DISTRIBUTION LIST
Quarterly Reports

AIR FORCE
Chief of Metallurgical Group
Flight Research Laboratory
WCRRL
Wright-Patterson Air Force Base, Ohio
Metallurgical Branch
Materials Laboratory
Research Division
Dayton, Ohio
Attn: Mr. I. Perlmutter
Wright Air Development Command
Wright-Patterson Air Force Base, Ohio
Attn: Power Plant Laboratory

NAVY
Bureau of Ordnance
Department of the Navy
Washington 25, D. C.
Attn: Re9a (John S. Nachtman)
Chief, Bureau of Ordnance
Navy Department
Washington 25, D. C.
Attn: Re5
Bureau of Aeronautics
Navy Department
Washington 25, D. C.
Attn: N. E. Promisel, AE-44
(Room 1W68)
Attn: Technical Library, TD-44

ARMY
Office of Chief of Ordnance (ORDTB)
Department of the Army
The Pentagon
Washington 25, D. C.
Attn: E. L. Hollady (2)
Ordnance Department
Springfield Armory
Springfield, Massachusetts
Attn: Mr. H. P. Langston
Watertown Arsenal
Laboratory Division
Watertown, Massachusetts
Attn: P. Kosting

ATOMIC ENERGY COMMISSION
Oak Ridge National Laboratory
Oak Ridge, Tennessee
Attn: Metallurgical Division
W. D. Hanly

Commaning Officer
Naval Air Material Center
Naval Base Station
Philadelphia, Pennsylvania
Attn: Aeronautical Materials Lab.

Director
Office of Naval Research
Department of the Navy
Branch Office
The John Crerar Library Building
Tenth Floor
66 E. Randolph Street
Chicago, Illinois
Attn: Mr. J. A. Bryson (2)

Chief of Naval Research
Department of the Navy
Washington 25, D. C.
Attn: Code 423 (2)

Director
Naval Research Laboratory
Washington 25, D. C.
Attn: Code 420, Metallurgy Division
Code 2020, Technical Library
NAVY (continued)

Bureau of Ships
Navy Department
Washington 25, D. C.
Attn: Code 343 (3)

Navy Liaison Officer for Guided Missiles
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

ONR London, c/o Fleet P. O.
Navy 100, New York, New York
For transmittal to
Armanent Research Establishment
Metallurgical branch
Ministry of Supply
Woolwich S. E. 18, ENGLAND

Commander NANTC
Pt. Mugu, California
Attn: Engineering Department

MISCELLANEOUS

 Battelle Memorial Institute
  505 King Avenue
  Columbus 1, Ohio
  Attn: Mr. Harry E. Goodwin

  British Joint Service Mission
  P. O. Box 165
  Ben Franklin Station
  Washington, D. C.
  Attn: Navy Staff (3)

  California Institute of Technology
  Pasadena 4, California
  Attn: Professor Pol Duwez
  Metallurgical Department

  Climax Molybdenum Corporation
  500 Fifth Avenue
  New York 18, New York

Bureau of Standards
Chemistry Division
Washington, D. C.
Attn: Dr. A. Brinner

  Climax Molybdenum Corporation of Michigan
  41410 Woodrow Wilson Avenue
  Detroit 3, Michigan
  Attn: Mr. A. J. Herzig

  Fansteel Metallurgical Company
  North Chicago, Illinois
  Attn: Dr. F. H. Driggs
  President

  General Electric Research Laboratory
  at the Knolls
  Schenectady, New York
  Attn: Mr. Robert M. Parke

  John Hopkins University
  Baltimore 18, Maryland
  Attn: Dr. Robert Haddin
  Dopt. of Mechanical Engineering

  National Advisory Committee for Aeronautics
  Lewis Flight Propulsion Laboratory
  Cleveland, Ohio

  National Advisory Committee for Aeronautics
  1724 F Street, N. W.
  Washington 25, D. C.
  Attn: Mr. Eugene B. Jackson

  Department of Metallurgy
  The Ohio State University
  Columbus, Ohio
  Attn: Dr. Rudolph Speiser

  Westinghouse Research Laboratories
  Metallurgical Department
  East Pittsburgh, Pennsylvania
  Attn: Howard Scott
  Manager, Metallurgical and Ceramic Department

  Bureau of Mines
  Albany, Oregon
  Attn: Dr. S. M. Shelton

  Bethlehem Steel Company
  Bethlehem, Pennsylvania
  Attn: Dr. John Marsh
S. Report
ON Contract N60k-22528 (NR 039-005)
For the period January 16 to April 15, 1953
The Ohio State University Research Foundation

PROTECTION OF MOLYBDENUM AGAINST CORROSION
AT HIGH TEMPERATURES

I. INTRODUCTION

With a view to developing a self-regenerative, protective oxide coating on molybdenum and molybdenum alloys, further data on the physical properties of the molybdates have been obtained. In particular the thermal stability of a number of molybdates has been determined by differential thermal analysis.

