MASTER

Fifth Annual Progress Report

Fundamental Studies of High-Temperature Corrosion Reactions

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A. OVERALL PROJECT

1. Personnel - In addition to the Principal Investigator Professor Robert A. Rapp, five researchers have received full or partial support on this contract during the past year:

a) Dr. Suresh Verma joined the project in August 1979. Dr. Verma received his graduate education and Ph.D. in 1972 at Liverpool University with Professors Whittle and Stringer. He has also conducted high-temperature corrosion research at Manchester and Cranfield Institutes of Technology. In his work on this project, Dr. Verma will adapt the SEM for hot-stage in-situ oxidation studies.

b) B. S. Lee has conducted research in the mechanism of reaction of molybdenum in gaseous sulfur environments. Mr. Lee should complete his Ph.D. thesis research within the next renewal period.

c) G. M. Raynaud received his B.S. degree in Electrochemistry from Grenoble Polytechnical University in France. Mr. Raynaud is conducting his M.S. thesis research on the study of the oxidation of Cu, Ni and Fe in the hot-stage SEM, which he should complete around December 1980.

d) In May 1979, Dr. S.N.S. Reddy completed 4 years of very productive solid-state electrochemical research in the fluoridation of solid copper and nickel, and in studies of the electronic conduction in CaF_2 and BaF_2 electrolytes. This research uncovered relatively large solubilities and high dif-

diffusivities for atomic fluorine in these metals, the first such data in the literature for any halogen in any metal. Dr. Reddy's research resulted in five publications and many presentations to date, and one further paper is pending. Currently, Dr. Reddy is employed as Research Metallurgist at Amoco Research Laboratory in Naperville, Illinois. Dr. Reddy intends to become a U.S. citizen.

e) In July 1979, Dr. C. F. (Rax) Chou completed his Ph.D. thesis on "The Effect of Oxygen on Conduction and Electrochemical Behavior of CaF_2 Electrolytes." The publication of this work is in preparation. At the present, Dr. Chou is working as a Research Metallurgist in the Babcock and Wilcox Research Laboratory in Alliance, Ohio.

2. Presentations and Publications of Past Year - A previously reported paper by Reddy and Rapp will appear in the March issue of Metall. Trans. B, and a copy of the galley proof is attached: S.N.S. Reddy and R. A. Rapp, "The Diffusivity and Solubility of Fluorine in Solid Nickel", Met. Trans., 11B, March (1980).

Another previously reported paper appeared in print, ~~and a reprint is attached~~

S.N.S. Reddy and R. A. Rapp, "Electronic Conduction in the Solid BaF_2 Single Crystal Electrolyte", J. Electrochemical Soc., 126, (1979) 2023-5.

A third paper has been recently submitted for publication, and a preprint is attached:

S.N.S. Reddy and R. A. Rapp, "Internal Fluoridation of

Ni-5.6% Alloy", submitted to Metall. Trans. B. in February 1980.

During the past year a number of oral presentations were made. "The Solubility and Diffusivity of Fluorine in Solid Nickel and Copper" was presented at the following laboratories or meetings in October 1979:

Universities of Osaka, Kyoto, Nagoya and Tokyo Institute of Technology in Japan, at an NSF-sponsored U.S.-Japan Seminar in Honolulu. (DOE travel funds were not involved in this foreign travel.) This talk was presented as a seminar at Purdue University on December 3, 1979, and is scheduled at Case-Western on March 4, 1980.

Within the next couple months, Professor Rapp will complete the final draft for an Audio-Lecture course on High-Temperature Corrosion for the American Chemical Society.

On April 4 and 5, Professor Rapp, with Professor R. W. Staehle, taught the AIChE course "Fundamentals of Corrosion" in Houston, Texas.

Professor Rapp is presently organizing a NACE initiated, but multisponsored, International Conference on High-Temperature Corrosion. The meeting will be held March 2-6, 1981 at the Radisson Scottsdale Hotel (Phoenix, AR). About 200 participants are expected. The proceedings will be published in a text suitable for graduate study instruction.

Throughout the past year, Professor Rapp has participated on a DOE-initiated NMAB Panel on Batteries; three two-day sessions in Washington and in Los Angeles were held. On April

25 and 26, Professor Rapp participated in the DOE (Tom Scott) Review of Batteries in Washington, D.C.

Upon the invitation of the DOE Materials Science Division, Professor Rapp (with Prof. D. Macdonald of OSU) organized a research panel review of the subject "Corrosion in Advanced Energy Systems". A national survey of corrosion problems was made, and a three-day meeting was held at Ohio State University on June 18-20. Later, a comprehensive report of the panel findings and research recommendations was written and presented orally at DOE Germantown Laboratories on October 30, 1979. The final report of this DOE research panel is presently being printed at University of Illinois.

Report on Research Progress

The previous research on metal fluoridation reactions has been essentially completed. The current research concerns two ongoing tasks: 1.) The In-Situ Study of Metal Oxidation Reaction (by S. Verma and G. Raynaud) and 2.) The Mechanism of Sulfidation of Molybdenum by Sulfur Gases (by B. S. Lee).

In the in-situ oxidation study, a used SEM microscope was acquired (\$15,000 OSU matching funds) and installed in July 1979. Dr. Verma and Mr. Raynaud arrived at Ohio State University in August and September 1979, respectively. In a period of about six months, these investigators have designed and built a very efficient and effective hot-stage into the SEM, and have provided a leak tube for the entry of non-condensable reactive gases to the specimen surface. Three preliminary oxidation runs, two for copper and one for a Ni-5%Cr alloy, at 850°C and $P_{O_2} = 2 \times 10^{-5}$ atm have shown exceptional promise for the continuous observation of the scale/gas interface at 10,000X and lower magnification. The experimental details and the preliminary results are presented in this report.

Most of the experiments by B. S. Lee reacting Mo in S_2 vapors have been completed, i.e., the temperature dependence of the kinetics have been established. Some further measurements will be made in S_2 vapors to establish the P_{S_2} -dependence of Mo sulfidation kinetics. Then similar studies will be conducted in H_2/H_2S gas mixtures and perhaps in $H_2/H_2S/H_2O$ gases. SEM characterization of the product scale and interpretation of the

results will continue.

In the following text, a detailed description of progress and results on the two tasks is presented.

