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On: PROTECTION OF MOLYBDENUM AGAINST
CORROSION AT HIGH TEMPERATURES

For the period: January 1, 1954 - March 31, 1954

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PROTECTION OF MOLYBDENUM AGAINST CORROSION AT HIGH TEMPERATURES

I. INTRODUCTION

During the period January 1, 1954 to March 31, 1954, work has proceeded in several areas outlined in the 'Future Work' section of the preceding report.¹

Work discussed in the present report is divided roughly into five areas:

- 1) Preparation of nickel molybdate of known high purity.
- 2) Observation of the conditions under which spalling is observed in nickel and cobalt molybdates.
- 3) Study of the mechanism of spalling.
- 4) Prevention of spalling and the study of reactions between various oxides and molybdates.
- 5) Testing of certain alloys to determine oxidation resistance and the nature and properties of oxidation products.

II. EXPERIMENTAL WORK

A. PREPARATION OF PURE MATERIALS

It was thought advisable to ascertain whether the molybdates as previously synthesized were correctly represented by the formulae NiMoO_4 and CoMoO_4 . The previous method consisted of boiling suspensions of stoichiometric proportions of the respective carbonates with molybdenum trioxide in water for prolonged periods. However, a dry method of preparation is likely to be superior to a wet method, such as that of

double decomposition between nickel nitrate and sodium molybdate in aqueous solution² where the pH of the solution must be carefully controlled in order to avoid simultaneous precipitation either of nickel hydroxides in alkali solution or of paramolybdates in acid solution. Nickel molybdate was therefore re-prepared by heating equimolecular proportions of nickel oxide (NiO) and molybdenum trioxide (MoO₃) in a Vycor tube in vacuo for 180 hours at 850°C. The resultant compound spalled on cooling. It was identified from its X-ray diffraction pattern as being identical with the ignited form of the nickel molybdate as previously prepared by wet methods. It was therefore assumed that the pure nickel molybdate has been prepared. It has already been shown by chemical analysis that nickel molybdate is weight stable on heating.³

B. OCCURRENCE OF SPALLING

It was shown in the previous report that molybdenum-nickel alloys, containing a sufficiently high percentage of nickel, form completely protective self-regenerative coatings on molybdenum in flowing air at 940°C. These coatings which consist predominantly of nickel molybdate spall violently from the alloy on cooling. Preliminary experiments have shown that molybdenum-cobalt alloys may also form almost completely protective coatings under the same conditions. The coating on the molybdenum-cobalt alloy consisted of cobalt molybdate, which is isomorphous with nickel molybdate and which spalled from the alloy in a similar manner on cooling.

Although cobalt molybdate produced on a molybdenum-cobalt alloy may not protect the alloy completely (whereas nickel molybdate is completely protective), much attention was paid to cobalt molybdate since it proved to be an easier substance to study. For example, it was easier to measure the weight stability of cobalt molybdate because spalling was so much less violent than in nickel molybdate. The differential thermal analysis pattern of cobalt molybdate was less complicated than that of nickel molybdate although similar. Three phases observed in differential thermal analysis were isolated in cobalt molybdate, though not in nickel molybdate, by quenching the compound from appropriate temperatures. It has nevertheless been considered to be legitimate to make some deductions about nickel molybdate from observations on cobalt molybdate because of the many similarities between the two.

In cobalt molybdate, unlike nickel molybdate, spalling occurs only on cooling, not on heating. Reheating followed by cooling results in further spalling. As in nickel molybdate, spalling could be prevented neither by very rapid nor by very slow cooling. Spalling will not occur in cobalt molybdate unless it is previously heated to at least 600°C for several hours.

A series of X-ray diffraction patterns was obtained for cobalt molybdate heated at different temperatures for varying periods of time and subsequently quenched. The following observations concerning temperature, time, and phases were noted.

1. A second phase, designated the intermediate temperature phase, appears on heating cobalt molybdate to 320°C and quenching. This was anticipated from the results of the differential thermal analysis. This phase does not spall.