These data indicate that only a few of the binary molybdates studied are thermally stable; the majority undergo crystalline phase transitions at elevated temperatures. This behavior is, of course, detrimental to the oxidation resistance of molybdenum alloys.

In the future, attempts are going to be made to stabilize some of the more promising oxide structures.

Section II of this report is a summary of the research on the structure and stability of binary molybdates completed in this quarter.

Section III is a progress report on the study of the kinetics of oxidation of molybdenum.

II. EXPERIMENTAL WORK

Experimental work has been divided into two sections.

A. FURTHER DATA ACCUMULATED ON THE NORMAL MOLYBDATES

The various molybdates have been arranged under their groups as indicated
in Mendeleef's periodic table in order to show likely chemical similarities.

**Group I**

**Sodium Molybdate**

**X-ray analysis**

As part of the total survey of molybdate structures anhydrous sodium molybdate (Na$_2$MoO$_4$) was studied. It was found to be cubic with $a_0 = 9.105\,\text{Å}$. Extinctions observed in the powder photogram suggest the space group is $F_{d3m}$. Table I summarizes the observed data.

<table>
<thead>
<tr>
<th>$d$</th>
<th>$I$</th>
<th>$hkl$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.255</td>
<td>70</td>
<td>111</td>
</tr>
<tr>
<td>3.206</td>
<td>80</td>
<td>220</td>
</tr>
<tr>
<td>2.734</td>
<td>100</td>
<td>311</td>
</tr>
<tr>
<td>2.085</td>
<td>5</td>
<td>331</td>
</tr>
<tr>
<td>1.857</td>
<td>25</td>
<td>422</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>511, 333</td>
</tr>
<tr>
<td>1.608</td>
<td>25</td>
<td>440</td>
</tr>
<tr>
<td>1.537</td>
<td>5</td>
<td>531</td>
</tr>
<tr>
<td>1.438</td>
<td>5</td>
<td>630</td>
</tr>
<tr>
<td>1.389</td>
<td>5</td>
<td>533</td>
</tr>
<tr>
<td>1.274</td>
<td>5</td>
<td>711, 551</td>
</tr>
<tr>
<td>1.216</td>
<td>10</td>
<td>642</td>
</tr>
<tr>
<td>1.135</td>
<td>15</td>
<td>731, 553</td>
</tr>
<tr>
<td>1.115</td>
<td>5</td>
<td>800</td>
</tr>
<tr>
<td>1.073</td>
<td>5</td>
<td>822</td>
</tr>
<tr>
<td>1.051</td>
<td>10</td>
<td>751</td>
</tr>
<tr>
<td>0.959</td>
<td>3</td>
<td>911, 753</td>
</tr>
<tr>
<td>0.9703</td>
<td>3</td>
<td>664</td>
</tr>
<tr>
<td>0.9516</td>
<td>5</td>
<td>931</td>
</tr>
</tbody>
</table>
Group II

Cadmium Molybdate

X-ray analysis

Cadmium molybdate was discussed in the preceding report but the X-ray data were not reported. Table II lists the data obtained subsequent to the date of the last report. Structure is scheelite type; \( a_0 = 5.14 \text{Å}, c_0 = 11.16 \text{Å} \).