1. In-Situ Studies of Metal Oxidation

(S. Verma and G. Raynaud)

A. Modification of SEM Specimen Stage to Include a Hot Stage and a Gas Pipe.

This research deals with the modification of a scanning electron microscope (Cambridge Model Mark IV) so that in-situ studies of metal oxidation could be carried out at a known temperature and in a controlled gaseous environment. A used SEM microscope was acquired and installed by Clark Houghton of Secondary Images in Hillsborough, Ohio. The instrument was equipped with a scintillator-photomultiplier device for collection of secondary electrons to produce the desired image.

There have been only two previous basic designs of a hot-stage for secondary electron microscopes¹⁻⁵ but neither of these seemed adequate for the present requirements. However, previous authors did describe a number of factors which are important for any hot-stage design. In particular, non-magnetic materials were recommended as materials of construction, and a clean dc power supply is required because any ripples present in the power supply would produce an alternating magnetic field to disturb the electron beam or decrease the signal/noise ratio. The use of radiation shields around the specimen heater to reduce the heat loss and protect the detector from radiation damage was also discussed. One of the authors^{1,2} used a biased grid between the detector and the heater to minimize the noise in the

picture due to thermionic electrons emitted from the sample or the heaters. In previous work^{3,5}, degassing of the specimen stage at high temperature was found to be a problem. Mostly, the use of ceramics in the construction of the hot-stage contributed to degassing at high temperatures. The correct positioning of a thermocouple was found to be important in all cases. But, no adverse effect of gas entry to the specimen chamber of the microscope was reported, especially when the volume of gas was small^{3,5}.

With these factors in mind, the specimen stage of this research was modified for high-temperature use. Various problems encountered with the modification and the resulting performance of the microscope are discussed here. The study of the nucleation and growth of surface oxide scales on metals and alloys at elevated temperature is currently in progress.

B. Specimen Stage

The original SEM specimen holder plate was replaced by a type-304 stainless steel plate of 0.6 cm thickness which supported the cylinder (3.17cm ID, 3.81cm OD) containing the specimen, heater, and the radiation shields. The whole assembly is shown in detail in Figs. 1-4. The specimen is surrounded by radiation shields made of molybdenum sheets of 0.04cm. thickness. Three shields (shown in Fig. 3) of diameters 1.27, 1.90 and 2.54 cm are insulated from each other at their bases by ceramic rings cut from alumina tubes. These shields also have similar slip-

over ceramic covers which are positioned after the specimen is placed in the shield assembly. The heating wire is double-wound

tungsten wire of 0.05cm diameter and is insulated from the specimen by ceramic alumina beads as shown in Fig. 3. The specimen is insulated at its top and bottom by thin slices of alumina tube. The specimen sits on a molybdenum circular disc supported by a spring within the first radiation shield. The initial vertical positioning of the specimen is fixed by the adjustment of the spring. The specimen and the three radiation shields contained within the stainless cylinder are mounted by a set of screws positioned at the bottom of the cylinder shown in Fig. 3. A Pt/Pt-Rh thermocouple is inserted into the hole at the bottom of the specimen and is mounted in such a way that the tip of the thermocouple touches the specimen near the oxidizing surface. To minimize the heat loss from the top and bottom of the assembly, additional radiation shields are used. Only one Mo shield of 0.04cm thickness was used at the bottom with three shields at the top. One of the top shields was mounted on the cold part of the stage for maximum efficiency.

The oxidizing gas is leaked to the top surface of the sample by a 0.10 cm ID 304 stainless steel pipe. Helical bellows in the gas pipe and a setscrew on the cylinder (shown in Figs. 1-4) helped to accomodate the movement of the stage in x-y-z direction without changing the position of the gas pipe on the surface.

As shown in Fig. 2, the ceramic ring positioned at the top of the sample was used to fix an electrical ground wire to the specimen. This grounding is very important to drain any electrostatic charge built up on the surface, without which good resolution could not be obtained⁶.

C. Heater and Power Supply

The heater was tungsten wire of 0.05cm diameter and was double-wound around the cylindrical sample to minimize any magnetic field effects. A diameter of 0.05cm was found to be suitable from preliminary calculations of the power requirements for the furnace. Because the heat transfer in vacuum takes place via radiation, the steady-state rate of heat transfer (Q_{h1}) from the heater (h) to the shield (1) could be written by Eq. 1:⁷

$$Q_{h1} = e_o \sigma (A_h T_h^4 - A_1 T_1^4) \quad (1)$$

where e_o is the emissivity (assumed equal for heater and shield), σ is the Stefan-Boltzmann constant, A_h the area of the heater wire, T_h the temperature of the heater wire, A_1 the area of the 1st shield, and T_1 the temperature of the first shield.

For no other heat transfer except radiation, similar relations could be used for the steady-state heat transfer from the first to the second shield, from the second to the third shield, as given by Eq. (2):

$$\begin{aligned} Q_{h1} &= e_o \sigma (A_h T_h^4 - A_1 T_1^4) = e_o \sigma (A_1 T_1^4 - A_2 T_2^4) \\ &= e_o \sigma (A_2 T_2^4 - A_3 T_3^4) = e_o \sigma (A_3 T_3^4 - A_4 T_4^4) \end{aligned} \quad (2)$$

where A_4 and T_4 are the area and the temperature of the stainless cylinder. For various assumed temperatures for the heater and the cylinder, the value of Q_{h1} was evaluated. Hence, the quantity of heat required to raise the temperature of the heater to a known value could be estimated by calculation. Once Q_{h1} or $I^2 R$ was known, selection of I (current) or R (resistance) was possible.

The power calculation was simplified further by assuming that the temperature of the specimen was the same as that of the first shield. The current I would then be given by:

$$I = \left(\frac{e_o \pi \sigma (A_1 T_s^4 - A_4 T_4^4)}{\rho_o \ell [1 + \alpha (T_h - T_i)]} \right)^{1/2} \times \frac{D}{2} \quad (3)$$

where ρ_o is the W resistivity^{8,9} at 20°C ($5.6 \times 10^{-8} \Omega m$), α is 4.5×10^{-3} , T_4 ambient temperature (20°C), ℓ the length of the heating wire, T_s the temperature of the sample, e_o the emissivity⁹ of molybdenum (0.6), D the wire diameter, and σ the Stefan-Boltzmann constant.

The current requirement calculated and experimentally found for heating the furnace to 800-1000°C was found to be in the range of 5-7 amperes. Actually, this calculation has been considerably refined to account for self-reflections by the individual shields.

