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PROTECTION OF MOLYBDENUM AGAINST CORROSION
AT HIGH TEMPERATURES

I. INTRODUCTION

With a view to developing a self-regnerative, 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.

<u>Group I</u>

<u>Sodium Molybdate</u>

<u>X-ray</u> analysis

As part of the total survey of molybdate structures anhydrous sodium molybdate (Na_2MoO_4) was studied. It was found to be cubic with $a_o = 9.105_8$Å. Extinctions observed in the powder photogram suggest the space group is F_{d3m}. Table I summarizes the observed data.

TABLE I. X-RAY DATA FOR SODIUM MOLYBDATE

d	I	hkl
5.255	70	111
3.206	80	220
2.734	100	311
2.085	5	331
1.857	25	422
1.749	20	511, 333
1.608	25	440
1.537	5	531
1.438	5	620
1.389	5	533
1.274	5	711, 551
1.216	10	642
1.195	15	731, 553
1.145	5	800
1.073	5	822
1.051	10	751
0.999	3	911, 753
0.9703	3	664
0.9546	5	931

Group II

Cadmium Molybdate

X-ray analysis

Cadmium molybdate was discussed in the preceeding 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; $a_o = 5.14\text{Å}$, $c_o = 11.16\text{Å}$.

TABLE II. X-RAY DATA FOR CADMIUM MOLYBDATE

d	I	hkl
3.025	9	112, 103
2.778	4	004
2.569	3B	200
1.886	10	204
1.822	3	220
1.654	9	116
1.559	8	312
1.395	2B	008
1.522	4	107, 224
1.286	1B	400
1.226	10	208, 316
1.185	2	332
1.168	2	307, 404
1.150	2	420
1.107	4	228
1.065	7B	1,1, 10; 424
1.016	3B	336
0.993	4B	512, 503, 433, 417
0.921	5B	3, 1, 10
0.946	3B	408
0.888	7B	428

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.

Formula	$Al_2(MoO_4)_3$
Appearance	Whitish powder
Solubility in water	Insoluble or very sparingly soluble
Hygroscopic or deliquescent	Neither
Crystalline phases	work in progress
Melting point	Decomposes before melting
Volatility and stability	Decomposes below 1000°C
Density	Not determined

Lanthanum Molybdate

Method of preparation	Stoichiometric proportions of molybdenum trioxide and lanthana were heated for 102 hours at 600°C and for a further 20 hours at 870°C
Formula	$La_2(MoO_4)_3$
Appearance	White powder
Solubility in water	Insoluble
Hygroscopic or deliquescent	Neither
Crystalline phases	See the account of the differential thermal analysis of lanthanum molybdate and of the X-ray analysis below
Melting point	977°C $\pm$ 10°C
Volatility and stability	Heating 0.1g at 1100°C for one hour results in melting but no weight change
Density	Not determined

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, $R^{=}(MoO_4)^{++}$, atomic arrangement and the lanthanum molybdate, $R_2^{=}(MoO_4)_3^{++}$, 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 $La_2(MoO_4)_3$, the modified or distorted lattice cannot be entirely discounted.

The apparent structure is tetragonal, a_o = 5.356Å, c_o = 11.91Å, c/a = 2.22.

TABLE III. X-RAY DATA FOR LANTHANUM MOLYBDATE

d	I	hkl
5.70	<1	
5.49	1	
4.85	<1	
3.182	10	112
2.958	3	004
2.666	4	200 (?)
2.342	2	211
2.287	≪1	
2.225	<1B	
2.130	<1B	
2.049	<1B	213 (?)
1.987	7	006, 204
1.891	5	220
1.756	6	116
1.710	≪1	
1.691	<1	215, 310
1.628	8	303, 312, 107
1.598	5	224
1.489	1	008
1.388	1B	323, 217
1.339	2B	400
1.301	5	208
1.289	7	316, 109

TABLE III. (continued)

d	I	hkl
1.235	4	332, 413
1.222	4	404
1.199	4	420
1.172	4	422
1.138	4	1, 1, 10
1.112	6	424, 406
1.066	4	(431 + 501), 336, 309
1.036	5B	512, (503 + 433)
0.9966	3VB	2, 2, 10; 521 (?)
0.9763	6	505, 435

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, Cr_2O_3, were heated in vacuo in a sealed Vycor tube for 96 hours at 825°C.
Formula	$Cr_2(MoO_4)_3$
Appearance	Mauve powder
Solubility in water	Insoluble
Hygroscopic or deliquescent	Neither
Crystalline phases	Work in progress
Volatility and stability	Decomposes below 1000°C
Density	Not determined

Group VIII

Ferric Molybdate

Method of preparation	Stoichiometric proportions of molybdenum trioxide and ferric oxide, Fe_2O_3, were heated in vacuo in a sealed Vycor tube for 96 hours at 816°C.
Formula	$Fe_2(MoO_4)_3$
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
Volatility and stability	Decomposes completely at 1000°C with evolution of molybdenum trioxide to ferric oxide, Fe_2O_3.
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.
Volatility and stability	Involatile and stable on heating for 46 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.