<table>
<thead>
<tr>
<th>d</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.778</td>
<td>004</td>
</tr>
<tr>
<td>2.569</td>
<td>200</td>
</tr>
<tr>
<td>1.886</td>
<td>204</td>
</tr>
<tr>
<td>1.822</td>
<td>220</td>
</tr>
<tr>
<td>1.654</td>
<td>116</td>
</tr>
<tr>
<td>1.556</td>
<td>312</td>
</tr>
<tr>
<td>1.395</td>
<td>008</td>
</tr>
<tr>
<td>1.522</td>
<td>107, 224</td>
</tr>
<tr>
<td>1.286</td>
<td>400</td>
</tr>
<tr>
<td>1.226</td>
<td>208, 316</td>
</tr>
<tr>
<td>1.185</td>
<td>332</td>
</tr>
<tr>
<td>1.168</td>
<td>307, 104</td>
</tr>
<tr>
<td>1.150</td>
<td>420</td>
</tr>
<tr>
<td>1.107</td>
<td>228</td>
</tr>
<tr>
<td>1.065</td>
<td>11, 10, 424</td>
</tr>
<tr>
<td>1.016</td>
<td>336</td>
</tr>
<tr>
<td>0.993</td>
<td>512, 503, 433, 417</td>
</tr>
<tr>
<td>0.921</td>
<td>3, 1, 10</td>
</tr>
<tr>
<td>0.946</td>
<td>408</td>
</tr>
<tr>
<td>0.888</td>
<td>428</td>
</tr>
</tbody>
</table>

Group III

Aluminum Molybdate

Method of preparation

Stoichiometric proportions of molybdenum trioxide and alumina were heated in vacuo in a sealed Vycor tube for four days at 825°C.
<table>
<thead>
<tr>
<th>Property</th>
<th>Lanthanum Molybdate Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$\text{La}_2(\text{MoO}_4)_3$</td>
</tr>
<tr>
<td>Appearance</td>
<td>White powder</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Hygroscopic or deliquescent</td>
<td>Neither</td>
</tr>
<tr>
<td>Crystalline phases</td>
<td>See the account of the differential thermal analysis of lanthanum molybdate and of the X-ray analysis below</td>
</tr>
<tr>
<td>Melting point</td>
<td>$977^\circ C \pm 10^\circ C$</td>
</tr>
<tr>
<td>Volatility and stability</td>
<td>Heating 0.1g at $1100^\circ C$ for one hour results in melting but no weight change</td>
</tr>
<tr>
<td>Density</td>
<td>Not determined</td>
</tr>
</tbody>
</table>

**X-ray Analysis of Lanthanum Molybdate**

The following table lists the X-ray data for lanthanum molybdate. With the exception of only a few lines, the data can be indexed in the tetragonal scheelite system. This is surprising considering the valence difference between...
the typical scheelite, $R^2(MO_4)^{2+}$, atomic arrangement and the lanthanum molybdate, $R_2^2(MO_4)_3^{2+}$, arrangement.

In order to account for this strange retention of the scheelite structure with the substitution of a trivalent cation for the usual bivalent cation, a deficiency structure or superlattice has been proposed. Although it is possible to account for the retention of the scheelite structure by assuming a slight shift in position of cation sites, until such time as the powder photogram can be completely indexed or until further single crystal work established definitely the structure of $La_2(MO_4)_3$, the modified or distorted lattice cannot be entirely discounted.

The apparent structure is tetragonal, $a_0 = 5.356 \overline{A}$, $c_0 = 11.91 \overline{A}$, $c/a = 2.22$.

<table>
<thead>
<tr>
<th>TABLE III. X-RAY DATA FOR LANTHANUM MOLYDATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>5.70</td>
</tr>
<tr>
<td>5.49</td>
</tr>
<tr>
<td>4.85</td>
</tr>
<tr>
<td>3.182</td>
</tr>
<tr>
<td>2.958</td>
</tr>
<tr>
<td>2.666</td>
</tr>
<tr>
<td>2.342</td>
</tr>
<tr>
<td>2.287</td>
</tr>
<tr>
<td>2.225</td>
</tr>
<tr>
<td>2.130</td>
</tr>
<tr>
<td>2.019</td>
</tr>
<tr>
<td>1.987</td>
</tr>
<tr>
<td>1.891</td>
</tr>
<tr>
<td>1.756</td>
</tr>
<tr>
<td>1.710</td>
</tr>
<tr>
<td>1.691</td>
</tr>
<tr>
<td>1.628</td>
</tr>
<tr>
<td>1.598</td>
</tr>
<tr>
<td>1.489</td>
</tr>
<tr>
<td>1.388</td>
</tr>
<tr>
<td>1.339</td>
</tr>
<tr>
<td>1.301</td>
</tr>
<tr>
<td>1.289</td>
</tr>
</tbody>
</table>
TABLE III. (continued)