In the experiments, current was drawn from a 12 volt battery of 500 ampere-hour strength and hence any adverse effects of ripples or ground loops present in any commercial dc supply were eliminated. One battery was found to be adequate for heating the furnace at 850°C for 10 hours after which time the heater terminals were changed to another battery while the initial battery was charged. This periodic change from one battery to another allowed long-term experimental runs to be conducted.

A variable resistor of 150 watts capacity in series with the heater and the battery helped to adjust the current in the

heater wire and hence manual control of the temperature was maintained. In tests conducted to this date, a maximum drift of only 15°C has been recorded. The fact that the tungsten wire resistance increases sharply with heating assists in the maintenance of a constant temperature⁸. Any temperature drop decreases the resistance which at fixed voltage increases the current automatically when other parameters are held constant.

D. Gas Pressure at the Sample Surface

A good vacuum is required for the electron gun and electron collection in the normal operation of the scanning electron microscope. But locally a higher gas pressure can be directed at the specimen surface by leaking gas at a known rate through a gas pipe near the surface of the sample. From the kinetic theory of gases, the Hertz-Langmuir equation given by Eq. (4) was used to evaluate the oxygen pressure at the surface of the sample:

$$J_{\max} = AP_i \sqrt{\frac{1}{(2\pi RTM_i)}}^{1/2} \quad (4)$$

where $J_{\max}$ is the maximum (or gross) molecular flow rate in mole/sec, P_i is the pressure in dynes/cm², M_i the molecular weight of gas (for O₂, 32 gm/mole), R the gas constant (8.314x10⁷ g cm² sec⁻² mol⁻¹ K⁻¹), T the temperature in °K, A the area (cm²) of exposed sample.

In order to use this equation for calculation of effective pressure P_i , the flux $J_{\max}$ must be known. If the gas flow at the surface is known, e.g., 3 cc/min, $J_{\max}$ would equal

$\frac{3}{60} \times \frac{10^{-3}}{22.4} \times \frac{273}{300} \frac{\text{mol}}{\text{sec}}$. For this value of J_{max} , P_i can be calculated and was found to equal 40.4 dynes/cm^2 or 2×10^{-5} atmosphere.

To calibrate the gas flow rate, a setup shown in Fig. 5 was used. Oxygen was passed from the gas cylinder so that part of it bubbled out in the bubbler and part passed through the capillary of the manometer. In this way, atmospheric pressure of oxygen was maintained on the higher pressure side of the manometer and U-tube. The oxygen flow through the capillary of the U-tube created a pressure difference in the two arms of the U-tube and was shown by the fluid height difference. The gas flow rate was calibrated against the difference in fluid height of the manometer. A graduated cylinder (shown by dotted lines in Fig. 5) was incorporated between the leak microvalve of the microscope and the manometer U-tube as shown. Oxygen was passed from one side of the U-tube and the microvalve of the microscope was opened at the other side. While oxygen was flowing through the system, a little soap solution was introduced to form a soap film in the graduated tube. Under the pressure differential, the soap bubble rose in the graduated tube and its volume displacement with time equalled the rate of oxygen flow into the microscope. The height difference in the U-tube was recorded for various flow rates. A plot of the flow rate vs the fluid height difference in U-tube then represents of calibration of the oxygen flow rate. In actual runnings of the microscope, obviously the graduated cylinder was removed and the set up shown by solid lines in Fig. 5 was used.

E. Collection of Secondary Electrons^{6,10}.

The radiation shields could obstruct the direct flow of secondary electrons such that low-energy electrons (0-50 ev) could be deflected or lost, increasing the noise of the image. To avoid this, the collector was kept at maximum value of 300V (positive relative to ground) to increase the signal/noise ratio. Further improvement in the image, especially for high-temperature runs, was made by decreasing the beam voltage while retaining the high-beam current⁶. This reduced the beam diffusion in the sample surface, so that secondary electrons from only the top few layers were collected to improve signal/noise ratio. Increasing the spot size by lowering the final lens current was also found to increase the signal/noise ratio.

The electrical grounding of the specimen was found to be very important^{6,10}. The specimen was therefore insulated from the rest of the stage and electrically grounded. This helped to drain any electrostatic charge accumulated on the surface of the specimen. Otherwise, surface charge tended to deflect the beam from the chosen spot and no resolution was achieved.

Interference from the photons reported by other authors^{1,2} was not found to be significant in our experiments conducted up to a temperature of 900°C. Masking of the secondary electron image by the photons may take place if experimental runs are conducted above 1000°C. Since we do not anticipate using temperatures higher than 1000°C, this problem may not arise.

F. Photography

A polaroid camera was available to take time-lapse photographs for events which occurred rather slowly, and a 16mm movie was adopted for the events that might take place during the start of the in-situ oxidation. To reduce future photography costs, we intend to adopt a 35mm camera to the microscope because a facility is available in the department for developing and printing. Also the movie film used in the runs reported here gave positive frames which were not suitable for printing. Prints used in this report are made from this positive film, and hence showed the reverse effect of the contrast. For example, any bright feature on the scanning electron image would be shown dark on all the prints.

G. Performance

The modified specimen stage of the scanning electron microscope has been successfully used up to a temperature of 850°C with $P_{O_2} = 2 \times 10^{-5}$ atm. Preliminary oxidation studies on pure (OFHC) copper and a Ni-5Cr sample gave interesting and promising results.

Copper

Preannealed copper was electropolished in a solution containing 70% phosphoric acid and 30% distilled water keeping the current density of 6-8A/dm² at 1.5V-2V and at 20°C. The sample was heated to 900°C for 0.5 h. in the microscope before lowering the temperature to 850°C. In 0.5 h. heating at 850°C, thermal etching revealed the grain structure clearly as shown in Fig. 6a. Figure 6a also showed some thermal faceting along

certain crystallographic directions, the orientations of these facets changed from grain to grain. Probably, the thermal faceted surfaces represented high index planes¹¹.

As is well known, surface orientation plays an important role in determining oxidation behavior^{11,12}. For example, oxygen adsorption on near low index planes has been reported and explained in terms of the misorientation in the planes (e.g. 4° off (111) planes) where a step/monolayer interaction leads to decomposition of the step into two nearest (321) steps¹¹.