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

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

* Number indicates relative peak height. (M) indicates line
shape is suggestive of a multiple line. (B) indicates line
is broad, ill-defined maximum.

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 appear-
ing 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 synthetioally 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 un-
certainty as to the nature of the sample material, particularly in regard to
the number of phases present.

TABLE V. X-RAY DATA FOR THREE HEATED NICKEL MOLYBDATES

A		B		C	
d	I	d	I	d	Peak Height
6.15	9	6.15	8	6.17	70
				5.485	1
				4.908	3
4.59	2	4.64	1B	4.646	2
		4.37	<1		
		4.08	<1	4.06	1
		3.69	2	3.696	4
3.46	9	3.50	4	3.494	7
				3.406	20
		3.167	1	3.154	2
3.08	10	3.076	10	3.083	67
2.86	1	2.864	2		
2.73	9	2.728	5B	2.739	6
				2.716	10
2.54	2	2.537	1B		
		2.460	≪1	2.461	1
2.43	1			2.423	2
		2.396	≪1	2.404	3
				2.326	1
2.31	3	2.313	?B	2.318	1
				2.304	1
2.164	3	2.182	3	2.185	5
		2.076	<1	2.086	4
2.056	8	2.054	9	2.059	25
		2.026	<1		
		1.973	<1		
		1.949	1	1.954	1
1.897	6	1.913	3	1.913	3
1.840	1				
		1.792	1		
1.703	5	1.713	4	1.713	4
1.625	4	1.631	<1		
		1.619	1	1.620	1
				1.595	2
1.586	5	1.588	4B	1.586	4
1.579	1				
		1.539	<1		
1.489	7	1.491	5VB	1.491	3
		1.472	<1		
1.442	1	1.456	2	1.459	1
		1.433	<1VB		
		1.4095	1	1.408	1
1.392	4	1.395	2	1.396	1
		1.384	1		
		1.282	1B		

TABLE V. (continued)

A		B		C	
d	I	d	I	d	Peak Height
1.273	2B	1.270	1B		
1.235	2	1.235	2	1.236	1
1.208	1	1.210	1B		
1.185	2	1.186	2B		
		1.163	<1B		
1.150	2B	1.483	2B		
		1.072	1		
		1.060	1		
1.040	2VB	1.043	2		
		1.034	<1		
		1.026	1		
0.919	2VB	0.921	3VB		

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.[2] 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 decom-
position. 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