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.235</td>
<td>4</td>
<td>332, 4313</td>
</tr>
<tr>
<td>1.222</td>
<td>4</td>
<td>404</td>
</tr>
<tr>
<td>1.199</td>
<td>4</td>
<td>420</td>
</tr>
<tr>
<td>1.172</td>
<td>4</td>
<td>422</td>
</tr>
<tr>
<td>1.138</td>
<td>4</td>
<td>1, 1, 10</td>
</tr>
<tr>
<td>1.112</td>
<td>6</td>
<td>424, 406</td>
</tr>
<tr>
<td>1.066</td>
<td>4</td>
<td>(431 + 501), 336, 309</td>
</tr>
<tr>
<td>1.036</td>
<td>5B</td>
<td>512, (503 + 433)</td>
</tr>
<tr>
<td>0.9966</td>
<td>3VB</td>
<td>2, 2, 10, 521 (?)</td>
</tr>
<tr>
<td>0.9763</td>
<td>6</td>
<td>505, 435</td>
</tr>
</tbody>
</table>

Group IV

Ceric Molybdate

The preparation of this molybdate presents certain difficulties. Preparation by reaction between ceric salts and sodium molybdate in aqueous solution is unlikely to prove successful for the following reason. A reaction of this type must not be carried out in strongly acid solution, since it results in precipitation of a polymolybdate instead of the normal molybdate. At the same time, the reaction may not be performed in a solution of pH value such that ceric hydroxide precipitates. Unfortunately, cerium has an amphoteric hydroxide so that the hydroxide precipitates in acid solutions. The range of pH over which the normal molybdate alone is precipitated is therefore likely to be small, so it would be difficult to prepare ceric molybdate by this method.

Repeated attempts to prepare ceric molybdate by heating stoichiometric proportions of ceric oxide and molybdenum trioxide in vacuo in sealed Vycor tubes at 800°C failed, and resulted in explosion of the glass tube. It appears therefore either that reaction between ceric oxide and molybdenum trioxide is slow, or that ceric molybdenum is unstable and its dissociation pressure at 800°C is considerable.
Group VI
Chromium Molybdate

Method of preparation

Stoichiometric proportions of molybdenum trioxide and chromium sesquioxide, Cr₂O₃, were heated in vacuo in a sealed Vycor tube for 96 hours at 825°C.

Formula

Cr₂(MoO₄)₃

Appearance

Mauve powder

Solubility in water

Insoluble

Hygroscopic or deliquescent

Neither

Crystalline phases

Work in progress

Volatile and stability

Decomposes below 1000°C

Density

Not determined

Group VIII
Ferric Molybdate

Method of preparation

Stoichiometric proportions of molybdenum trioxide and ferric oxide, Fe₂O₃, were heated in vacuo in a sealed Vycor tube for 96 hours at 816°C.

Formula

Fe₂(MoO₄)₃

Appearance

Green powder

Solubility in water

Insoluble. It was observed however that on heating in water the green powder turns brown, presumably indicating that the ferric molybdate molecule either hydrolyzes or hydrates.

Hygroscopic or deliquescent

Neither

Crystalline phases

Work in progress
Melting point
Decomposes before melting

Volatile and stability
Decomposes completely at 1000°C with evolution of molybdenum tri-oxide to ferric oxide, Fe₂O₃.

Density
Not determined

**Nickel Molybdate**

Crystalline phases
See the account of the differential thermal analysis of nickel molybdate and of the X-ray analysis below.

Volatile and stability
Involatile and stable on heating for 16 hours at 972°C

**X-ray Analysis of Nickel Molybdate**

Photograms and spectrograms have been made of two forms of nickel-molybdenum-oxygen compounds.

The photogram and spectrogram of the as-prepared nickel molybdate both give evidence of a low-symmetry structure as indicated by a large number of lines and considerable line broadening and distortion of line shape. The latter features are often indicative of a slight distortion from a more symmetric structure or of poorly defined crystallinity. It has not yet been possible to ascertain the structure of the as-prepared nickel molybdate, but the coarse X-ray data are presented in Table IV.
It is observed that the structure of nickel molybdate changes on heating. The following table gives a comparison of the X-ray data obtained from three heated samples.

Column A contains data for the naturally formed oxidation product appearing on the surface of a Mo-15% Ni alloy heated in air at 1600°F (871°C) for 5 hours. These data are identical with those obtained from a similar sample heated in air at 1800°F (982°C) for 5 hours.