In our scaling experiments, as soon as oxygen was leaked in the microscope "dendritic" or needle-like oxide nuclei were seen spontaneously. Photograph 6(b) was taken after 0.5 minute oxidation and random nucleation of oxides was evident. It was not possible to observe adsorption phenomena, only the nucleation of the oxide was seen. There is some tendency for the oxide to grow along the direction of the facets described earlier and at right angle to them giving an epitaxial initial scale. After 3-5 minutes, preferential nucleation both at grain boundaries and along the thermal facets became apparent (see Fig. 6, b,c,d). These oxide mounds grew along with a uniform oxide film between them (see Fig. 6e). Such nuclei have been seen by other authors working with thin films of copper where preferred nucleation and growth of oxide on certain planes were observed¹³.

During growth, interesting features including accommodation of growth strains by void formation at oxide grain boundaries were seen. A void shown in the center of Fig. 7a was formed

after 4 hours of oxidation, but within 15 minutes it was filled up by the growing oxide (see Fig. 7b). Because these prints were made from a positive film, a dark void on the screen appeared white in the center of the photograph.

The process of void creation and repair was seen at many grain boundaries elsewhere, and clearly indicated the usual perforation of the scale, often professed by Mrowec for sulfide scales¹⁴. The fact that the repaired void appeared lighter in color (it appears dark in Fig. 7b because of the positive film used) is not clearly understood at this time, but the possibility that the newly grown oxide was electrically charging in the microscope due to the presence of strain cannot be ruled out.

Other features noticed on the growing oxide was the presence of a whisker protruding out at the top of an oxide mound (see Fig. 8 a-d). The discrete crystal faces of the mound changed to a spherical shape and simultaneously the whisker grew in size as shown in the sequence of Fig. 8. Figure 8 (a) also showed some "shadow" effects for the thin oxide film near the base of the mound; these shadows are thought to be result from strain in the thin film caused by the growing mound. The "shadow" effect was reduced after 10 minutes as shown in Fig. 8b. During this interval, some strain relief might have taken place. The occurrence and filling of voids also suggested that during the oxide growth on pure copper local strains are generated. Appearance of the dark line in Fig. 8c is assumed to be a broken whisker (formerly grown at the mound) lying on the surface.

This copper specimen was cooled to room temperature and examined by the optical and scanning electron microscope. The optical photograph shown in Fig. 9a showed few interesting features except that the size of the oxide scale varied from place to place. Figure 9b showed the sample in another SEM. The presence of the voids and considerable debris is obvious, especially at grain boundaries. Probably, most of the debris seen at room temperature resulted from the thermal cycle. Without a hot stage, the post-oxidation SEM examination would not reveal that the debris resulted from cooling. This finding suggests that our equipment is ideal for the study of thermal cycling effects on metal oxidation.

Ni-5Cr Specimen

A coldrolled and annealed Ni-5 Cr alloy was polished mechanically by 600-grit silicon carbide paper and examined in the SEM. At room temperature, scratches could clearly be seen. The contrast of the scratches changed on heating to 850 °C possibly due to strain relief. As soon as oxygen was leaked to the surface, the brightness of the surface changed suggesting a uniform effect of oxygen on the surface but no nuclei could be seen at 200X magnification.

Oxide protrusions appeared along the direction of polishing after 15 minutes (see Fig. 10 a-d). Oxide started appearing at other sites after 30 minutes and were later found to be associated with the metal grain boundaries. Higher magnification showed chromium-rich globules at grain boundaries as shown in Fig. 10e.

The specimen was cooled to room temperature and examined in another (SEM) microscope equipped with an x-ray detector. Examination of the surface showed protrusions, as indeed were seen earlier (see Fig. 11a), and the x-ray image taken for chromium and nickel showed (see Fig. 11 b,c) the oxide protrusions were rich in chromium compared to the matrix. The background surface oxide which had appeared green on visual examination was found to contain both nickel and chromium as seen in Fig. 11 a,b and c.

Summary and Suggestions for Future Research

These preliminary results show that the modified heating stage is working well and many tasks suggested in the last proposal can now be studied. Copper oxidation has shown many interesting features and this anisotropic oxidation behavior on certain planes warrent the use of single crystal at some stage during the next year. Other pure metals planned for study are iron, nickel and chromium in the same temperature range (i.e., 700-950°C). After the oxidation of metals is completed, efforts would be shifted to alloys. Chromia-formers like Fe-25Cr (ferritic alloy), Fe-20Cr-25Ni (austenitic alloy) and alumina-formers such as Fe-25Cr-5Al will be studied.

Further modification of the stage is necessary since the stage used so far does not have the tilt which is often necessary to examine the depth of growing oxide. Either an oblique cut sample at a fixed known angle can be adopted, or the stage should be modified. Both of these methods are under present consideration and a combination of both should solve the problem.

The hot-stage SEM is already equipped with an scintillator-photomultiplier device which collects and accelerates the secondary electrons to give an electronic image. But the emission of secondary electrons has no relationship between their intensity and atomic numbers so the contrast produced by secondary electrons is not so suitable for multiphase, multi-component scales as would be back-scattered electrons. This was the major drawback of the secondary electron image of the Ni-5Cr alloy where a lack of contrast existed between various oxide phases formed on the alloy. The contrast of a back-scattered electron image depends on the composition of the specimen due to a relationship between the intensity of back-scattered electrons and the atomic numbers of the specimen⁶. Hence it is suggested to purchase a back-scattered electron detector which would be very useful in differentiating alloy components in the scale, e.g., aluminum oxide from chromium oxide.

To differentiate between two growing oxides as discussed earlier, if the back-scattered electron image does not produce enough contrast, then x-rays that are emitted from the oxide surface should be collected and analysed. For this purpose, either the x-rays are used as they arise (non-dispersive), or particular wave lengths are selected (dispersive) with the aid of a crystal spectrometer or pulse-height analyser¹⁰. Which one of these two would be adopted would depend on the availability and the cost of a second-hand x-ray detector.

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Figure 1. Photograph Showing the Modified Stage.

st - Specimen stage

mv - Microvalve

G - Gas pipe

R - Radiation Shield, (R' for top and R'' for bottom shield)

E - Ground wire of the stage

T - Thermocouple wire

H - Heater wire or power connection

C - Cylinder

Figure 2. Photograph Showing the Heating Stage and its Parts.

- C - Cylinder
- C' - Ceramic ring
- E - Ground wire
- R - Radiation shields
- S' - Specimen

Figure 2A. Schematic Cross-Sectional Drawing of Heating Stage.

Figure 3. Photograph Showing the Specimen, Heater, Shields, and Cylinder.