2. On heating to temperatures above 320°C and quenching, the intermediate temperature phase appears, together with a third phase, which will be designated the high temperature phase. Increase in either the time or the temperature of heating results in an increase of the proportion of the high temperature phase present and an increase in the tendency to spall. (A similar phenomenon was noted in magnesium molybdate.) It is only when a considerable proportion of the high temperature phase is formed that spalling occurs.
3. If the temperature is sufficiently high and the time sufficiently long, then only the high temperature phase, which spalls on cooling, is observed.

This may indicate a sluggish phase transition. Such a sluggish transformation was also noted in magnesium molybdate¹ and is not uncommon. For example, there is an inversion temperature in wollastonite, CaSiO_3 , to pseudo-wollastonite at 1125°C ($\pm 10^\circ\text{C}$) in which the conversion is slow enough to make necessary exposures of up to 50 days at constant temperature in establishing the inversion temperature.⁴ Crystallographic evidence indicates that in a sluggish type of transition, a rearrangement of bonds and a major change of symmetry take place; whereas in a rapid type of transition, the change of symmetry is minor and involves no breaking of bonds. The two types have been called reconstructive and displacive transitions, respectively, by Buerger.⁵

C. MECHANISM OF SPALLING

The mechanism of spalling in nickel and cobalt molybdates has not yet been determined conclusively. The reason, in large degree, is the inability to study the phases existing at elevated temperatures and,

in lesser degree, the present incomplete nature of the data assembled from quenched samples and differential thermal analysis curves. It can be stated only that the phenomenon of spalling appears to be intimately associated with a particular phase transition known to exist in nickel and cobalt molybdates.

Light may be shed on the mechanism of spalling by use of a high temperature X-ray powder diffraction camera presently in the process of acquisition. However, for the time being, despite the lack of fundamental knowledge of the mechanism of spalling, work has progressed in an attempt to prevent spalling.

D. PREVENTION OF SPALLING

An attempt was made to prevent spalling of molybdates first in the pure compounds rather than directly in molybdates formed on the surface of molybdenum alloys. It was thought that this would be likely to throw some light on the mechanism of spalling and that it would also indicate more quickly which alloys might be tested successfully to give self-regenerative protective coatings which do not spall.

The principal method of spalling prevention employed has been the addition of other compounds to the pure molybdates. However, when additives are found which interact with and prevent spalling in molybdates, it is almost impossible to predict whether these will function in the same way on a molybdenum alloy. The formation of compounds on the surface of an alloy during oxidation depends on a number of factors such as the free energy of the compounds formed, mutual diffusion rates of the

metals forming the alloy, diffusion of anions and cations through the scale, solubility of the oxides in one another, interactions between the various compounds formed, etc.^{6,7} However, many of these data are particularly scarce. In the interest of testing as many different oxides as possible, experiments were performed on the synthetically prepared oxides on the assumption that although a material which was stable and did not spall in the free oxide state may do so when produced on an alloy surface, still there is little likelihood for success for an oxide or molybdate coating on an alloy which cannot be stabilized or prevented from spalling when in the free state. These assumptions permit a rapid screening of experiments and provide a key for designing more fruitful experiments with alloys.

It has been observed that when spalling does not occur, only the intermediate temperature phase of cobalt molybdate is found. By the addition of suitable components, the intermediate phase structure can be preserved at room temperature after quenching from temperatures of 1000°C to 1100°C (the present limit of testing temperatures) and spalling does not occur. The phenomenon is also observed in nickel molybdate in which the intermediate temperature phase had never been isolated previously. X-ray diffraction patterns indicate that the intermediate phase probably is stabilized by taking the additional component into solid solution with the intermediate temperature parent phase.

Selection was made of additional components (generally oxides) to add to the molybdates in an attempt to stabilize them, employing one or more of the following criteria.

1. The oxides were known or expected to form on the surface of molybdenum alloys.
2. The atomic radii and valences of the cations of the oxides were such that it seemed likely that a solid solution of the cation in one of the forms of the cobalt or nickel molybdates could exist, perhaps stabilizing the structure by virtue of a greater electronegativity or bond strength or more favorable atomic packing.
3. The cations were small enough that the diffusion rates of the ions in an alloy are likely to be appreciable, thus bringing the ion to the surface of the alloy where it could react to form the desired oxide or molybdate.