Column B contains data obtained from a sample of synthetically prepared nickel molybdate which had been heated at 1023°C for 17-1/2 hours.

Column C contains data obtained from a sample of synthetically prepared nickel molybdate which had been heated to constant weight (2 hours) over a Meker burner (ca. 1000°C).

Although tentative indexing of the data in column B has been accomplished in the tetragonal system, the results are not presented here, as there is uncertainty as to the nature of the sample material, particularly in regard to the number of phases present.

TABLE IV. X-RAY DATA FOR AS-PREPARED NICKEL MOLYBDATE

<table>
<thead>
<tr>
<th>d</th>
<th>r^*</th>
<th>d</th>
<th>r^*</th>
<th>d</th>
<th>r^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.94</td>
<td>85</td>
<td>3.104</td>
<td>8</td>
<td>2.09</td>
<td>10 (M)</td>
</tr>
<tr>
<td>6.51</td>
<td>85</td>
<td>2.994</td>
<td>100 (M)</td>
<td>2.053</td>
<td>10</td>
</tr>
<tr>
<td>5.13</td>
<td>10</td>
<td>2.861</td>
<td>22</td>
<td>1.992</td>
<td>12</td>
</tr>
<tr>
<td>4.192</td>
<td>14</td>
<td>2.77</td>
<td>5 (B)</td>
<td>1.908</td>
<td>10</td>
</tr>
<tr>
<td>4.107</td>
<td>14</td>
<td>2.676</td>
<td>20 (M)</td>
<td>1.87</td>
<td>5 (B)</td>
</tr>
<tr>
<td>3.874</td>
<td>20</td>
<td>2.465</td>
<td>8 (M)</td>
<td>1.81</td>
<td>4 (B)</td>
</tr>
<tr>
<td>3.761</td>
<td>24</td>
<td>2.38</td>
<td>5 (B)</td>
<td>1.76</td>
<td>5</td>
</tr>
<tr>
<td>3.362</td>
<td>12</td>
<td>2.236</td>
<td>8 (M)</td>
<td>1.75</td>
<td>5</td>
</tr>
<tr>
<td>3.301</td>
<td>60</td>
<td>2.168</td>
<td>8</td>
<td>1.716</td>
<td>15 (M)</td>
</tr>
<tr>
<td>3.233</td>
<td>56</td>
<td>2.149</td>
<td>12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Number indicates relative peak height. (M) indicates line shape is suggestive of a multiple line. (B) indicates line is broad, ill-defined maximum.
<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>Peak Height</td>
<td>Peak Height</td>
<td>Peak Height</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.15</td>
<td>6.17</td>
<td>6.185</td>
<td>1</td>
</tr>
<tr>
<td>4.59</td>
<td>4.64</td>
<td>4.646</td>
<td>2</td>
</tr>
<tr>
<td>3.69</td>
<td>3.59</td>
<td>3.596</td>
<td>4</td>
</tr>
<tr>
<td>3.50</td>
<td>3.167</td>
<td>3.167</td>
<td>7</td>
</tr>
<tr>
<td>2.86</td>
<td>3.076</td>
<td>3.076</td>
<td>10</td>
</tr>
<tr>
<td>2.73</td>
<td>2.728</td>
<td>2.728</td>
<td>5</td>
</tr>
<tr>
<td>2.54</td>
<td>2.537</td>
<td>2.537</td>
<td>1</td>
</tr>
<tr>
<td>2.43</td>
<td>2.436</td>
<td>2.436</td>
<td>2</td>
</tr>
<tr>
<td>2.31</td>
<td>2.313</td>
<td>2.313</td>
<td>3</td>
</tr>
<tr>
<td>2.164</td>
<td>2.182</td>
<td>2.182</td>
<td>5</td>
</tr>
<tr>
<td>2.056</td>
<td>2.076</td>
<td>2.076</td>
<td>4</td>
</tr>
<tr>
<td>1.897</td>
<td>1.913</td>
<td>1.913</td>
<td>3</td>
</tr>
<tr>
<td>1.840</td>
<td>1.792</td>
<td>1.792</td>
<td>1</td>
</tr>
<tr>
<td>1.703</td>
<td>1.713</td>
<td>1.713</td>
<td>4</td>
</tr>
<tr>
<td>1.625</td>
<td>1.631</td>
<td>1.631</td>
<td>1</td>
</tr>
<tr>
<td>1.586</td>
<td>1.588</td>
<td>1.588</td>
<td>4</td>
</tr>
<tr>
<td>1.579</td>
<td>1.539</td>
<td>1.539</td>
<td>1</td>
</tr>
<tr>
<td>1.489</td>
<td>1.491</td>
<td>1.491</td>
<td>3</td>
</tr>
<tr>
<td>1.442</td>
<td>1.456</td>
<td>1.456</td>
<td>2</td>
</tr>
<tr>
<td>1.392</td>
<td>1.405</td>
<td>1.405</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>
TABLE V. (continued)