- E - Ground wire
- C' - Ceramic ring for specimen insulation
- H - Heater wire
- R'' - Radiation shield for bottom
- R' - Radiation shield for top
- R - Radiation shields

Figure 4. Detailed Assembly - Partially Disassembled to Show Features.
R - Radiation shield, (R' for top and R'' for bottom shields).
S' - Specimen
ST - Stage
T - Thermocouple
C - Cylinder
G - Gas pipe

Figure 5: Apparatus for monitoring and calibrating gas flow into microscope.

Figure 6: Photomicrographs at 1000X showing Cu specimen surface when heated in SEM to 850°C in $P_{O_2} = 2 \times 10^{-5}$ atm.

- (a) heated for 0.5 hr. in vacuum
- (b) heated for 0.5 min. in O_2
- (c) heated for 3 min. in O_2
- (d) heated for 7 min. in O_2
- (e) heated for 40 min. in O_2
- (f) heated for 2.5 h. in O_2

Figure 7: SEM photographs of in-situ oxidation of pure Cu oxidized at 850°C for 4.5 and 4.75 h. in $P_{O_2} = 2 \times 10^{-5}$ atm (2000X)

- (a) Shows voids at grain boundaries (arrows)
- (b) Shows that some voids appearing in (a) have been filled by growing oxide.

Note - contrast is opposite due to use of positive film.

Figure 8: SEM photograph of in-situ oxidation of pure Cu oxidized at 850°C in $P_{O_2} = 2 \times 10^{-5}$ atm (5000X)

- (a) after 4.5 h. oxidation
- (b) after 4.75 h. oxidation
- (c) after 5.0 h. oxidation
- (d) after 5.5 h. oxidation.

Note - contrast is opposite due to use of positive film.

Figure 9(a): Optical micrograph showing surface of pure copper oxidized at 850°C in $P_{O_2} = 2 \times 10^{-5}$ atm. (100X)

(b): SEM micrograph of same surface at 800X. Note oxide debris apparently spalled from grain boundaries.

Figure 10: Sequence of SEM Micrographs during in-situ oxidation of Ni-5Cr alloy at 850°C in $P_{O_2} = 2 \times 10^{-5}$ atm.

- (a) After 30 s. oxidation (2000X)
- (b) After 60 s. oxidation (2000X)
- (c) After 0.5 h. oxidation (2000X)
- (d) After 5 h. oxidation (2000X)
- (e) After 5 h. oxidation (5000X)

Note: contrast is opposite due to use of positive film.

Figure 11(a): Electron image of Ni-5Cr alloy oxidized at 850°C in $P_{O_2} = 2 \times 10^{-5}$ atm, after cooling to room temperature. (5000X)

- (b): Cr X-ray image of section shown in (a)
- (c): Ni X-ray image of section shown in (a)

The High-Temperature Sulfidation of Molybdenum

by

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I. Introduction

For the past year, construction of the previously described experimental apparatus was completed and a number of modifications were made. Figure 1 shows the improved experimental apparatus. In the first couple of experimental runs, the total length of the quartz spring (Item 2 of Fig. 1) 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.

When the sample was lowered into the reaction zone, the column temperature decreased because part of the limiter (Item 4 of Fig. 1) that was previously outside the column absorbed heat from the column. But after about 10 minutes, the column again reached the constant temperature.

To monitor the temperature of the connection between the main column and the sulfur reservoir, a quartz cylinder (Item 14 of Fig. 1) 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 above that of the sulfur

reservoir.

In the initial experimentation 1 atm of flowing Ar gas was used as a carrier for the sulfur vapor, but because of severe oscillations of the spring caused by the convection inside the reaction chamber, it was later decided to conduct the experiment with the elemental sulfur in vacuum. The very high sensitivity of the quartz spring accentuated the severity of any oscillations.

Sulfidation experiments conducted in the Knudsen (free molecular) pressure regime ($\lambda \gg D$) were highly reliable and good kinetic data were obtained. A comparison with other investigations is not possible, because no previous research has been done in this temperature range with elementary sulfur.

A transitional kinetic behavior was found in the temperature range used (700°C ~ 900°C). Below about 750°C, time-independent (linear) kinetics were observed and at higher temperatures (850°C, 900°C) a parabolic time-dependence was obeyed. Dutrizac¹ reported linear kinetics up to 550 C, and Gerlach and Hamel² and Fueki et al³, reported parabolic kinetics at higher temperatures (850°C ~ 950°C) for reactions in H₂/H₂S gas mixtures.

The kinetic data obtained from this investigation will be useful to decide the possible utilization of Mo in gaseous environments involving high sulfur activities but low oxygen activities. The sodium-sulfur high-temperature battery represents one such application.

The morphologies of the MoS₂ product scales were studied utilizing the X-ray diffraction method and the SEM. Upon combining

the kinetic data, morphologies and X-ray diffraction information, a reasonable tentative mechanism for the sulfidation of Mo has been proposed.

At the initiation of this fundamental study of Mo sulfidation, we proposed to use three different atmospheres; pure sulfur vapor, H_2/H_2S gas mixtures and $H_2/H_2S/H_2O$ atmospheres. So far, the sulfur vapor experiments have been nearly completed. After the next few experiments, the apparatus must be modified to avoid the oscillations previously encountered in gases at higher pressures. The experiments should be completed within the year. Some more detailed presentations of results follows.

II. Experimental Apparatus and Procedures

The quartz spring TGA balance for sulfidation research described in the previous proposal was designed and constructed.

After some modifications, this apparatus was successful in establishing sensitive weight changes. Although the thermal expansion coefficient of quartz is very low and positive, the length of the quartz spring (Figure 2) decreases as the column temperature was raised, and vice versa. Then during kinetic runs the spring column was insulated and the column temperature was maintained constant and monitored. The spring constant at $25^\circ C$ is $39.9 \mu g / 0.1 \text{ mm}$. To measure the spring constant at the column temperature used, first a quartz sample of $M + \Delta M$ (g) 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. Table I shows the spring

constants for the column temperature used.

To avoid the formation of any oxides on the sample during residence in the column (at 300°C) prior to the experiment, the sulfur reservoir was heated for more than one or two hours before the sample 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 sample was submitted to the same procedure. The quartz specimen did not gain any weight in 2 hours. In addition to continuous measurements, before and after each experimental run, the weight of the sample was measured and the spring constant was recalculated. Table I lists the values of the spring constant.