The material selected from the large number fulfilling one or more criteria were chromic oxide, alumina, ferric oxide, silica, magnesium molybdate, calcium molybdate, titanium dioxide, manganese dioxide, nickel wolframate, and zirconia. These were heated in equimolecular proportions with nickel molybdate and cobalt molybdate at temperatures of 1000°C to 1100°C for periods of one to two days. After heating, the mixtures were allowed to cool in air and were watched for spalling. X-ray diffraction patterns were obtained in order to see if the mixtures had undergone any reaction. It was not always easy to tell if the amount of spalling had decreased, relative to that observed in the pure molybdates, since dilution of the molybdates with a second component necessarily makes spalling appear less.

Three general types of situations occurred when oxides were heated with molybdates: stabilization of the intermediate form of the molybdate with resultant elimination of spalling, reduction of spalling without any apparent reaction of the constituents, and reaction of the molybdate and

oxide to produce a spinel type oxide with the loss of molybdenum trioxide previously associated with the molybdate.

1. Molybdate structure stabilization

a. Magnesium molybdate-cobalt molybdate system. Molybdates were heated at 984°C for 21 hours. Spalling did not occur on cooling. The intermediate form of cobalt molybdate was the only structure observed in the X-ray diffraction pattern. Stabilization is due apparently to the effect of magnesium atoms in substitutional solid solution.

b. Aluminum oxide-cobalt molybdate system. Constituents were heated at 985°C for 17 hours. Spalling did not occur on cooling. Intermediate and high temperature phases of cobalt molybdate were observed together with alumina. If stabilization is due to solid solution of aluminum atoms, apparently the reaction has not gone to completion but sufficient intermediate form is present to prevent visible spalling.

c. Silica-cobalt molybdate system. Constituents were heated at 1135°C for 46 hours. Spalling was not observed on cooling. The diffraction patterns consisted principally of the intermediate temperature form of cobalt molybdate, with some high temperature form being observed.

d. Manganese dioxide-nickel molybdate system. Constituents were heated at 1111°C for 22 hours. Spalling did not occur on cooling. The only structure observed was isomorphous with the intermediate form of cobalt molybdate and was presumed to be the intermediate form of nickel molybdate, not previously isolated in pure nickel molybdate.

2. Reduction of spalling without interaction of phases.

Spalling was reduced in intensity and amount in nickel molybdate by the addition of titanium dioxide, silica, magnesium molybdate, calcium molybdate, and zirconia. Only the patterns of the molybdate high temperature phase and the normal pattern of the additive were observed on examination by X-rays.

3. Spinel formation

- a. Ferric oxide-nickel molybdate and ferric oxide-cobalt molybdate systems. Constituents were heated at approximately 1100°C for about 24 hours. Spalling did not occur on cooling. The structure observed on cooling gave only the pattern of a spinel type structure. Apparently all the molybdenum was lost as molybdenum trioxide and the remaining stable oxides had the formulae $\text{NiO}\cdot\text{Fe}_2\text{O}_3$ and $\text{CoO}\cdot\text{Fe}_2\text{O}_3$, respectively. The lattice parameters were found to be approximately 8.34Å. As a check, the nickel-iron-oxygen spinel was prepared by heating together the respective oxides. The X-ray diffraction pattern was identical with that previously observed.
- b. Alumina-nickel molybdate system. Constituents were heated as for the ferric oxide - nickel molybdate system. The resulting product was a nickel-aluminum-oxygen spinel with a lattice parameter of approximately 8.04 Å.
- c. Other systems. Preliminary studies indicate the same type of reaction occurs in the systems alumina-cobalt molybdate, chromic oxide - cobalt molybdate, and chromic oxide - nickel molybdate.

Mixed oxides of the spinel type are well known for their protective properties on steels. In addition, Iitaka and Miyake⁷ have observed that the marked non-oxidizing properties of Nichrome alloy are explained by the formation of a film of $\text{NiO}\cdot\text{Cr}_2\text{O}_3$ on the surface. The spinel structure is observed in a large number of oxides of the general type $\text{AO}\cdot\text{B}_2\text{O}_3$. Minerals have been observed in which the A positions are shared between two or three metals. Only small differences in lattice parameters are observed among the oxide spinels. The spinel structure is known to be exceedingly flexible as to composition and generally quite stable.