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Peak Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.273</td>
<td>2B</td>
<td>1.270</td>
<td>1B</td>
</tr>
<tr>
<td>1.235</td>
<td>2</td>
<td>1.235</td>
<td>2</td>
</tr>
<tr>
<td>1.208</td>
<td>1</td>
<td>1.210</td>
<td>1B</td>
</tr>
<tr>
<td>1.185</td>
<td>2</td>
<td>1.186</td>
<td>2B</td>
</tr>
<tr>
<td>1.163</td>
<td>&lt;1B</td>
<td>1.183</td>
<td>2B</td>
</tr>
<tr>
<td>1.150</td>
<td>2B</td>
<td>1.072</td>
<td>1</td>
</tr>
<tr>
<td>1.040</td>
<td>2VB</td>
<td>1.060</td>
<td>1</td>
</tr>
<tr>
<td>0.919</td>
<td>2VB</td>
<td>0.921</td>
<td>3VB</td>
</tr>
</tbody>
</table>

B. DIFFERENTIAL THERMAL ANALYSIS

1. EXPERIMENTAL PROCEDURE

The technique consists briefly in heating under the same conditions the sample under test and a substance which has no polymorphic changes, in this case alumina. The differential temperature between the two is recorded. Where no change in phase of the sample occurs, the differential temperature is approximately zero, though in practice it may vary slightly. At a phase change, the evolution or absorption of heat in the sample causes an abrupt change in the differential temperature, which is recorded by a Brown Electronik differential recorder. In this way the thermal behavior of the samples may be easily followed. Much research has recently been devoted to development of this type of apparatus, the details of which are quite complicated. They are described fully by Robert L. Stone.¹

2. PLOTTING OF DIFFERENTIAL THERMAL ANALYSIS RESULTS

The results are presented graphically in Figures 1 to 34. The position of the horizontal lines indicates the temperatures at which the transition
occurs, and the lengths of these lines as drawn, or else as indicated numerically in cm, are the same as those of the deflections shown on the differential thermogram; that is, they are proportional to the differential temperatures. The horizontal lines to the left indicate exothermic transitions; those to the right, endothermic transitions.

Many of the molybdates show an unusual but reproducible complexity of thermal behaviors. X-ray photograms of the molybdates at various temperatures are needed in order to elucidate this behavior.

3. RESULTS

**Group II**

**Calcium Molybdate (Figures 1, 2, 3, 4, 5, 6)**

Figure 1 (heating of calcium molybdate to 1000°C) shows four endothermic transitions. The first two deflections are rather small. It is dubious whether they correspond to transitions in calcium molybdate. Cooling (Figure 2) gives four exothermic transitions as expected, although all these do not occur at the temperatures at which the corresponding endothermic changes occur. Reheating of the sample (Fig. 3) gives only three endothermic transitions. The cooling curve (Fig. 4) shows three exothermic transitions as expected. Again the temperatures of transition do not correspond. Reheating (Fig. 5) and cooling (Fig. 6) seem to indicate that the lowest transition is lost, i.e., supercooling to room temperature occurs at this point.

The above is an empirical description of the thermal analysis of calcium molybdate. It is already known that calcium molybdate decomposes at 965°C. Since the decomposition temperature has been exceeded in each experiment, it must be realized that Figures 1, 2, 3, 4, 5, and 6 do not refer to the same
substance. Only Figure 1 refers to pure calcium molybdates; the subsequent figures each refer to calcium molybdate in different states of partial decomposition. These diagrams will be better understood when supplemented by further analytical and high temperature X-ray studies.

**Strontium Molybdate**

Strontium molybdate shows one endothermic transition at about 600°C which appears reversibly on cooling (Figures 7 and 8).

**Barium Molybdate**

Barium molybdate exhibits no transitions up to 1020°C (Figures 9 and 10).