Table I. Spring Constants

Sample Temperature	Inert Sample	Sulfidation Experiment
800°C	42.1 $\mu\text{g}/0.01\text{mm}$	41.7 $\mu\text{g}/0.01\text{cm}$
	41.3 $\mu\text{g}/0.01\text{mm}$	
850°C		42.6 $\mu\text{g}/0.01\text{cm}$
		43.5 $\mu\text{g}/0.01\text{cm}$
900°C		43.8 $\mu\text{g}/0.01\text{cm}$

III. Results and Discussion

1. Composition of Scale

From the X-ray diffraction pattern of the scale, it was apparent that MoS_2 is the only corrosion product phase. Other investigators ^{1,2} who studied the sulfidation of pure Mo using a H_2 and H_2S mixture at $800^\circ\text{C} \sim 950^\circ\text{C}$ also reported that MoS_2 was the only sulfide in the scale from the electron diffraction results.

An Ellingham stability diagram for the Mo-S-O system at 800°C , Figure 3, shows that MoS_2 is the only stable phase for the sulfur pressure of 0.03 torr and an oxygen pressure estimated at 10^{-8} atm.

2. Scale Morphology

The morphology of the scale changes as the reaction temperature was changed. But the scale always exhibits a uniform thickness and columnar grains as shown in Figure 4a. There was no spalling of the scale. The original surface condition affects the morphology of the scale somewhat and scratches on the 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. Figure 4b shows the top surface morphology of the sulfidized coupon. Further, evidence for inward sulfur diffusion is shown in Figure 5a and b. This kind of edge (or ledge) morphology is characteristic of inward diffusion of anions and scale formation at the metal/scale interface.

As seen in Figure 6, Mo grain boundaries are not sulfidized preferentially. Thus, if scaling rates should differ for different surfaces, a difference in grain size cannot explain the effect.

3. Kinetics

Four different surfaces were used to study the kinetics of sulfidation in S_2 vapor. Samples purchased from Alfa Chemical were used either as-received or with a ground and polished (to 1 μ alumina) surface. Other samples from Climax Molybdenum Company had a larger grain size than Alfa samples; the same two surface preparations as described above were used for the Climax specimens. The kinetic curves showed that the polished surfaces and as-rolled surfaces did not show significant differences in sulfidation behavior (as will be discussed later). The as-rolled surfaces were always uniform and clean, but it was not possible to prepare the polished surfaces to the exact same condition for all the runs so most of the experiments were conducted with as-received surfaces. Dutrizac³ reported that the rate of molybdenum sulfidation was only slightly dependent on the surface roughness. He examined three samples having different surface conditions for Mo sulfidation at 523°C in 42 torr total sulfur pressure. His linear rate constant for an electropolished specimen was $36 \times 10^{-3} \text{ mg/cm}^2 \text{ hr}$; that for a specimen abraded with emery paper was $44 \times 10^{-3} \text{ mg/cm}^2 \text{ hr}$. The rate constant for the as-received metal, which had been rolled to a smooth finish, was $45 \times 10^{-3} \text{ mg/cm}^2 \text{ hr}$. These results further justify the use of the as-rolled condition as a representative surface.

As shown in Figure 7, another reason for using the as-rolled surface was the observation that half of the ground and polished specimens did not gain weight for 1 to 2 hours at the beginning

of the sulfidation. A possible cause for this behavior is the formation of a passivating oxide film. Until the reaction chamber reaches the desired temperature, the sample is maintained in a zone at 200 to 400°C for about 5 to 6 hours. Although the whole system is evacuated, P_{O_2} may approximate 10^{-8} atm, while P_{S_2} is virtually zero. Under these conditions, the oxide MoO_2 is stable, so that nucleation of the oxide can occur. A polished sample has many scratches and surface damage to provide more sites for oxide nucleation than the as-rolled sample. Perhaps the displacement reaction,

is very slow. Thus when the surface of the sample is covered with oxide crystals the initial sulfidation of the specimen would be slow. Figure 7 is the kinetic curve for sulfidation of the Alfa sample ground and polished to 3 μ alumina and sulfidized at 800°C in P_{S_2} of 0.03 torr. The curve is initially linear, but after about 0.15 mg/cm² gain, further linear kinetics exhibit a slower rate. After some time, in this Period II, there is no weight gain for awhile, but this is followed by a curve (Period III) which approximates a parabola. The next Period IV, shows continuous sequences of 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.

Above 800°C the kinetic curves more closely approached parabolic behavior, and at 900°C the curves were indeed quite parabolic. Thus, 800°C is approximately the transition temperature from linear to parabolic behavior, but this transition is gradual.

Dutrizac,³ as already mentioned, reported linear kinetics in the temperature range of 400 to 550°C and Gerlach and Hamel² and Fueki et al¹ reported parabolic kinetics at the temperature range 800 to 950°C. Dutrizac³ observed that lower values of P_{S_2} favored more parabolic kinetics. However, the effect of P_{S_2} on kinetics will also be studied in our future work.

Figures 8 to 12 are the kinetic curves for as-rolled Alfa samples at different temperatures. The photographs show the surface morphology of the sample after the run. At lower temperatures, the linear behavior for initial kinetics is clear, but for temperatures higher than 800°C, general parabolic behavior is apparent. Figure 13 is the plot of $\ln k_p$ vs $1/T$ showing the initial and secondary linear rate constants. For temperatures higher than 800°C the kinetic constants are not described as an extension of the low temperature behavior.

Figures 14 and 15 report kinetic curves for Climax molybdenum specimens. Figures 16 through 18 describe the kinetics for as-rolled Climax specimens. Linear initial behavior is clearly seen in Figure 16. Figure 19 is an Arrhenius plot of $\ln k_p$ vs. $1/T$ for both as-rolled and polished Climax samples. The slopes, which represent the activation energies for the rate limiting step, are about the same as those for the Alfa specimens in Figure 13.

Figure 20 is the kinetic curve for the as-rolled Alfa sample at 850°C and Figures 21 and 22 are parabolic plots of weight gain vs $t^{1/2}$ for $P_{S_2} = 0.08$ and 0.03 torr, respectively. These linear plots indicate that parabolic behavior is obeyed at the higher temperature ($T \geq 850^\circ\text{C}$). Questions which arise from these results include:

- (1) What causes the break in linear kinetics between period I and II at lower temperatures?
- (2) What are the mechanisms and the rate limiting steps for each period?
- (3) What causes the slope change in the plot of weight gain vs. $t^{1/2}$ for higher temperatures?

To answer these questions, the orientation relations between the sulfide and metal were studied.

