) vs \( t^{\frac{1}{2}} \) were used to calculate the parabolic rate constants.
Specimens with four different surface finishes were sulfidized at 900°C and in $P_{S_2}$ of 0.32 torr for 10 minutes, and the results are shown in Table III. As can be seen in Table III, the weight gains for the first 10 minutes are not negligible.

A spring constant of $42 \mu g/0.01 \text{ mm}$ was used for the experimental temperature ranges for 800 - 950°C. Spring column temperature ranged from 200 to 230°C. Estimated error for this spring constant is less than 0.7% (see Appendix D).

Table 3.

Weight gains per unit area for Mo specimens after sulfidation at 900°C and in $P_{S_2} = 0.32$ torr for 10 minutes.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Weight Gain (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Climax Mo ground to 400 grit sand paper</td>
<td>$2.39 \times 10^{-2}$</td>
</tr>
<tr>
<td>Climax Mo, as-rolled</td>
<td>$7.32 \times 10^{-2}$</td>
</tr>
<tr>
<td>Climax Mo, polished to 1μm alumina</td>
<td>$5.92 \times 10^{-2}$</td>
</tr>
<tr>
<td>Alfa Mo, as-rolled</td>
<td>$8.26 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
2. Kinetics

At temperatures higher than 850°C, the scaling behavior was clearly parabolic. At first, the plots of $\Delta m$ vs $t^{\frac{1}{2}}$ showed straight lines, then after the scale reached some thickness, the slope began to change to a lower value. After that stage, the scaling behavior was sequences of weight gains and interruptions, as was the case of Period III of the lower temperature curves.

Figures 42 - 50 are the kinetic results for different temperatures and $P_{S_2}$.

Figure 51 is an Arrhenius plot for the parabolic sulfidation of Alfa as-rolled specimens. The activation energy for sulfidation was estimated to be 147.3 KJ/mol (35.2 Kcal/mol).
Fig. 42. Sulfidation kinetics for Alfa as-rolled specimen at $850^\circ$C, $P_{S_2} = 0.11$ torr.
Fig. 43. Sulfidation kinetics for Alfa as-rolled specimen at 850°C, $P_{S_2} = 0.2$ torr.
Fig. 44. Sulfidation kinetics for Alfa as-rolled specimen at 850°C, $P_{S_2} = 1$ torr.
Fig. 45. Sulfidation kinetics for Alfa as-rolled specimen at 900°C, \( P_{S_2} = 0.11 \) torr.
Fig. 46. Sulfidation kinetics for Alfa as-rolled specimen at 900°C, $P_{S2} = 0.32$ torr.
Fig. 47. Sulfidation kinetics for Alfa as-rolled specimen at 900°C, $P_{S_2} = 1$ Torr.
Fig. 48. Sulfidation kinetics for Alfa as-rolled specimen at 900°C, $P_{S_2} = 2.6$ torr.
Fig. 49. Sulfidation kinetics for Alfa as-rolled specimen at 950°C, $P_{S_2} = 0.05$ torr.
Fig. 50. Sulfidation kinetics for Alfa as-rolled specimen at 950°C, $P_{S_2} = 1$ torr.
Fig. 51. Arrhenius plot for the parabolic sulfidation of Alfa as-rolled specimens.
3. The Dependence of the Parabolic Rate on $P_{S_2}$

Figure 52 is a plot of $k_p$ vs $\ln P_{S_2}$ for three different temperatures, 850, 900 and 950°C. As shown in this plot, the parabolic rate shows some dependence on $P_{S_2}$ at low sulfur activities. However, at higher $P_{S_2}$, $k_p$ is independent of $P_{S_2}$. The significance of this will be discussed in detail later.

4. Morphology and Scale Composition

The scale morphology at the scale/gas interface at higher temperatures looks quite different from the one formed at lower temperature. As shown in Figure 53, the scale does not appear to be porous.

When the scales formed at temperatures lower than 800°C, for which the kinetics were linear, were spalled off by bending the specimens, they showed bare metal with metallic color. However, when the scales formed at higher temperatures were similarly removed, the remaining surfaces were not bare metals, but showed a very thin layer of gray color with a slight gold tone. When the sulfidized specimen was bent, the outermost layer (MoS$_2$) cracked easily and could be removed with a fine pointed tweezers. However, the innermost layer was adherent to the metal.
Fig. 52. $P_{S_2}$ dependence of the parabolic rate constant.
Fig. 53. MoS$_2$ scale of Alfa specimen reacted at 900°C in P$_{S_2}$ = 0.11 torr. 20 hrs. 5KX.
Figure 54 shows the top of the inner layers formed at 900°C in $P_{S_2} = 0.11$ torr. The bottom picture shows the inner layer after the specimen was heavily bent. The inner scales formed at 850 and 900°C were not thick enough to show the cross-sections of the scales.