**Magnesium Molybdate**

The compound was prepared by evaporation of an aqueous solution of magnesium molybdate to give the compound \( \text{MgMoO}_4 \cdot 2\text{H}_2\text{O} \). The differential thermal analysis (Figures 11, 12) shows two extremely large endothermic transitions at 150°C and 250°C. Their size and the method of preparation of magnesium molybdate indicate that they correspond to the loss of successive molecules of water of crystallization.

One exothermic inflection, believed to indicate a phase change, occurs at 820°C. The high temperature phase is retained on cooling to room temperature. The hydrated molybdate does not reform on cooling, a conclusion supported by weight change experiments on reheating (Figure not shown). No inflections are found on the D.T.A. curve, as expected.

**Cadmium Molybdate**

Figure 13 indicates that cadmium molybdate has one endothermic transition on heating at 525°C. On cooling (Fig. 14), the transition splits into two...
Horizontal scale in arbitrary units of differential temperature for all figures.
Cooling of NiMoO$_4$
Fig. 30

Heating of NiMoO$_4$
Fig. 31

Cooling of NiMoO$_4$
Fig. 32

Heating of NiMoO$_4$
Fig. 33

Cooling of NiMoO$_4$
Fig. 34
distinct transitions, although these have only a small temperature interval between them. A high-temperature X-ray study is needed before an explanation can be attempted.

**Group III**

**Lanthanum Molybdate**

One endothermic inflection (Fig. 15) occurs in the differential thermal analysis curve at 915°C. It is so small in magnitude that it seems dubious whether it indicates a crystalline transition. The melting point is marked by an endothermic transition (shown as a dotted line on Fig. 15) at 977°C. The inflection at 915°C does not reappear on cooling (Fig. 16) nor on reheating (figure not shown).

**Group IV**

**Lead Molybdate**

Lead molybdate (Figures 17, 18) shows no transitions up to 1005°C.

**Thorium Molybdate**

Thorium molybdate (Fig. 19) shows one endothermic transition at 94°C on heating. The high-temperature phase (Fig. 20) is retained on cooling to room temperature and no further transitions are observed on reheating (figure not shown).

**Group VIII**

**Cobalt Molybdate**

Heating of cobalt molybdate (Fig. 21) gives two endothermic transitions at 312°C and 343°C. The high-temperature form above 343°C apparently supercools (Fig. 22) and does not, of course, reappear on reheating (figure not shown).
Nickel Molybdate

Figures 23, 24, 25, 26, 27, 28, 29, 30, 31, and 32 represent heating, cooling, and consecutive reheating and cooling runs performed on the same specimen. The inflections of Figure 24 (cooling of nickel molybdate) correspond neither in direction nor in temperature to those obtained by heating (Fig. 23). Reheating results again in a change of transitions (cf. Fig. 23 showing exothermic transitions at 438°C and 449°C and Fig. 25 showing only one endothermic transition at 677°C). Cooling (Fig. 26) results in five small exothermic transitions. Further reheating and cooling (Fig. 27 and 28) show a similar phenomenon. Figures 29 and 30 show that if nickel molybdate is heated to a point which is below that of the high temperature transition (A, Fig. 27), then on cooling the low temperature transformations B, C, D, in Figure 28 are missing. Figures 31 and 32 show the same phenomenon repeated. Five rather more pronounced inflections are shown on Figure 32, which was obtained at a rather slower rate of cooling, as compared to four in Figure 28.

Figures 33 and 34 represent experiments conducted on a sample of nickel molybdate which previously had been ignited for 2 hours over a Beker burner. The results differ from the other diagrams obtained, indicating that further changes have occurred.

4. CONCLUSION

All those molybdates that it was planned to prepare have now been prepared, with the exception of ceric molybdate which presents exceptional difficulties (see above). Of those compounds, magnesium, strontium, cadmium, barium, lead, and cobalt molybdates are stable and solid at 1000°C. Lanthanum and thorium molybdates are stable and solid up to almost 1000°C. Lead and barium molybdates show no phase changes up to 1000°C. Cobalt, thorium, lanthanum, and magnesium
molybdates have high temperature phases which supercool easily to room temperature and show no further phase changes on reheating. These last six molybdates therefore seem to be particularly promising.

