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R E P O R T

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Investigation of Protection of Molybdenum Against
Corrosion at High Temperatures

Subject of Report Status during April 16 to July 15, 1953

Submitted by J. W. Spretnak and Rudolph Speiser

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ONR Contract N6onr-22528 (NR 039-005)
For the period April 16 to July 15, 1953
The Ohio State University Research Foundation

Protection of Molybdenum Against Corrosion
at High Temperatures

I. INTRODUCTION

In an attempt to develop a self-regenerative, protective oxide coating on molybdenum, work has now been concentrated in two directions. Section A of this report deals with the oxidation resistance of certain molybdenum alloys and of molybdenum coated with various metals. Where possible, the surface products formed during heating these samples have been identified. It is hoped that this type of experiment will throw a light on the properties, such as crystal structure and density, required in a coating in order that it may prove protective on molybdenum. With this end in view, those metals, enumerated in the previous report¹, which form stable molybdates and therefore have some possibility of producing protective coatings on molybdenum have been alloyed with molybdenum. In those cases in which the relative atomic diameters of the metals and molybdenum indicate that the solubility of the metals in molybdenum will be negligible, the metal has been coated on molybdenum. Oxidation tests have then been carried out.

Experiments show that nickel molybdate at high temperatures formed a highly protective coating on molybdenum which is broken by spalling on cooling. This result led to the beginning of a thorough investigation of the properties of nickel and cobalt molybdates, which is reported in Section B.

II. EXPERIMENTAL WORK

A. OXIDATION RESISTANCE OF MOLYBDENUM ALLOYS AND OF MOLYBDENUM COATED WITH VARIOUS METALS

Oxidation tests in flowing air at high temperatures were performed using the apparatus and procedure described by J. F. Mosher^{1,3} in previous reports. This technique permits weighing of the oxidizing specimen at any time during the test.

Molybdenum-nickel Alloy

was
An oxidation test at 960°C/performed on a molybdenum - 20% nickel alloy formed by arc-melting molybdenum and nickel. The results are presented in Figure 1. The weight changes may be explained as follows. Section AB of the diagram represents a rapid loss in weight as molybdenum trioxide evaporated from the sample. BC shows the specimen losing weight less rapidly as a protective coating begins to form. CD shows the specimen gaining weight as oxygen is absorbed in the formation of more of the protective coating. Over the region DE the weight of the specimen approaches a constant value; sufficient coating forms to give more complete protection. These results are not in agreement with those presented by the Battelle Memorial Institute.² On removing the sample from the furnace it was seen to be covered with a green powder which spalled off on cooling in a manner characteristic of nickel molybdate. This green powder was identified, using an X-ray spectrometer, as being predominantly the high-temperature form of nickel molybdate, although a second unidentified substance was also present.

Molybdenum-cobalt Alloy

Results of an oxidation test at 944°C on a molybdenum - 7% cobalt alloy formed by arc-melting molybdenum and cobalt are presented in Figure 2. The