Figures 55 shows the fractured cross-sections of the scales formed at 950°C in $P_{S_2} = 0.05$ torr. In these pictures, the outer scale exhibits a laminated or layered structure, while the inner scale exhibits a blocky equiaxed structure.

In Figure 56, the top picture shows the backside of the MoS$_2$ scale, and the bottom picture shows the topview of the inner scale. Although these two surfaces contacted each other, the sizes of crystals of the two surfaces are obviously different. Actually, MoS$_2$ crystals are columnar (needle-shaped), and the diameter of the needle is in the range of $0.2 \mu m$. The diameter of the blocky crystals of the inner layer is in the range of $0.6 - 0.8 \mu m$. Figure 57 shows the MoS$_2$ crystals remaining on the surface of the inner scale, and the sizes of the two different crystals can be compared.

In Figure 58, the top picture shows the backside of the inner scale, and the bottom picture shows the surface of the metal beneath the inner scale. This metal surface shows the traces of the crystals of the inner scale.
Fig. 54. Inner scale formed on Alfa specimen reacted at 900°C in $P_{S_2} = 0.11$ torr. 20 hrs. 2KX.
Fig. 55. Cross-section of a scale formed on Alfa as-rolled specimen reacted at 950°C in $P_{S_2} = 0.05$ torr for 21 hours. 5KX.
Fig. 56. a. Backside of the MoS$_2$ scale formed at 900°C in P$_S$ = 2.6 torr. 8.5 hrs. 5KX.
b. top view of the inner scale beneath the MoS$_2$ scale described in a. 5KX.
Fig. 57. MoS$_2$ crystals remaining on the surface of the inner scale formed at 900°C in $P_{S_2} = 2.6$ torr. 8.5 hrs. 5XX.
Fig. 58.  
a. Backside of the inner scale formed at 900°C in $P_{S_2} = 2.6$ torr, 8.5 hrs. 5KX.  
b. Surface of the metal beneath the inner scale described above. 5KX.
Adhesive tape was applied to the surface of the MoS\textsubscript{2} scale, and the specimen was bent couple of times, and the MoS\textsubscript{2} scale was successfully removed leaving only the inner scale adherent to the metal, as shown in Figure 59.

An X-ray diffraction pattern was made from this inner layer using the General Electric diffractometer with Cu K\textsubscript{α} radiation and a Ni filter, and is shown in Figure 60. It can be concluded without doubt that this phase is Mo\textsubscript{2}S\textsubscript{3}.

5. Mo\textsubscript{2}S\textsubscript{3} Scale

No investigators have previously reported the existence of the Mo\textsubscript{2}S\textsubscript{3} inner scale beneath the MoS\textsubscript{2} scale in sulfidation, but the formation of Mo\textsubscript{2}S\textsubscript{3} is not surprising. As shown in the Ellingham-type diagram in Figure 4, for all temperatures, there exists a narrow regime of log $P_{S_2}$ where Mo\textsubscript{2}S\textsubscript{3} is stable.

Based on the Ellingham diagram, only a Mo\textsubscript{2}S\textsubscript{3} could be formed if the sulfur activity were kept low enough. At 900°C, the sulfur reservoir was heated to a temperature below but close to the melting temperature of sulfur(119°C) to give a sulfur pressure of about 0.02 torr, and the Mo\textsubscript{2}S\textsubscript{3} scale with a very small amount of MoS\textsubscript{2} on the
Fig. 59. Inner scale formed at 950°C in $P_{S_2} = 0.05$ torr. 23 hrs.

a. 5KX.  b. 1KX.
Fig. 60. Diffraction pattern from the inner scale formed on Alfa Mo at 900°C in $P_{S_2} = 1$ torr.
surface was formed. The rate of scaling was very slow, as shown in Figure 61. Figure 62 shows the top surface of the Mo$_2$S$_3$ scale which was intentionally fractured by bending to show the cross-section of the scale.

At 900°C, when a higher pressure of 0.037 torr sulfur was used, only MoS$_2$ was formed.

At 945°C, with the sulfur reservoir temperature of 107°C, only Mo$_2$S$_3$ was formed. Figure 63 shows the diffraction pattern from this scale, and all the peaks from the scale were identified as those from Mo$_2$S$_3$. From the Table IV in Appendix, sulfur pressure was estimated to be about $0.0076 \text{ torr} (10^{-5} \text{ atm})$.