These observations on spinels and past experimental evidence indicate that molybdenum base alloys can be protected from oxidation by at least three basically different means of production of self-regenerative oxide coatings:

- (1) Production of a nonspalling regenerative coating by chemical combination of the constituents of a binary alloy with oxygen (e.g., CaMoO_4)
- (2) Production of a protective regenerative coating by chemical combination of molybdenum and one alloying material with oxygen which is then stabilized by simultaneous or subsequent reaction with the second alloying element (e.g., nickel molybdate stabilized with manganese)
- (3) The production of a nonspalling regenerative coating by chemical combination of two alloying elements with oxygen with evolution of molybdenum trioxide until a sufficient coating is built up to be protective (e.g., spinel formation).

In addition to these methods, two others are possible which conceivably could be demonstrated as practical by further experimentation:

- (1) The Price-Thomas technique, in which one or more alloying elements are oxidized preferentially to molybdenum in a reduced partial pressure of oxygen, thus creating a protective coating of the alloying element oxides or combinations thereof. (This technique, however, does not permit the automatic regeneration of a coating and hence defects therein are not self-healing.)
- (2) The technique wherein the alloy is oxidized in air with the formation of nonprotective oxides, or combinations thereof, following which the alloy is heated in a reduced partial pressure of oxygen, thus decomposing the oxides to different compounds which react, or react on subsequent heating, to form a protective coating. This may be regarded as a modified Price-Thomas technique.

E. OXIDATION TESTS

1. Apparatus and procedure

Apparatus and technique for oxidation tests were described in previous reports.^{3,8} The technique permits weighing of the oxidizing sample at any time during the test.

Tests were performed for purposes of determining

- a. Whether oxidation products of the anticipated type and properties would actually form on alloys
- b. Whether such oxidation products would enhance the oxidation resistance of the alloy.

2. Tests on binary alloys forming molybdate coatings

Oxidation tests have been performed on a 62% molybdenum - 38% nickel alloy* at 930°C and on a 60% molybdenum - 40% cobalt alloy at 960°C. These alloys correspond to the compositions of single phases, δ in the molybdenum-nickel system⁹ and ϵ in the molybdenum-cobalt system.^{10,11} However, metallographic examination of the molybdenum-nickel alloy shows it to be multiphased. The nickel alloy produces a completely protective coating of the high temperature phase of nickel molybdate. The cobalt alloy produces an almost completely protective coating of the high temperature phase of cobalt molybdate. Both coatings spall on cooling.

* All alloys have been prepared by arc melting methods. Compositions noted are intended compositions only; no chemical analyses have been made.

3. Tests on ternary alloys with stabilized molybdate coatings

Figure 1 represents the oxidation of the alloy 63% molybdenum-25% cobalt - 12% silicon at 960°C. The alloy forms an almost completely protective coating which does not spall. This observation is substantiated by the fact that the alloy was removed from the furnace at point A (Figure 1), allowed to cool, and replaced without either resultant alteration in weight or alteration of slope of the oxidation curve. Manual examination of the coating showed it to be extremely hard and adherent. Its diffraction pattern showed that it consisted predominantly of the intermediate temperature phase of cobalt molybdate with traces of the high temperature phase. The lines of metallic molybdenum were also present. It is believed that this is due to the fact that the coating is so thin, as is further demonstrated by the small weight gain, that the molybdenum beneath it produced its own pattern superimposed on that of the coating.

Calculations based on the weight gain and an estimated density of cobalt molybdate give the thickness of the coating as about 0.025 mm (0.001"). No traces of either SiO_2 or MoSi_2 were found, indicating that these compounds are not producing the protection.^{12,13,14} Protection is due most probably to the silicon-stabilized intermediate form of cobalt molybdate.