4. Orientation of the Sulfide Grains in the Scale.

(1) Orientation of the Mo metal grains, Figure 23a is the X-ray diffraction pattern of the as-rolled surface of a Alfa Mo specimen. The $\{110\}$ peak at $40.54^\circ(2\theta)$ which is expected to exhibit the highest intensity is very small. Instead, the peaks from $\{200\}$ and $\{211\}$ are very strong. This means that the surface of the as-rolled Alfa Mo specimen is predominantly comprised of $\{100\}$ planes. Climax specimens have a slightly lesser degree of preferred orientation. Figure 24 is a schematic diagram of the Mo specimen. An SEM examination showed that the unreacted Mo sheet has a layered surface structure resulting from rolling. (Figure 25).

Figure 24. Schematic diagram for surface of as-rolled Mo specimen.

However, because grinding and polishing should remove this layered surface, but such surface preparation did not affect the kinetics, the layered structure of as-rolled surfaces is not critical to sulfidation kinetics.

2. Orientations of the sulfide crystals in scales

Figure 23b is the X-ray diffraction pattern from the Mo specimen after sulfidation. In Figure 23b, MoS_2 should exhibit the highest peak at 14.75° (2θ), but this peak is missing. Instead, the planes $\{101\} \text{MoS}_2$ and $\{100\} \text{MoS}_2$, from the pyramidal and prism planes, respectively, show strong peaks. By comparing Figure 23a and b, all Mo peaks have decreased in intensity except the one at 58.65° (2θ), which results because the peak from $\{110\} \text{MoS}_2$ at 58.24° (2θ) is overlapping. Missing peaks in diffraction patterns are caused by the preferred orientation of crystals. For the absence of peaks from the basal planes, the predominant arrangement of the sulfide crystals on Mo $\{100\}$ is the one drawn schematically in Figure 26. As seen in the picture, this arrangement is favored, because the lattice parameter "a" of the MoS_2 is a good match

with that of Mo, and the lattice parameter "c" of MoS_2 is about four times that of "a" for Mo. Thus, the epitaxial relations are described by $\{100\}_{\text{MoS}_2} \parallel \{100\}_{\text{Mo}}$ and $\{001\}_{\text{MoS}_2} \parallel \{100\}_{\text{Mo}}$.

Figure 27a is the X-ray diffraction pattern from the MoS_2 scale on Mo. After most of the scales was removed from the sample by grinding, another X-ray diffraction pattern was made and Figure 27b was obtained. This time the peak from the basal planes indeed appear. So the $\{001\}_{\text{MoS}_2}$ peak can result either from the lower part of the columnar scale and from the underlying surface A of Figure 28, or only from the surface A. In the latter case, a MoS_2 scale of random orientation may form beneath the outer columnar scale. This inner (last-formed) scale may be more compact and protective.

The SEM was used to check the existence of a compact inner scale layer, but as seen in Figure 29, such a layer does not seem to exist beneath the columnar scale. This possibility will be investigated further for a very thick scale.

At this point, the recovered MoS_2 diffraction peak seems to arise from the columnar scale and the surface A.

The fact that MoS_2 crystals grow predominantly with their basal planes normal to the $\{100\}$ Mo surface so that the MoS_2 $\{001\}$ is missing from the pattern of the external surface can be explained as follows. The $\{100\}$ Mo surface planes are covered by the MoS_2 film which has its basal planes perpendicular to the surface, as shown in Figure 30. At small angles less than 7° , the X-ray cannot penetrate to crystals with basal planes parallel to the surface. The thickness of the oriented (first formed) outer scales,

δ , is not known, but it can be quite small. Figure 31 suggests that the outermost scale is different from the lower part of the scale.

5. Proposed Mechanism

With the information from the kinetic study and the morphology of the sulfide scales, a mechanism for molybdenum sulfidation can be considered.

1) Macroscopic.

As mentioned earlier, sulfur is obviously transported through the MoS_2 scale to form new crystals at the Mo/MoS_2 interface. The Pilling-Bedworth ratio ($\bar{V}_{\text{MoS}_2}/\bar{V}_{\text{Mo}}$) is about 3.5. Then, for the scale to grow, new crystals must push the existing scale out towards the surface. At higher temperature ($>850^\circ\text{C}$), where the scale must exhibit high plasticity, the required plastic deformation can be accomplished without any cracking of the scale, similar to the high-temperature oxidation of zirconium and zirconium. At lower temperatures ($<800^\circ\text{C}$) new scale formation at the Mo/MoS_2 interface will introduce stresses exceeding some critical value, so that the necessary scale deformation introduces microcracks in the scale. Figure 32 shows that some of the scale grains are pushed out at the surface.

So long as the scale is thin (and therefore plastic), this mechanism becomes important. Such behavior is common to the oxidation of refractory metals (Nb, Ta, Hf, Zr) whose oxides are grown by anion transport.

2. Microscopic Structure

a. Lower temperatures ($\sim < 800^{\circ}\text{C}$).

The sizes of the individual sulfide crystal range from 0.1 to 0.2 μm as shown in Figure 33. Thus, the more obvious columnar "grains" are not one grain, but are made of thousands of small crystals as shown in schematic diagram of Figure 34. Thus, any parabolic kinetics of Mo sulfidation are surely limited by grain boundary diffusion because of the enormous area of the grain boundaries. In Figure 7, Period I and Period II showed linear kinetics. In the first periods, as shown in Figure 33, the initial scale is relatively porous, which means that transport of $\text{S}_2(\text{g})$ should be a fast process compared to the rate-limiting step which can be either the dissociation of S_2 or, more likely, the diffusion of sulfur ions or atoms along the grain boundaries of an adherent compact inner scale of about constant thickness (Loriers mechanism).

At the beginning of the sulfidation, porous scale is forming. Somehow the crystal particles do not grow larger than some critical size, probably because of the particular structure of the MoS_2 crystals (Figure 35). Such a layered structure permits only anisotropic diffusion of sulfur between the basal planes. When one grain of Mo reacts with S_2 , as shown in Figure 36, it can produce MoS_2 grains of several different equivalent epitaxial orientations. Because of the big mismatch between MoS_2 crystals, they cannot grow.