A marker experiment was conducted with the sputtering technique previously described, and as shown in Figure 64, the gold markers remained on the surface of Mo$_2$S$_3$, indicating inward diffusion of sulfur.

According to the Ellingham diagram, Figure 4, Mo$_2$S$_3$ should also form at lower temperatures, for instance at 800°C. However, the sulfur activity should be as low as $10^{-9}$ atm. Ellingham-type stability diagram for Mo-S-O system at 800°C, Figure 5, shows that the $P_{O_2}$ should be lower than $10^{-20}$ atm to avoid the formation of MoO$_2$. It was not possible to generate this condition for this work, because the TGA system was evacuated only to $10^{-5}$ torr ($1.3 \times 10^{-8}$ atm) before sulfur vapor was introduced.
Fig. 61. Kinetic rate of Mo$_2$S$_3$ formation on Alfa as-rolled specimen at 900°C in $p_{S_2}$ = 0.02 torr.
Fig. 62. Mo$_2$S$_3$ scale formed on Alfa specimen at 900°C for 4 hours. 1,000X.
Fig. 63. Diffraction pattern from the scale formed on polished Climax No at 945°C in $P_{S_2} = 0.0076$ torr.
Fig. 64. Gold markers remaining on the surface of the Mo$_2$S$_3$ scale formed on polished Alfa specimen at 945°C in $P_{S_2} = 7.6 \times 10^{-3}$ torr for 3 hrs. 2KX.
A sulfidation experiment was designed using a cracked specimen with an idea that at the tip of the crack, the sulfur activity must be low enough to form $\text{Mo}_2\text{S}_3$.

A specimen with a crack (estimated crack depth $50 \, \mu\text{m}$) was sulfidized at $800^\circ\text{C}$ in $P_{S_2} = 0.03$ torr. Figure 65 shows the surface of the crack before sulfidation.

As shown in Figure 66, at the mouth of the crack, only $\text{MoS}_2$ was formed. However, at the crack tip, as shown in Figure 67, two different kinds of crystals were formed. The larger crystals are $\text{Mo}_2\text{S}_3$, and the smaller ones are $\text{MoS}_2$.

This experiment indicates that at lower temperatures $\text{Mo}_2\text{S}_3$ can be formed if the $P_{S_2}$ is locally low enough. The sulfidation experiments at lower temperatures ($700 - 800^\circ\text{C}$) did not show any $\text{Mo}_2\text{S}_3$ phase, although the $P_{S_2}$ at the $\text{MoS}_2$/Mo interface should be low enough to form $\text{Mo}_2\text{S}_3$ at the later stage of the sulfidation (e.g., Period III).

Thus, it is concluded that the nucleation of $\text{MoS}_2$ is favored kinetically at the scale/metal interface even if $\text{Mo}_2\text{S}_3$ is stable thermodynamically and forms on the free surface (crack surface).
Fig. 65. The surface of a crack formed in a Climax Mo specimen. 8KX.
Fig. 66. Sulfide crystals formed at the mouth of a crack at 800°C in $P_{S_2} = 0.03$ torr. 5KX.

Fig. 67. Sulfide crystals formed at the crack tip in the same specimen as above. 5KX.
6. Proposed Mechanism

The kinetics of sulfidation of pure molybdenum at temperatures higher than $850^\circ C$ show parabolic behavior, which indicates that the diffusion of sulfur ions or molecules is the rate limiting step for the sulfidation.

From the kinetic results, the following questions can arise:

a. Why does the slope change after some thickness of the scale in a plot of $\Delta m$ vs $t^{1/2}$?

b. In the first stage, before the slope changes, what kind of diffusion process is the rate limiting step, bulk diffusion or grain boundary diffusion?

Because the rate limiting step is also very important in the discussion of the first question, the second question will be discussed first.

Frivaz and Mooser\(^{19}\) reported that MoS\(_2\) is an n-type semiconductor. For the n-type semiconductor scales, generally (especially in oxidation) the ideal Wagnerian parabolic scale growth is nearly independent of any change in the oxidant gas pressure, because the equilibrium concentration of the anion vacancies in the scale next to metal is many orders of magnitude higher than that in equilibrium with the gas phase, and the change of the defect gradient due to the change in oxidant activity is therefore negligible.
However, this independence of the kinetic rate on oxidant pressure is valid only when the outside gas pressure is tens of orders of magnitude higher than the metal/scale equilibrium gas pressure. As shown in Figure 4, for the sulfidation of pure Mo, the gaseous oxidant pressure is only two orders of magnitude higher than the MoS₂/Mo₂S₃ equilibrium gas pressure at 950°C. So, the change in the concentration of point defects caused by the oxidant gas activity is not negligible for the Mo-S system.