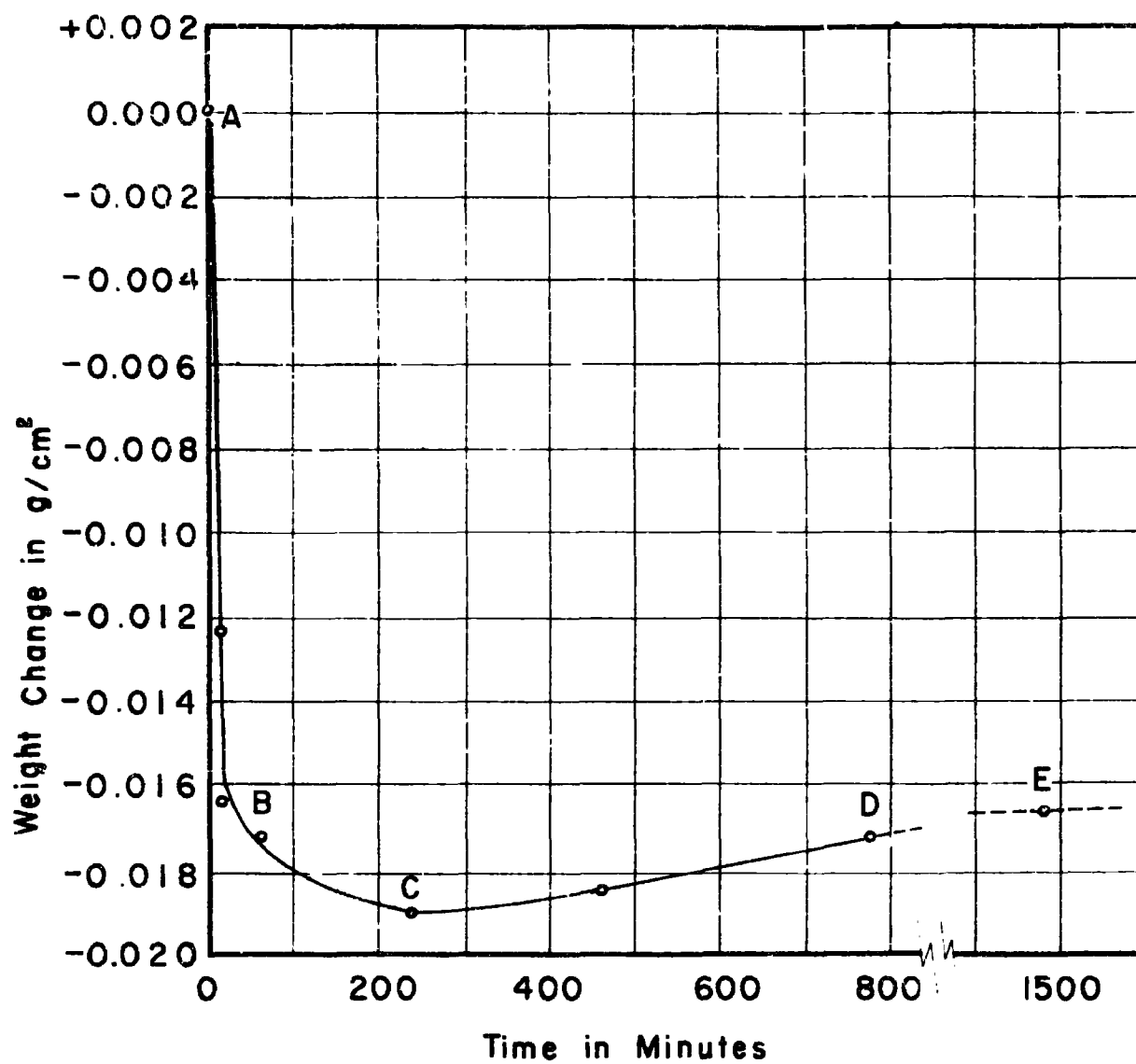


Fig.1 Oxidation Curve for a Mo-20 %
Ni Alloy at 960 ° C

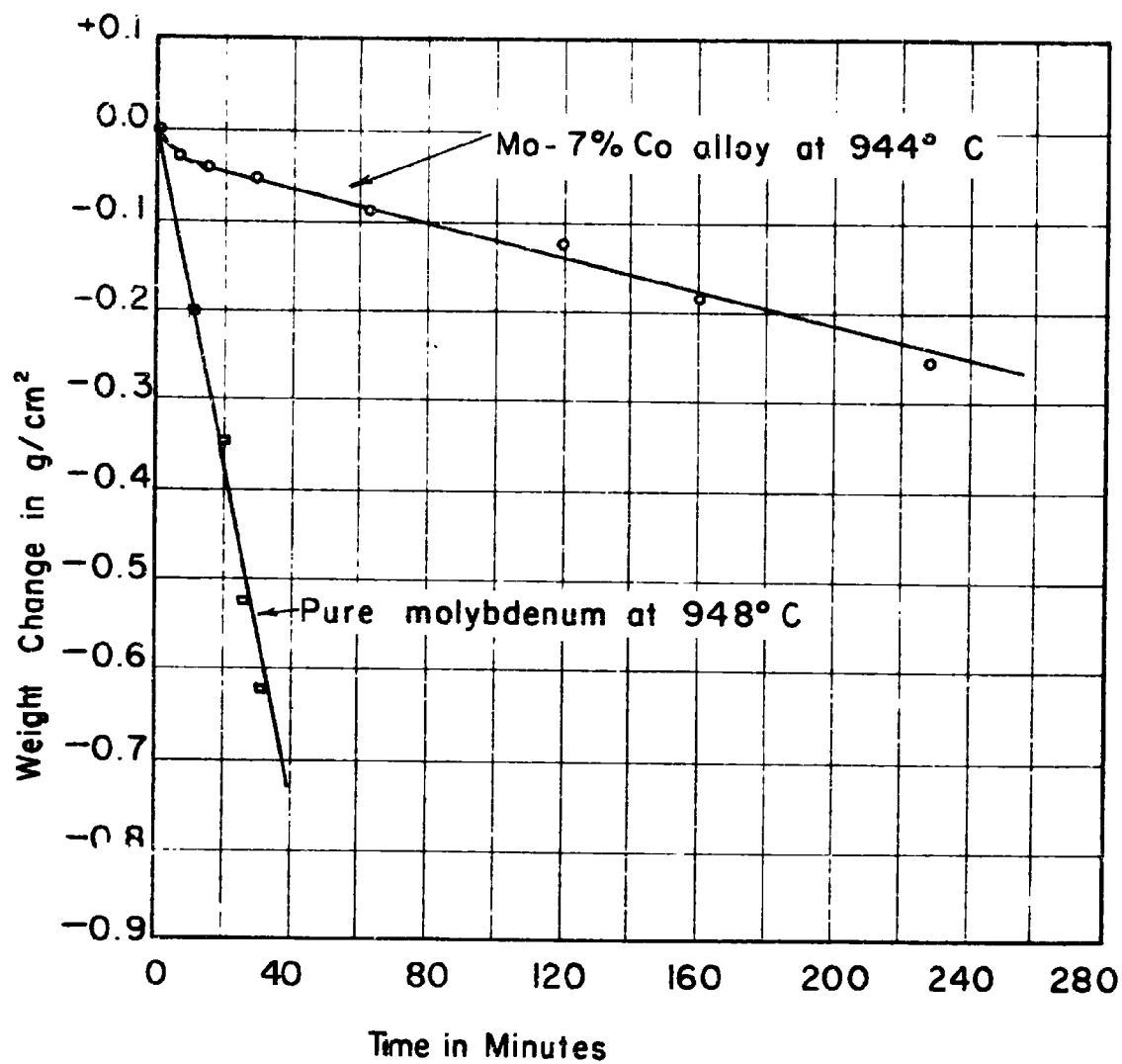


Fig. 2 Comparison of Oxidation Characteristics
of a Mo-7% Co Alloy and High Purity
Molybdenum

rate of evaporation of pure molybdenum under the same conditions is shown on the same diagram. It is seen that a partial protective coating forms on this alloy, reducing the rate of volatilization of molybdenum 90%. On removing the alloy from the furnace it was observed that it was coated with a dark purple powder. This was identified by the X-ray spectrometer as being predominantly the high temperature form of cobalt molybdate, although a second unidentified substance was also present.

Molybdenum-cadmium Alloy

A solution of cadmium in molybdenum was formed by heating together a piece of molybdenum sheet and some cadmium for two days at 950°C in vacuo in a sealed vycor tube. Under these conditions a solution of about 0.2% of cadmium was produced in the molybdenum sheet. An oxidation test was performed on this specimen at a comparatively low temperature, 690°C. It was hoped that this temperature was sufficiently low to avoid the volatilization of cadmium or cadmium oxide, which both have a high vapor pressure, and sufficiently high to lead to the formation of cadmium molybdate on the surface of the alloy. Unfortunately this was not the case. The coating formed on the specimen under these conditions was shown by the X-ray diffraction to contain little or no cadmium molybdate. It consisted of a mixture of cadmium oxide, and of molybdenum trioxide with a high degree of preferential orientation with growth occurring perpendicular to the $[110]$ crystal planes of MoO_3 . The results of the oxidation test of this alloy are presented in Figure 3, together with results obtained under the same conditions with a pure molybdenum sample. It can be seen that the coating produced was completely non-protective.