The same alloy tested for 19 hours at about 1100°C oxidizes quite rapidly. The coating spalled on cooling. It consisted predominantly of the high temperature phase of cobalt molybdate. The intermediate temperature phase was completely absent.

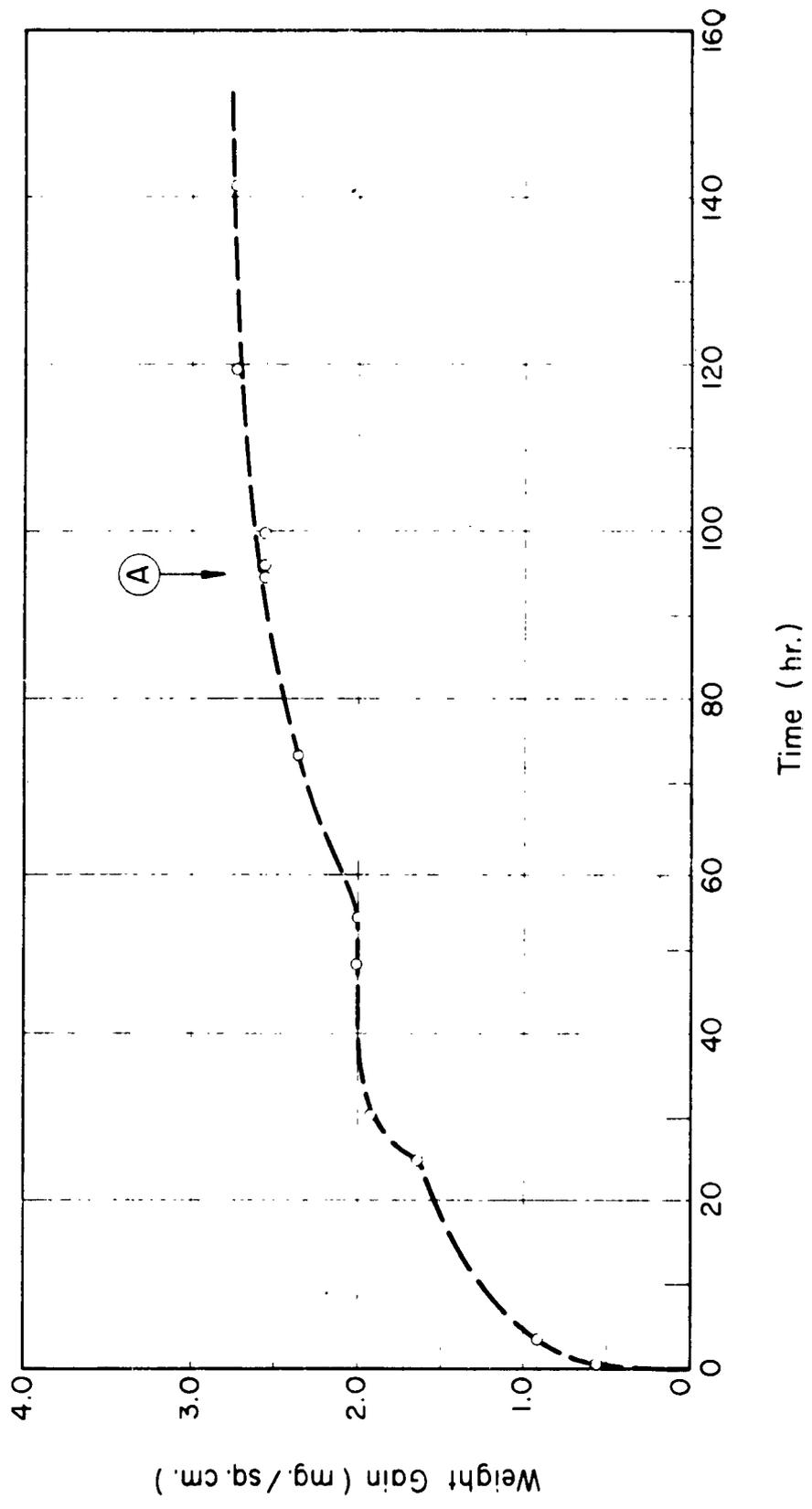


Fig. 1. Oxidation Curve for Alloy 63% Mo, 25% Co, 12% Si
 Testing Temperature - 960° C.