At equilibrium,

\[ S^X_S \longrightarrow V^{\cdot\cdot}_S + \frac{1}{2}S_2 + 2e' \]

\[ K = \frac{[V^{\cdot\cdot}_S][P_{S_2}]^2[e']^2}{[S^X_S]} \]

while, \[ [e'] = 2[V^{\cdot\cdot}_S], \quad [S^X_S] = 1. \]

K becomes,

\[ K = 4[V^{\cdot\cdot}_S]^3(P_{S_2})^{1/2} \]

and

\[ [V^{\cdot\cdot}_S] = K'(P_{S_2})^{-1/6} \]
The ionic conductivity, $\sigma_{\text{ion}}$ or $D_S$ should be proportional to $[V_{\text{S}^2}]$. Then, $\sigma_{\text{ion}} \propto K'(P_{S2})^{-1/6}$.

From Eq. (7) on page 8,

$$\tilde{K} \propto k_p \propto K' \left\{ (P_{S2}^i)^{-1/6} - (P_{S2}^o)^{-1/6} \right\},$$

where $P_{S2}^i$ and $P_{S2}^o$ are the equilibrium $P_{S2}$ at the metal/scale and scale/gas interface, respectively.

If we plot $k_p$ vs $\ln P_{S2}^o$, the slope will be,

$$\frac{d k_p}{d \ln P_{S2}^o} = \frac{d}{d \ln P_{S2}^o} K' \left\{ (P_{S2}^i)^{-1/6} - (P_{S2}^o)^{-1/6} \right\}$$

$$= \frac{1}{P_{S2}^o} \frac{d P_{S2}^o}{d P_{S2}^o} K' \left\{ (P_{S2}^i)^{-1/6} - (P_{S2}^o)^{-1/6} \right\}$$

$$= \frac{K'}{6} (P_{S2}^o)^{-1/6}$$

So, the slope of the curve is a function of temperature and $P_{S2}^o$. As the outside $P_{S2}$ increases, the slope decreases, and as the temperature increases, the slope increases.
Figure 52 is a plot of \( k_p \) vs \( \ln P_{S_2}^0 \), and this shows that slope of the curve decreases as \( P_{S_2}^0 \) increases, and the slope increases as the temperature increases.

Thus, at least qualitatively, it can be said that the dependence of \( k_p \) on the outside \( P_{S_2} \) is consistent with a change in the point defect concentration in response to a change in the gaseous \( P_{S_2} \) pressure.

If grain boundary diffusion were the rate limiting diffusion step, the diffusivity of sulfur through grain boundaries should probably not depend importantly on \( P_{S_2}^0 \), and the slope of the plot \( k_p \) vs \( \ln P_{S_2}^0 \) would not change much.

As discussed before, Zelikman reported the melting point of MoS\(_2\) as 1185°C, and 850-950°C would seem sufficiently high for the bulk diffusion to predominate.

For these reasons, it is believed that bulk diffusion of sulfur ions over anion vacancies is the rate limiting step for the parabolic sulfidation.

The observed dependence of \( k_p \) on the outside sulfur pressure(Figure 52) answers another question. As mentioned before, Gerlach and Hamel reported the activation energy for sulfidation as 198.7 KJ/mol, while Fueki et al reported 325.5 KJ/mol. These values are higher than the one from this work, 147.3 KJ/mol.
These differences can be explained qualitatively. Both previous works were conducted using $H_2/H_2S$ gas mixtures, but the investigators used a constant gas mixture ratio at each temperature rather than constant sulfur activity ($P_{S_2}^*$) to calculate the activation energy of sulfidation.

Fueki et al used temperatures ranging from $800^\circ C$ to $950^\circ C$ and a 1:1 ratio of $H_2/H_2S$ gas mixture. As shown in Appendix II, for the gas mixture ratio of 1:1, the equilibrium $P_{S_2}^*$ at $800^\circ C$ is 0.18 torr, while that at $950^\circ C$ is 4.2 torr. As previously discussed, the sulfur pressure dependence of $k_p$ is more evident at low $P_{S_2}^*$, and the $k_p$ at 0.18 torr $P_{S_2}^*$ should be much lower than that expected for 4.2 torr of $P_{S_2}^*$. Thus the activation energy calculated from the constant gas mixture ratio is higher than the one from the constant sulfur activity experiments.