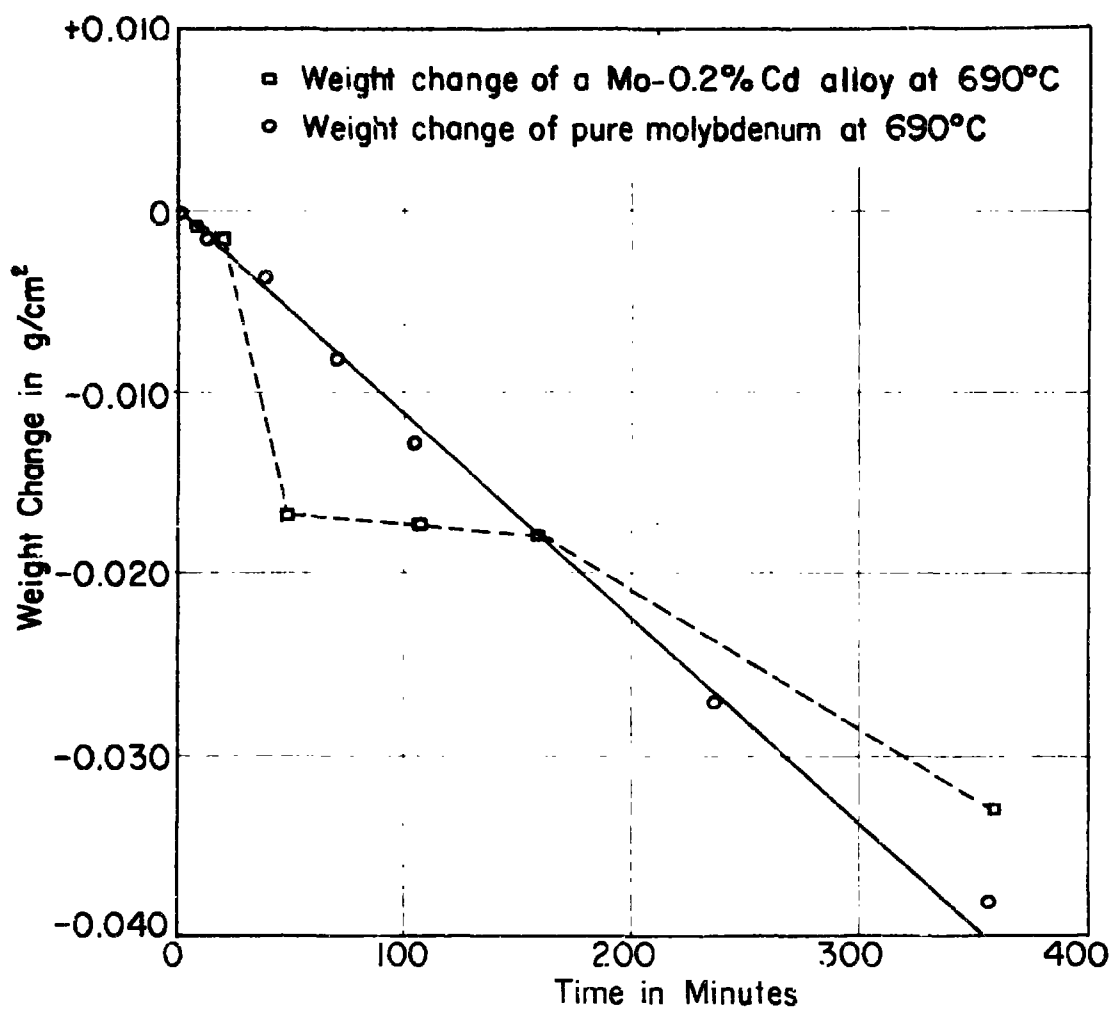


Fig. 3 Comparison of Oxidation Characteristics of a Mo-0.2% Cd Alloy and High Purity Molybdenum

Molybdenum Coated with Magnesium, Lead and Barium

The ratios of the atomic radii of magnesium, lead, and barium to that of molybdenum are such that it is extremely unlikely that any of these metals will go into solution in molybdenum. Molybdenum specimens were therefore completely coated with films of magnesium, lead, and barium. This was done by evaporation of these metals in vacuo from a hot molybdenum filament, according to the standard technique described by S. Dushman.⁴ Oxidation tests at about 950°C were performed on these specimens. It was realized that self-regenerative coatings could not be made in this manner, but it was hoped that molybdates would form on the surface of these specimens during their testing, and that the protection afforded by these coatings could be measured during the test. Unfortunately results were negative, since these specimens all volatilized completely a few minutes after the beginning of the oxidation tests. The coatings did not reduce the rate of volatilization of molybdenum. It is not possible to draw further conclusions.