It is noted that lanthanum molybdate, \( \text{La}_2(\text{MoO}_4)_3 \), has a melting point of 977°C, whereas the substance reported in the last report (No. 5) as \( \text{La}_2\text{O}_3 \cdot 4.5\text{MoO}_3 \) melts above 1070°C. It has been noted that in all observed cases the addition of molybdenum trioxide (melting point 795°C) to a substance of melting point above 795°C results in a lowering of the latter melting point. It is believed possible, therefore, that the compound reported as \( \text{La}_2\text{O}_3 \cdot 4.5\text{MoO}_3 \) probably contains less molybdenum trioxide than was previously thought. The chemical analysis of this substance needs rechecking.

The differential thermal analyses of those compounds showing complicated thermal behavior such as that exhibited by nickel molybdate have little significance until supported by further high temperature X-ray studies. Hence, no attempt has been made to explain these particular experiments as yet. They have simply been reported empirically.

The case of nickel molybdate is particularly interesting, since it is known that nickel molybdate forms on molybdenum at high temperatures a protective coating which is damaged by spalling on cooling. It is believed from the differential thermal analysis work, that spalling of nickel molybdate on cooling is due to a phase change, not to strain. Further work should show whether elimination of this phase change can result in elimination of spalling.

5. ERRATUM

In the previous report (page 10, Report No. 5, on Contract N6onr-22528 (NR-0344-404)) the density of magnesium molybdate was given as 2.208 g/cc. This figure actually refers to the hydrated salt \( \text{MgMoO}_4 \cdot 5\text{H}_2\text{O} \). The density of anhydrous magnesium molybdate is not yet known.
III. KINETICS OF OXIDATION OF MOLYBDENUM

Previous work (see previous Quarterly and Technical Report) had indicated some interesting features. The irreproducibility of results, as a result of the source of supply and the effects of the etch or pickling procedure in 30% (by weight) HNO₃, required further investigation.

The work was continued at the arbitrary temperature of 1200°F while various combinations of surface preparation were compared with previous results. Advantage was taken of the fact that MoO₃, of all the oxides of molybdenum, is soluble in NH₄OH. By abrading, etching, and washing in NH₄OH, oxidizing and comparing with previous results, it was noted that the new results agreed favorably with the samples which were abraded but not etched. This confirmed the fact that an etch in HNO₃ produces a layer of MoO₃ which protects against oxidation at 1200°F. This fact coupled with previously reported lack of protection at temperatures above 1300°F, using a pickling surface preparation, would indicate the following:

(1) Below that temperature where sublimation of MoO₃ is appreciable, an even, coherent layer of MoO₃ on molybdenum sheet will protect against oxidation.

(2) Attempts to obtain this coherent layer of MoO₃ in air have been unsuccessful.

(3) Etching in HNO₃, a strong oxidizing agent, will lead to the deposition of a thin, coherent protective layer of MoO₃.

Further investigations into possible satisfactory surface preparations have shown that the following procedure will produce a surface which will yield reproducible results for rates of oxidation:
(1) Etch sample in 30% (by weight) HNO₃. Time in etchant 10 seconds after reaction is visible.

(2) Wash in stream of distilled water to stop reaction and remove loose material.

(3) Soak in boiling 1 normal NH₄OH for 1 hour.

(4) Wash in stream of distilled water.

(5) Wash in acetone.

(6) Soak in acetone for 12 to 30 hours.

(7) Dry in air, just before oxidation.

Samples prepared in the above manner show rates of oxidation which agree with abraded and unetched molybdenum samples.

Therefore the state of progress at the present is that a satisfactory surface preparation has been found which will give reproducible results. Accurate rates of oxidation of sheet samples may now be obtained and after a determination of the rate of sublimation of MoO₃ is available, these results can be corrected to give oxidation rates of molybdenum. Work has been started to obtain rates of sublimation of MoO₃ and oxidation rates of molybdenum.
REFERENCES


ACKNOWLEDGEMENT

Technical contributions to this report have been made by:

Dr. Rudolph Speiser
Dr. J. W. Spretnak
Dr. Holly Gleiser
Mr. William L. Larsen
Capt. John F. Mosher, USAF

NOTE: In submitting this report it is understood that all provisions of the contract between The Foundation and Cooperator and pertaining to publicity of subject matter will be rigidly observed.

Investigator
Dr. J. W. Spretnak Date 4-24-53

Supervisor
Rudolph Speiser Date 4/29/53

FOR THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION

Executive Director
Ornan C. Wolford Date 4/29/53