Gerlach and Hamel used a higher temperature range, 900-1050$^\circ C$, and for the constant $H_2/H_2S$ gas mixture ratio of 1:1, $P_{S_2}^*$ ranged from 1 torr to 8.15 torr as shown in Appendix B. At these higher values of $P_{S_2}^*$, the $P_{S_2}^*$ dependence of $k_p$ is not strong, so that Gerlach and Hamel reported a lower value of 198.7 KJ/mol than the 325.5 KJ/mol of Fueki et al.
Let us consider the question of why the slope in a plot of $\Delta m/A$ vs $t^{1/2}$ changes after some scale thickness. As shown in the Ellingham diagram in Fig. 4, for all temperatures, there exists a narrow regime of $\log P_{S_2}$ where Mo$_2$S$_3$ is stable. At the beginning of a sulfidation experiment, for example at $P_{S_2} = 0.03$ torr, MoS$_2$ is stable, and MoS$_2$ begins to form. As the sulfidation progresses, the Mo/MoS$_2$ interface should reach a local metastable equilibrium with a $P_{S_2}$ value that is higher than the equilibrium $P_{S_2}$ for Mo/Mo$_2$S$_3$ coexistence. So long as the sulfur transport process can maintain this $P_{S_2}$ (Mo/MoS$_2$) at the MoS$_2$/Mo interface, only MoS$_2$ crystals will be formed and grow.

But as the scale grows, the rate of sulfur influx decreases according to Fick's first law. Then, after the scale reached some critical thickness, it becomes difficult to maintain the metastable $P_{S_2}$ (MoS$_2$/Mo), and the $P_{S_2}$ at the interface becomes lower. At this time Mo$_2$S$_3$ becomes stable, and begins to form. Because of the slower growth rate of Mo$_2$S$_3$, as discussed before, the onset of the Mo$_2$S$_3$ formation will slow down the sulfidation rate, and cause a change in the slope of $\Delta m/A$ vs $t^{1/2}$ plot curve. Then series diffusion of S through MoS$_2$ and Mo$_2$S$_3$ will provide rate control.
In addition to the $\text{Mo}_2\text{S}_3$ formation reaction at the $\text{Mo}_2\text{S}_3$/Mo interface, the following reaction would also proceed at the MoS$_2$/Mo$_2$S$_3$ interface,

$$\text{Mo}_2\text{S}_3 + \frac{1}{2}\text{S}_2 \rightarrow 2 \text{MoS}_2.$$ 

7. Separation of the Defect Concentration and Diffusion Coefficient

The technique developed by Rosenberg$^{29}$ for the separation of defect concentration and diffusion coefficient was attempted in this work for the Mo-S system. This technique will be explained using the Mo-S system as an example.

First, application of the method is possible if volume diffusion of ionic defects in the sulfide(or oxide) layer is the rate limiting step in the process of metal sulfidation(or oxidation), if local equilibria are maintained at metal-sulfide and oxide-gas interfaces, and if the sulfide layer is compact, monophase, and well adherent to the metal.

When the thickness of the MoS$_2$ scale, $X$, is very large compared to the thickness increase for a short time, $\Delta X$, the concentration gradient of the anion vacancies would appear as in Figure 68.
Fig. 68. Sulfur vacancy concentration profile in MoS$_2$ scale for the gaseous $P_{S_2}$ of 0.03 torr.

Fig. 69. Sulfur vacancy concentration profile in MoS$_2$ scale for the gaseous $P_{S_2}$ of 5.3 X 10$^{-13}$ torr.
Now, if the gaseous $P_{S_2}$ were changed to $5.3 \times 10^{-13}$ torr, the gradient would become flat as shown in Figure 69 when the system reaches an equilibrium. In doing this, the MoS$_2$ scale would desorb some sulfur to create more vacancies.

If the gaseous sulfur pressure is returned to the original value ($3 \times 10^{-2}$ torr), the defect concentration profile returns to the one before interruption (Figure 68). This time the specimen will gain weight. This weight gain rate can be interpreted mathematically, by solving the Fick's second law,

$$\frac{\partial C(X)}{\partial t} = D \frac{\partial^2 C(X)}{\partial X^2} \quad \cdots \quad (10)$$

with the initial and boundary conditions that

$$\begin{align*}
C(X) &= C_o \quad \text{for all} \ X \quad \text{at} \ t = 0, \\
C(X) &= C_o \quad \text{at} \ X = 0 \\
C(X) &= C_1 \quad \text{at} \ X = x \\
\end{align*}$$

where $C(X)$ represents the vacancy concentration, and $D$ represents the diffusivity of sulfur ions.

The solution of the Eq. (10) has two simple limiting forms. At the beginning of the reaction,

$$\Delta m = B \ t^{\frac{1}{2}} \ (t \ll x^2/D)$$

where $B = 1.12 \ D^{\frac{1}{2}} c_0$.  