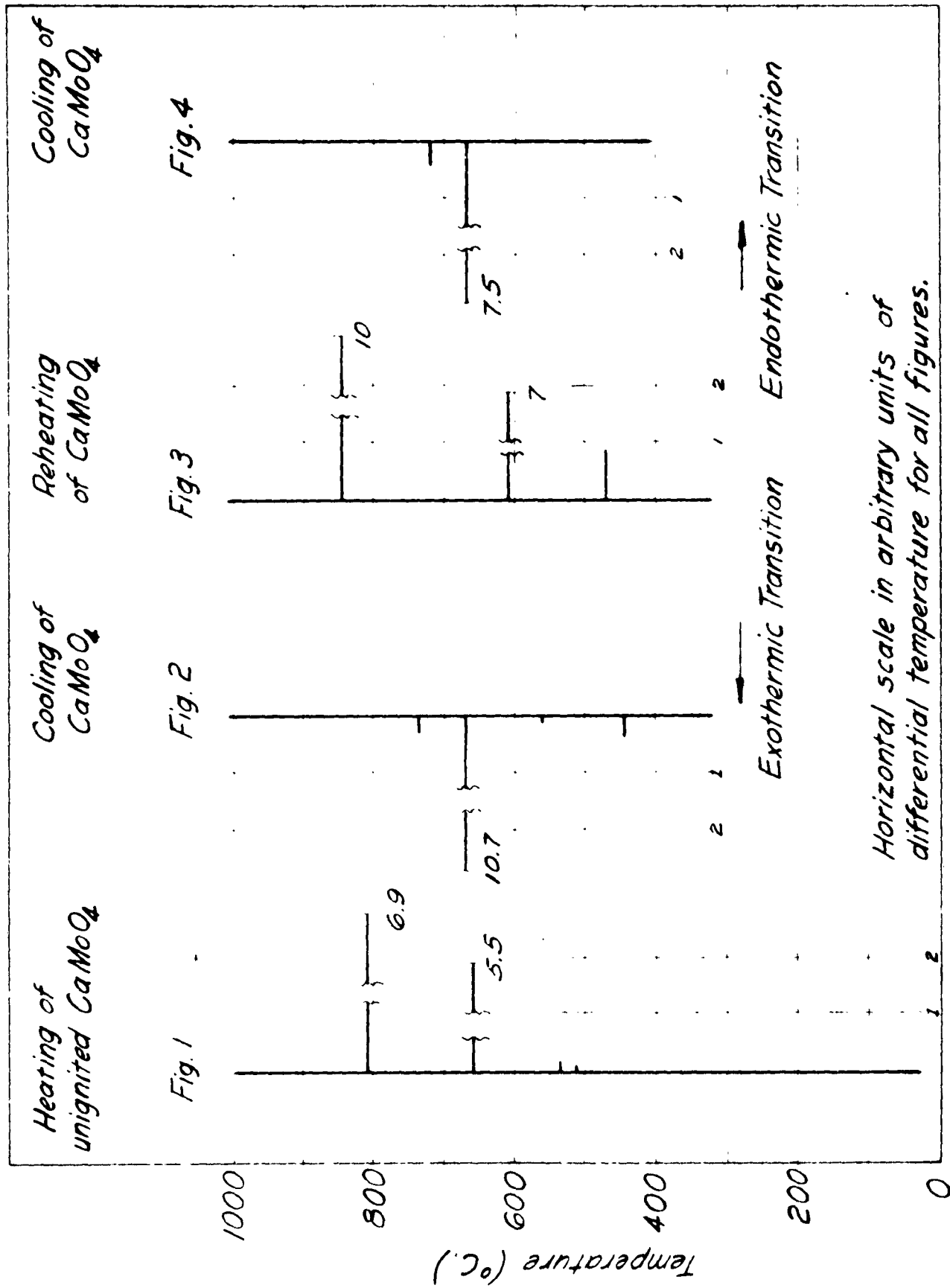Barium molybdate exhibits no transitions up to 1020°C (Figures 9 and 10).
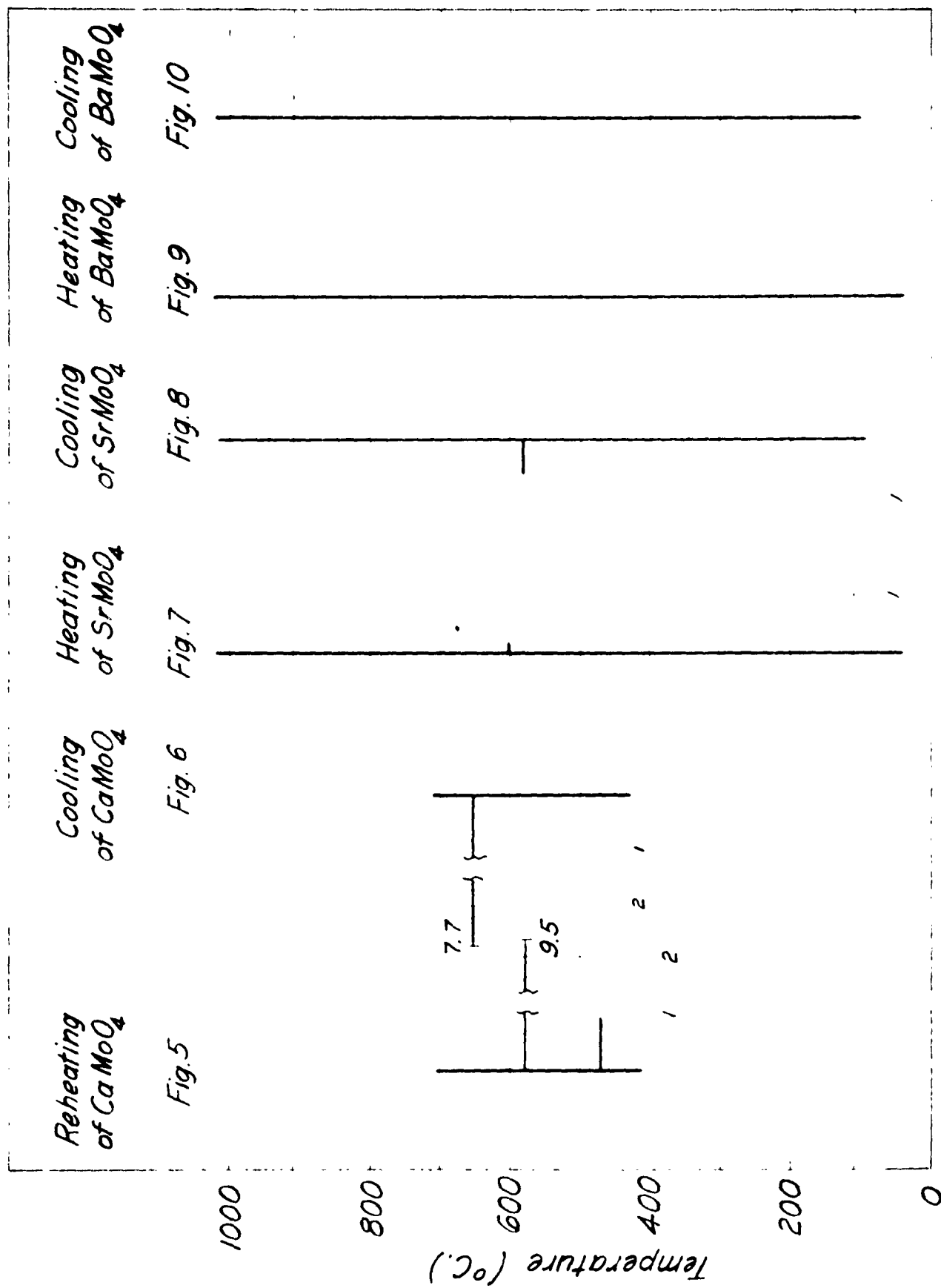
Magnesium Molybdate