B. NICKEL MOLYBDATE AND COBALT MOLYBDATE

Differential thermal analyses indicate that both nickel and cobalt molybdates have two transition points.¹ Three crystalline phases may therefore be expected in each compound. The high-temperature forms of these molybdates have now been obtained by heating them to the appropriate temperature followed by quenching in water. These forms are isomorphous, as are the low-temperature forms. Inefficient quenching of a heated sample leads to varying mixtures of the three forms being produced. This led to the probably erroneous idea recorded in the previous report that the structure of these molybdates varies with the period of heating. It was also previously thought that there was some possibility that one of the transition

points of cobalt molybdate might correspond to the equation, $\text{CoMoO}_4 \cdot n\text{H}_2\text{O} \longrightarrow \text{CoMoO}_4 + n\text{H}_2\text{O}$. Weight change measurements made on cobalt molybdate, however, indicate that this is not so, and that all three forms of cobalt molybdate, and probably, by analogy, nickel molybdate, are anhydrous.

In cobalt molybdate the intermediate form has been isolated by heating cobalt molybdate to 320°C and quenching in water. It was found impossible to isolate the intermediate form of nickel molybdate in this manner. Quenching nickel molybdate from 422°C led to the high-temperature form being produced. Quenching from 420°C led to the low-temperature form being produced. It may be concluded that either it is not possible to supercool this form of nickel molybdate, or that the form exists only in the extremely narrow range 420°C to 422°C. It is probable that its eventual isolation will show it to have the same crystalline form as the intermediate form of cobalt molybdate.

Tests were also made by quenching nickel molybdate into ice water in order to study further the nature of the spalling sometimes observed upon cooling from elevated temperatures. The following results were obtained:

1. No spalling was observed in samples heated below the transition point.* The X-ray pattern was substantially as reported for the low temperature (as prepared) form in the previous report.¹ However, in addition to this pattern, it was observed that at temperatures as much as 40°C below the transition point, there is evidence of the appearance of the principal lines of the high-temperature form.

* Note: Since it was not possible to isolate by quenching a phase between the two transition points indicated by differential thermal analysis, they are referred to here collectively as a single transition point.

2. Samples quenched from temperatures just above the transition point show no spalling and yield the typical high temperature form diffraction pattern, but with the addition of one or two extra lines which do not conform with the principal lines of the low temperature form nor with the expected lines of some intermediate phase, based on the assumption of isomorphism with cobalt molybdate for which an intermediate form has been isolated.

3. Samples quenched from a temperature approximately 400°C above the transition point spalled violently. The X-ray diffraction pattern for the spalled material was identical with that of the unspalled material quenched from lower temperatures which were yet within the high temperature phase region, except that, the "extra" lines, noted in the preceeding paragraph, did not appear.

From these results the following conclusions are drawn:

1. The true transition points have probably not yet been determined. Apparently reactions are sluggish and dependent upon rates of heating or cooling.

2. Spalling is probably not due to a phase change of a principal fraction of the material but is probably largely a mechanical phenomenon. However, the appearance of "extra" lines in samples of unspalled material indicates the possibility of the reaction being suppressed by small amounts of a phase which has undergone a transition, this however, being a transition to a phase other than the usual low temperature phase or an intermediate phase corresponding to that observed in cobalt molybdate.

3. Further study of this phenomenon of spalling is needed. It is necessary to obtain further information on the effect of cooling rates, and

the effects of cyclic heating and cooling in addition/^{to}making a further study of the factors which tend to suppress spalling on cooling.

III. GENERAL CONCLUSIONS AND FUTURE WORK

It is emphasized that although data are not complete at this point, nevertheless there is definite evidence that not only is nickel molybdate, a naturally-forming oxidation product, very protective at high temperatures, but also that the destructive spalling occurs only under certain conditions of cooling. Furthermore, on the basis of evidence so far obtained, it appears that it may be possible to deduce the spalling suppressing mechanism and perhaps enhance its action sufficiently to cause the protective form of nickel molybdate to remain on the sample surface at room temperature.

It is anticipated that work will continue in an effort to gain a better understanding of the mechanism of the oxidation protection afforded by nickel molybdate and of its temperature-dependent adherence qualities.

Attempts will also be made to form continuous coatings of magnesium, strontium, cadmium, barium, lead, lanthanum and thorium molybdates on molybdenum, followed by tests to measure their protectivity.

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

Investigator J. W. Spretnak Date 8-6-53

Supervisor Rudolph Speiser Date 8-6-53

FOR THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION

Executive Director Gran C. Woolpert Date 8-6-53

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