Later in the reaction,

$$\Delta m = Q + RT \left( t > \frac{x^2}{2D} \right)$$

where \( Q = \frac{XC_0}{3} \) and \( R = \frac{DC_0}{X} \).

From the values of \( B \) and \( R \), we can get \( D \) and \( C_0 \).

Experiment:

A molybdenum specimen was sulfidized at 800°C and in \( P_{S_2} = 0.03 \) torr until further weight gain was slow. Then the system was evacuated to lower the sulfur activity. The specimen lost weight, which was quite fast and in larger magnitude than expected. When the original \( P_{S_2} \) was reintroduced, the rate of weight gain was parabolic. When further weight gain was negligible, the total weight of the specimen was below the original weight (before evacuation). Furthermore, sometimes the weight loss because of the evacuation was even more than the weight that the molybdenum specimen gained since the beginning of the sulfidation.

After studying the Ellingham diagram, Figure 5, it was concluded that when the system is evacuated, sulfur activity goes down, and \( \text{MoO}_2 \) becomes stable. The vapor pressure of \( \text{MoO}_3 \) over \( \text{MoO}_2 \) is quite high, and this caused the weight loss. When original \( P_{S_2} \) was restored, the following reaction might have caused part of the
weight gain

\[
\begin{align*}
\text{MoO}_2 + S_2 & \rightarrow \text{MoS}_2 + O_2 \\
111.94 \text{ g/mol} & \rightarrow 127.94 \text{ g/mol}
\end{align*}
\]

Since so much uncertainty was involved, it was concluded that this technique cannot be used for elemental sulfur experiment.

8. Formation of Molybdenum Oxides

In one experiment, after running the system more than 56 hours, a leak developed, and MoO\textsubscript{2} was formed on the surface of MoS\textsubscript{2}. Figure 70 shows the MoO\textsubscript{2} crystals formed on MoS\textsubscript{2}. MoO\textsubscript{2} has a monoclinic structure.

In another experiment, a small amount of air was leaked into the system intentionally after molybdenum specimen was sulfidized for some time, and white fume of MoO\textsubscript{3} was generated almost instantly. Figure 71 shows the MoO\textsubscript{3} crystals (larger crystals) and MoO\textsubscript{2} crystals formed on MoS\textsubscript{2}.

The following reactions must be very fast.

\[
\begin{align*}
2 \text{MoS}_2 + 3 O_2 & \rightarrow 2 \text{MoO}_3 + 2 S_2 \\
\text{MoS}_2 + O_2 & \rightarrow \text{MoO}_2 + S_2
\end{align*}
\]
Fig. 70. MoO$_2$ crystals formed on MoS$_2$. 5KX.
Fig. 71. MoO$_3$ crystals (larger crystals) and MoO$_2$ crystals formed on MoS$_2$. 2KX.
C. Sulfidation of Pure Molybdenum in $\text{H}_2/\text{H}_2\text{S}$ Gas Mixtures

The kinetic results from the sulfidation experiments in $\text{H}_2/\text{H}_2\text{S}$ gas mixture are shown in Figures 72 - 75. Figure 76 shows the Arrhenius plot for the sulfidation in $\text{H}_2/\text{H}_2\text{S}$ gas mixture. The results from the elemental sulfur experiments and those of previous works are also plotted for comparison.

As shown in Figure 76, the parabolic rate constants for the $\text{H}_2/\text{H}_2\text{S}$ environment were almost one order of magnitude higher than those from the elemental sulfur environment at 850 and 900°C.

However, at 940 and 950°C, $k_p$ from $\text{H}_2/\text{H}_2\text{S}$ gas mixture experiments were far lower than expected. After the experimental runs at higher temperatures (~950°C), the ends of the inside tubes were colored with dark green and metallic color as shown in Figure 77.

An X-ray diffraction pattern was made from the part with dark green color, and one peak appeared at the position of the highest peak of $\text{MoS}_2$. So, there is a good possibility that $\text{MoS}_2$ is deposited on the surface of the tube.

An X-ray diffraction pattern was also made for the surface with metallic color, but those peaks were not identified.
McCabe\textsuperscript{12} noted that MoS\textsubscript{2} seems not to be volatile, so it is reasonable to propose that gaseous MoS\textsubscript{3} was formed by the following reaction:

$$\text{MoS}_2 + \text{H}_2\text{S} \rightarrow \text{MoS}_3 + \text{H}_2$$

This MoS\textsubscript{3} is unstable and decomposes to MoS\textsubscript{2} with a reaction

$$\text{MoS}_3 \rightarrow \text{MoS}_2 + \frac{1}{2} \text{S}_2$$

on colder parts of the reaction chamber.