The compound was prepared by evaporation of an aqueous solution of magnesiu
molybdate to give the compound[3] $MgMoO_4 \cdot 2H_2O$. 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

Fig. 1 — Heating of unignited $CaMoO_4$

Fig. 2 — Cooling of $CaMoO_4$

Fig. 3 — Reheating of $CaMoO_4$

Fig. 4 — Cooling of $CaMoO_4$

Exothermic Transition

Endothermic Transition

Horizontal scale in arbitrary units of differential temperature for all figures.

Temperature (°C)

Reheating of CaMoO₄ — Fig.5

Cooling of CaMoO₄ — Fig.6

Heating of SrMoO₄ — Fig.7

Cooling of SrMoO₄ — Fig.8

Heating of BaMoO₄ — Fig.9

Cooling of BaMoO₄ — Fig.10

Temperature (°C)

1000   800   600   400   200   0

Heating of MgMoO₄ — Fig.11
Cooling of MgMoO₄ — Fig.12
Heating of CdMoO₄ — Fig.13
Cooling of CdMoO₄ — Fig.14
Heating of La₂(MoO₄)₃ — Fig.15
Cooling of La₂(MoO₄)₃ — Fig.16
Heating of PbMoO₄ — Fig.17

Temperature (°C.)

1000   800   600   400   200   0

10.7   ≃18

Cooling of PbMoO₄ — Fig. 18

Heating of Th(MoO₄)₂ — Fig. 19

Cooling of Th(MoO₄)₂ — Fig. 20

Heating of CoMoO₄ — Fig. 21

Cooling of CoMoO₄ — Fig. 22

Heating of NiMoO₄ — Fig. 23

Temperature (°C.)

1000   800   600   400   200   0

Fig.24 — Cooling of NiMoO₄

Fig.25 — Heating of NiMoO₄

Fig.26 — Cooling of NiMoO₄

Fig.27 — Heating of NiMoO₄

Fig.28 — Cooling of NiMoO₄

Fig.29 — Heating of NiMoO₄

Temperature (°C.)