While the crystal may extend basal planes in growth at the

Mo/MoS₂ surface, it is not able to extend laterally, because of the existence of differently oriented epitaxial crystals. Thus MoS₂ grains can only grow normal to the c direction. However, as the scale grows thicker, it becomes more compact, and the individual grains cannot easily extend laterally. So crystals with basal planes parallel to the metal surface become more favorable, when the thickness of the scale reaches some value. Because of the slow diffusion rate for sulfur normal to the basal plane, the randomization of the original epitaxial orientation may represent the break between Period I and Period II. For these reasons, the value δ in Figure 30 is estimated at about 0.5 μm .

The current study of the effect of P_{S₂} on kinetics should provide further insight into the rate-limiting step. At the end of the Period II, the scale is thick enough to make the diffusion of sulfur the rate-limiting step. As a result, Period III shows parabolic behavior which may end when the increased thickness of and decreased plasticity of the scale prevent further plastic deformation, so that fracturing is introduced.

b. Higher Temperature (> 850°C)

As the reaction temperature is increased, the number of intercrystalline pores or tunnels decreases, and the (grain-boundary) diffusion step becomes the rate-limiting step. At 800°C, the kinetic curve shows some semblance of parabolic behavior and at temperatures higher than 850°C the kinetics are perfectly parabolic.

When the thickness of the scale reaches some critical thick-

ness ($\approx 0.6 \text{ mg/cm}^2$) the growth of new MoS_2 crystals at the Mo/MoS_2 interface becomes difficult because of the large thickness of existing scale. The breaks in Figures 21 and 22 are probably explained in this way. Figure 37a shows that the surface of the sulfidized sample at 900°C is not porous. Figure 37b shows that a whole row of MoS_2 crystals can be extruded outward at the scale/gas interface.

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Figure 1. Schematic Drawing of Experimental Setup for Molybdenum Sulfidation Study.

Figure 2. Quartz Spring for Measurement of Rates of Sulfidation of Molybdenum

Figure 3. Ellingham type stability diagram for Mo-S-O System at 800°C

Figure 4. a. MoS₂ scale on as-rolled Mo sample sulfidized at T=800°C, P_{S₂} = 0.03 torr

b. Top view of sulfidized Mo specimen in a.

Figure 5. a. Edge of the sulfidized annealed molybdenum sample
 $T=800^{\circ}\text{C}$ $P_{\text{S}_2} = 0.03$ torr 14 hr.
 b. Edge of the sulfidized rolled sample mag; 5k

Figure 6. MoS₂ scale on annealed ground and polished Mo surface
T = 800°C, P_{S₂} = 0.03 torr (5k)

Figure 7. Kinetic curve for Alfa sample polished to 3μ Alumina.

Figure 8. Molybdenum sulfidation kinetics for as-rolled Alfa specimen at $706^\circ C$, $P_{S_2} = 0.03 \text{ torr}$.

Figure 9. Molybdenum sulfidation kinetics for as-rolled Alfa specimen at 750°C , $P_{S_2} = 0.03 \text{ torr}$.

Figure 10. Molybdenum sulfidation kinetics for as-rolled Alfa specimen at 800°C , $P_{S_2} = 0.03 \text{ torr}$.

Figure 11. Molybdenum sulfidation kinetics for as-rolled Alfa specimen at 850°C , $P_{S_2} = 0.03 \text{ torr}$.

wt. gain $\frac{\text{mg}}{\text{cm}^2}$
scale thickness $\approx 5 \mu$

Figure 12. Molybdenum sulfidation kinetics for as-rolled Alfa specimen at 900°C , $P_{\text{S}_2} = 0.03 \text{ torr}$.

as rolled α sample

Figure 13. Arrhenius plot for sulfidation of as-rolled Alfa Molybdenum at $P_{S_2} = 0.03$ torr.

Figure 14. Sulfidation kinetics for polished Climax Molybdenum specimen at 750°C , $P_{\text{S}_2} = 0.03 \text{ torr}$.

Figure 15. Sulfidation kinetics for polished Climax Molybdenum specimen at 800°C , $P_{\text{S}_2} = 0.03 \text{ torr}$.

Figure 16. Sulfidation kinetics for as-rolled Climax Molybdenum specimen at 750°C , $P_{\text{S}_2} = 0.03 \text{ torr}$.

Figure 17. Sulfidation kinetics for as-rolled Climax Molybdenum specimen at 800°C , $P_{S_2} = 0.03 \text{ torr}$.

Figure 18. Sulfidation kinetics for as-rolled Climax Molybdenum specimen at 850°C, $P_{S_2} = 0.03$ torr.

Figure 19. Arrhenius plot for the sulfidation of Climax samples.

Figure 20. Sulfidation kinetics for as-rolled Alfa Mo specimen at 850°C , $P_{S_2} = 0.08 \text{ torr}$.

Figure 21. Sulfidation kinetics for as-rolled Alfa Mo specimen at 850°C , $P_{S_2} = 0.08 \text{ torr}$.

Figure 22. Sulfidation kinetics for as-rolled Alfa Mo specimen at 850°C, $P_{S_2} = 0.03 \text{ torr}$.

Figure 23. a. X-ray Diffraction Pattern for Mo.
 b. X-ray diffraction pattern for Mo + MoS_2

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inside structure of Mo sample
2000X

Figure 25. Layered surface structure of the rolled Mo sheet.

Figure 26. Schematic diagram of the MoS₂ growing epitaxially on the surface of Mo (100).

Figure 27. a. X-ray Diffraction Pattern for Mo + MoS_2 Scale.
b. X-ray Diffraction Pattern after removing the surface layer of MoS_2 .

Figure 28. Columnar MoS_2 scale and underlying surface A.

Figure 29. a) Cross-section of a sulfidized Climax specimen 1000X
b) Surface A scratched to indicate presence of adherent sulfide layer 2000X

Figure 30. Schematic diagram for the preferred orientation in the outer MoS_2 scale layer.

Figure 31. Cross-section of MoS_2 scale of Alfa specimen.

Figure 32. Surface of Sulfidized Climax Mo specimen reacted at 750°C in $P_{S_2} = 0.03$ torr.

Figure 33. MoS₂ scale formed on polished Climax Mo specimen reacted at T = 800°C and P_{S₂} = 0.03 torr for 2 hrs. (scale thickness ~ 1.3 μm) 1000X

Figure 34. Schematic diagram of the columnar MoS₂ scale.

Figure 35. Layered structure of MoS_2 .

Figure 36. Schematic diagram of the possible MoS₂ formation on Mo.

Figure 37. MoS_2 scale of Alfa specimen reacted at 900°C in $\text{P}_{\text{S}_2} = 0.03$ torr (5000X).