It is proposed that the formation of the volatile species (probably MoS\textsubscript{3}) caused the deviation of the kinetic rates at $\sim 950^\circ$C.

Now, the reason for the large discrepancy between the data from elemental sulfur and H\textsubscript{2}/H\textsubscript{2}S experiments should be discussed.

Simkovich\textsuperscript{30} suggested that hydrogen present in the aggressive medium may be incorporated as a proton into the crystal lattice of the scale, which results in a change at the concentration of defects in the scale.

This suggestion can be used to explain the above mentioned discrepancy. Protons can easily enter into the interstitial site of the MoS\textsubscript{2} lattice, and to satisfy the electrical neutrality condition, more sulfur ions (S\textsuperscript{2–}) should fill the sulfur vacancies. As result, the number
of the sulfur vacancies will decrease. On the assumption
that the diffusivity of H\(^+\) inside the MoS\(_2\) lattice is
not high, the gradient of the sulfur vacancy concentration
(see Fig. 68) becomes higher than the one in elemental
sulfur atmosphere, and induces higher sulfidation rates
in H\(_2\)/H\(_2\)S atmospheres.
Fig. 72. Sulfidation kinetics for Alfa polished specimen at 950°C, $P_{S_2} = 1$ torr. $P_{H_2S}/P_{H_2} = 0.7$. 

$T = 950°C$

$P_{H_2S}/P_{H_2} = 0.7$

$P_{S_2} = 1$ torr.
Fig. 73. Sulfidation kinetics for Alfa polished specimen at 940°C. $P_{H_2S}/P_{H_2} = 1$. 
Fig. 74. Sulfidation kinetics for Alfa polished specimen at 900°C. \( P_{S_2} = 1 \text{ torr, } P_{H_2S}/P_{H_2} = 1 \).
Fig. 75. Sulfidation kinetics for Alfa polished specimen at 850°C. \[ T = 850^\circ \text{C} \]
\[ P_{S_2} = 1 \text{ torr} \]
\[ \frac{P_{H_2S}}{P_{H_2}} = 1.7 \]
Fig. 76. Arrhenius plot for the parabolic sulfidation in elemental sulfur and $\text{H}_2/\text{H}_2\text{S}$ gas mixture.
Fig. 77. Colors of the deposits after the experimental runs at $\sim 950^\circ C$
V. SUMMARY AND CONCLUSIONS

The kinetics and mechanism of sulfide scale growth on pure molybdenum have been investigated in an elemental sulfur ($S_2$) and $H_2/H_2S$ gas mixture atmosphere for the temperature range of 700 - 950°C. A high sensitivity quartz spring ($40 \mu g/0.01$ mm) was used to monitor the weight gain of the specimen. Sulfur vapor was generated from an independently heated liquid sulfur reservoir and ranged in pressure from 0.03 to 2.6 torr.

Conclusions are the following:

1. Below about 750°C, time-independent (linear) kinetics were observed and the linear scaling rate was on the order of $10^{-8}$ g/cm$^2$.sec. (2.03 $\times 10^{-8}$ g/cm$^2$.sec, for example, at 706°C, $P_{S_2} = 0.03$ torr).

2. The activation energy for the linear sulfidation kinetics is $103.4 \pm 21.2$ KJ/mol.

3. For temperatures higher than 850°C, clear parabolic behavior was observed. The parabolic rate constants are on the order of $10^{-11}$ g$^2$/cm$^4$.sec.

4. The activation energy for the parabolic sulfidation kinetics is about 148 KJ/mol.
5. For all the experimental temperatures, the sulfide scales have uniform thickness and columnar structure. The sulfide crystals have strong epitaxial relationship with the metal.

6. For the linear kinetics, sulfide crystal nucleation process is believed to be the rate limiting step. It is also believed that the microcrystalline scale caused by the two different epitaxial orientation of MoS$_2$ crystals makes the scale porous.

7. For parabolic behavior, a bulk diffusion process of sulfur ions is the rate limiting step. After the scale reaches some thickness, Mo$_2$S$_3$ crystals begins to form, and this reduces the kinetics somewhat.

8. The parabolic rate constants of sulfidation in H$_2$/H$_2$S gas mixtures were about one order of magnitude higher than those from elemental sulfur experiments.
APPENDIXES
I. Calculation of the $P_{S_2}$ over Liquid Sulfur

The following equation was obtained by Meisen and Bennet\textsuperscript{31}, and was used for calculation of the liquid vapor pressure.

\[ \ln P = a + bT + c/T + d/T^2 \]

where $P$ denotes the total pressure and $T$ the absolute temperature.