Cooling of NiMoO₄
Fig. 30

Heating of NiMoO₄
Fig. 31

Cooling of NiMoO₄
Fig. 32

Heating of NiMoO₄
Fig. 33

Cooling of NiMoO₄
Fig. 34
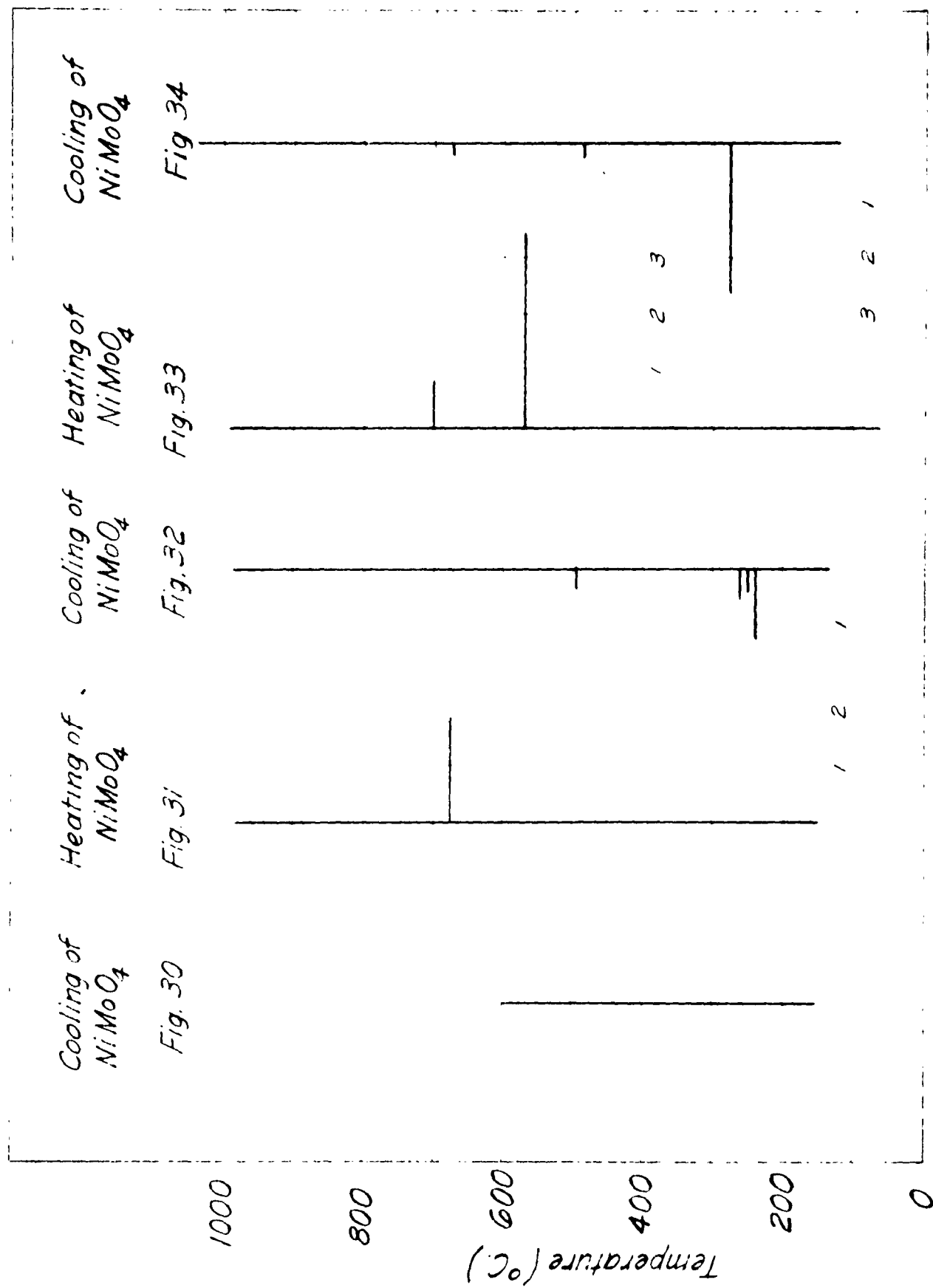
Temperature (°C)

1000

800

600

400

200

0

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 re-heating (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 940°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 Meker 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 difiiculties (see above). Of these 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, $La_2(MoO_4)_3$, has a melting point of 977°C, whereas the substance reported in the last report (No. 5) as $La_2O_3 \cdot$ 4.5 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 $La_2O_3 \cdot 4.5MoO_3$ probably co tains 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-034-404)) the density of magnesium molybdate was given as 2.208g/cc. This figure actually refers to the hydrated salt[3] $MgMoO_4 \cdot 5H_2O$. 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% (be weight) HNO_3, 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 MoO_3, of all the oxides of molybdenum is soluble in NH_4OH. By abrading, etching, and washing in NH_4OH, 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 HNO_3 produces a layer of MoO_3 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 MoO_3 is appreciable, an even, coherent layer of MoO_3 on molybdenum sheet will protect against oxidation.

(2) Attempts to obtain this coherent layer of MoO_3 in air have been unsuccessful.

(3) Etching in HNO_3, a strong oxidizing agent, will lead to the deposition of a thin, coherent protective layer of MoO_3.

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) HNO_3. 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 NH_4OH 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 MoO_3 is available, these results can be corrected to give oxidation rates of molybdenum. Work has been started to obtain rates of sublimation of MoO_3 and oxidation rates of molybdenum.

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