4. Tests on ternary alloys which produce spinel type oxides

Tests were performed on the alloy 60% molybdenum - 20% nickel - 20% iron at approximately 920°C and 1110°C. At 920°C the surface product, which spalled on cooling, consisted of ferric oxide, the high temperature phase of nickel molybdate, and the nickel-iron spinel, $\text{NiO} \cdot \text{Fe}_2\text{O}_3$. At 1110°C the surface product again spalled on cooling. The scale consisted of the high temperature phase of nickel molybdate and the spinel $\text{NiO} \cdot \text{Fe}_2\text{O}_3$. Apparently the spinel can form on the alloy. In the above case it did not form a protective coating. This may have been true only because it did not completely cover the alloy surface.

An oxidation test was performed on the alloy 62% molybdenum - 20% nickel - 18% chromium at 950°C. The scale spalled on cooling. It consisted of the high temperature phase of nickel molybdate plus chromic oxide. No spinel type oxide was present, the temperature presumably being too low for its formation. During a short-time preliminary test, the sample lost weight quite rapidly. The chromium alloy will be tested at a higher temperature in order to see if a protective spinel forms.

A preliminary, short-time, oxidation test of the alloy 63% molybdenum - 25% cobalt - 12% aluminum was performed at 954°C. The oxidation product spalled from the surface of the alloy on cooling. It consisted predominantly of the high temperature phase of cobalt molybdate, although some of the intermediate temperature phase and some alumina were present. It is believed that this alloy contained a lower percentage of aluminum than the nominal composition reported. If the test were conducted at a higher temperature, a spinel would be expected to form.

An alloy of 63% molybdenum - 20% nickel - 17% titanium oxidized completely in 22 hours at 950°C so that an oxidation curve cannot be accurately presented, nor were the surface products available for examination.

III. SUMMARY

The mechanism of spalling has not yet been established conclusively. It is hoped that future work, especially high temperature X-ray diffraction studies, will permit a fuller understanding of the crystal structure of the phases, and of the fundamental mechanism of the phase changes, in the materials which spall.

It has been observed that spalling of nickel and cobalt molybdates is associated with a phase which appears upon quenching only after heating above certain temperatures. If the phase designated the 'intermediate temperature phase' can be preserved at room temperature by means of the introduction of another component, spalling can be suppressed. This has been accomplished in the case of nickel molybdate by the use of manganese dioxide and in the case of cobalt molybdate by the use of silica, magnesium molybdate, or alumina. It has also been shown that the reaction required to produce the stabilized intermediate phase will occur on the surface of an alloy as well as in the free materials.

It has been shown that oxidation products obtained from certain molybdenum base alloys will react to form spinel type oxides. This has been accomplished with mixtures of compounds and by oxidation of the appropriate alloy. This opens up a new area of possibilities for the

production of self-regenerative protective oxide coatings for molybdenum alloys.

In addition to showing that spalling can be prevented and that the production of spinel type oxides on the surface of molybdenum alloys is possible, oxidation tests have also demonstrated that molybdenum alloyed with 25% cobalt and 12% silicon is very oxidation resistant at 960°C. A slight adjustment of alloy composition may render the oxide coating completely protective.

IV. FUTURE WORK

A. MECHANISM OF SPALLING

The study of the fundamental mechanism of the spalling of molybdates will be continued employing refined differential thermal analysis techniques and, when it becomes available, a high temperature X-ray diffraction camera. In conjunction with this work, attempts will be made to identify the crystalline forms of the phases already observed and isolated, many of which are not reported in the literature.

B. PREVENTION OF SPALLING

Work will be continued in an effort to find more ways to prevent spalling in nickel and cobalt molybdates. Testing will be continued whenever possible on actual alloys of compositions designed to produce the stabilized molybdate coating.

C. SPINEL FORMATION

The formation of spinel type oxides of metals feasible for use as alloying elements in molybdenum will be studied further. Testing may be continued on certain alloys of compositions designed to produce coatings composed of spinel type oxides.

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