For the total pressure in torr,

\[ a = 5.01600 \]
\[ b = 0.00542412 \]
\[ c = 1,439.83 \]
\[ d = -2,208,580 \]
II. Calculation of the $P_{S_2}$ in the Reaction Chamber at High Temperature.

The mean free path for the sulfur molecules ($S_2$) was calculated to be less than 0.2 cm at 25°C for lowest total sulfur pressure used (0.03 torr). The diameter of the reaction chamber is about 6 cm, and the reaction chamber was considered to be in the viscous pressure regime and the pressure inside the chamber to be uniform everywhere.

At equilibrium, for the reaction

$$i \text{ S}(l) \longrightarrow S_i(g),$$

equilibrium constant $K$ is

$$K = \frac{P_{S_i}}{a_i S(l)}.$$

$$\Delta G^0 = -RT \ln K = -RT \ln \frac{P_{S_i}}{a_i S(l)}$$

$$\frac{P_{S_i}}{a_i S(l)} = \exp(-\Delta G^0 RT), \text{ and}$$

$$P_{S_i} = a_i S(l) \exp(-\Delta G^0 RT).$$

For 540°C, for example, vapor pressure over liquid sulfur is 2583 torr$^{-1}$. So for total $P_{S_2} = 0.03$ torr, $a_{S(l)}$ is $1.16 \times 10^{-5}$. As a result, the following is true.

$$a_{S(l)}^2 \gg a_{S(l)}^3 \gg a_{S(l)}^4 \ldots .$$
Thus, $P_S_i$'s for $i > 3$ can be neglected, and it was concluded that for the experimental temperatures for this work, gaseous sulfur was mainly consisted of $S_2$.

III. Vapor pressure of solid and liquid sulfur

Table 4

Vapor pressure of solid and liquid sulfur

<table>
<thead>
<tr>
<th>$P_{\text{Total}}$ ($10^{-9}$)</th>
<th>$T, ^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-9}$</td>
<td>294</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>310</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>328</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>349</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>375</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>408</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>449</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>509</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>592</td>
</tr>
<tr>
<td>1</td>
<td>717.75</td>
</tr>
</tbody>
</table>
APPENDIX B

To get the gas mixture ratio for the desired $P_{S_2}$, the following calculations were used, and the graph in Fig. 78 was drawn.

\[ 2 \text{H}_2 + S_2 \rightarrow 2 \text{H}_2S \]

\[ K = \frac{(P_{H_2S})^2}{(P_{H_2})^2 P_{S_2}} = \frac{1}{P_{S_2}} \left( \frac{P_{H_2S}}{P_{H_2}} \right)^2 \]

\[ \frac{P_{H_2S}}{P_{H_2}} = (P_{S_2} \cdot K)^{\frac{1}{2}}, K = \exp \left( -\frac{\Delta G^0}{RT} \right) \]

\[ \Delta G^0 = -43,160 + 26.7 T \text{ (from ref. 33)} \]

Using the same calculations, $P_{S_2}$ for the $P_{H_2S} / P_{H_2} = 1$ for different temperatures were obtained, and are shown in the Table IV.

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Fig. 78. \( \frac{P_{H_2S}}{P_{H_2}} \) for different \( P_{S_2} \) at different Temp.
Table IV. $P_{S_2}$ for $\frac{P_{H_2S}}{P_{H_2}} = 1$

for different temperatures.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$P_{S_2}$ (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.18</td>
</tr>
<tr>
<td>850</td>
<td>0.44</td>
</tr>
<tr>
<td>900</td>
<td>1.00</td>
</tr>
<tr>
<td>950</td>
<td>2.13</td>
</tr>
<tr>
<td>1000</td>
<td>4.3</td>
</tr>
<tr>
<td>1050</td>
<td>8.15</td>
</tr>
</tbody>
</table>
Two flowmeters purchased from Matheson were used for H$_2$S and H$_2$, and they were calibrated using a soap bubble technique. The calibration curves are shown in Figures 79 and 80.
Fig. 79. Calibration curve for $H_2$. 
Fig. 80. Calibration curve for $\text{H}_2\text{S}$. 

relative position of the float

flow rate (cc/min.)
APPENDIX D

The spring constant was measured to be $40 \, \mu g/0.01\text{mm}$ for spring column temperature of $25^\circ\text{C}$, and $42 \, \mu g/0.01\text{mm}$ for $200^\circ\text{C}$. Assuming a linear behavior, a plot for spring constant vs temperature was drawn as shown in Fig. 81.

For higher temperature kinetics measurements ($850$-$950^\circ\text{C}$), a spring constant of $42 \, \mu g/0.01\text{mm}$ was used, and the error was calculated to be less than $0.07 \%$.

Fig. 81. Spring constants as a function of the spring column temperature
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