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ADHERENT ELECTROPLATING
ON MOLYBDENUM

by

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BIBLIOGRAPHY

- (1) Addicks, L., "Silver in Industry", Reinhold Publishing Corp., 1940
- (2) American Society for Testing Materials, Letter from R. B. Saltcnstall, Oct. 19, 1951
- (3) Blum, W., and Hogaboom, G. B., "Principles of Electroplating and Electroforming", McGraw-Hill Book Co. Inc., 1949
- (4) Buckley, H. E., "Crystal Growth", Wiley & Sons, 1951
- (5) Cannizzaro, J. J., assignor to Westinghouse Electric Corp., U. S. Patent #2, 443, 651, "Process for Electroplating on Tungsten"
- (6) Clark, G. L., Pish, G., and Weeg, L. E., "Applied Physics", 1944
- (7) Climax Molybdenum Company, Letter from N. L. Dsuble, Oct. 23, 1944
- (8) Hansen, M., Der Aufbau der Weistofflegierungen, Ver lag von Julius Springer, Berlin, 1936, Edwards Brothers, Inc.
- (9) International Nickel Co., Telephone conversation with Dr. Wesley and Letter from Climax Molybdenum Co., 1951
- (10) Kohl, W. H., "Materials Technology for Electron Tubes", Reinhold Publishing Corp., 1951
- (11) Mantell, C. L., "Industrial Electrochemistry," Mc Graw-Hill Book Co., Inc., 1950
- (12) Massachusetts Institute of Technology Research Laboratory of Electronics, "Tube Laboratory Manual", 1951
- (13) Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. II, Longman's Green and Co., 1930
- (14) "Metal Finishing", Letter from W. A. Raymond, Oct. 9, 1951
- (15) "Metal Progress", July, 1951, Molybdenum A New High Temperature Metal, R. K. Parke
- (16) "Metals Handbook", The American Society for Metals, 1948
- (17) "Modern Electroplating", The Electrochemical Society, 1942
- (18) Molybdenum - Practical Structural Material, Gelok, J., Westinghouse Engineer 7, 156, Sept., 1947
- (19) "Product Engineering", Jan., 1952, "Molybdenum - Our Most Promising Refractory Metal, Harwood, J. J.

- (20) Sachs, G., and Van Horn, K., "Practical Metallurgy" American Society for Metals, 1940
- (21) U. S. Dept. of Commerce, National Bureau of Standards, Letter from W. Blum, Oct. 18, 1951
- (22) Westinghouse Electric Corporation, Lamp Division, Letter from A. Korbelak, Oct. 17, 1951

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SUMMARY

Molybdenum, due to its high temperature properties, and potential supply, is becoming a very important structural material, particularly in the field of electronics; however, it is not new in this part of industry. As temperatures go higher and higher in various fields, the need for satisfactory materials becomes of paramount importance.

One of the ways in which to overcome the disadvantages of poor surface stability, brazing difficulties, and surface resistance to high frequency conduction, is by electroplating. Until recently there has been no satisfactory method for obtaining adherent deposits. The purpose of this report has been to investigate these recent processes and devise a method by which the average plating installation may obtain adherent electroplated deposits on molybdenum.

The following method, devised by the author, was found to give satisfactory adherence of nickel on flexible sheet molybdenum: After degreasing, the part is etched anodically in 95% sulfuric acid for one minute at 9 volts and then rinsed in cold running water. It is then rinsed in an ammonium hydroxide solution, followed by cold running water. The molybdenum is then treated cathodically for one minute at 9 to 10 volts in 95% sulfuric acid. After this, it is rinsed in cold water and nickel plated in a low ph Watt's bath.

The following method, also devised by the author, was found to be satisfactory for nickel plating rigid pieces of molybdenum for brazing purposes. After degreasing, the part is etched in a solution of three parts water, two parts sulfuric acid, and one part nitric acid. It is then rinsed and dipped in hot hydrochloric acid. The part is rinsed again and plated with nickel in a low ph Watt's bath.

The following method devised by A. Korbela² of Westinghouse Corporation is satisfactory for obtaining adherent nickel plating on flexible sheet molybdenum. After degreasing, the part is etched anodically in 60% sulfuric acid for 30 seconds at 10 volts. After rinsing and dipping in a caustic bath (caustic soda, commercial cleaner or equivalent), the part is neutralized in a 5-10% sulfuric acid dip. After rinsing, the part is chromium plated for 20-60 seconds at 1 amp/in.² The molybdenum is then rinsed and transferred to a high chloride nickel strike (Wood's bath).

Another method for obtaining adherent deposits on molybdenum is a method used by RCA Victor. This involves spraying the part with a mixture of nickel and silver oxides and firing in line II at 950°C. for 15 minutes.² The part may then be plated with any desired metal.

INTRODUCTION

(19)

Molybdenum and its alloys are being used more and more in applications calling for a metal to withstand high temperatures. Because of its availability and its properties, it is rapidly becoming one of the most promising refractory metals where materials are needed to construct equipment which will operate in excess of 1800°F. By referring to Table I, one may see the metals on which future developments in these high temperatures depend.

TABLE I
PROPERTIES OF REFRACTORY METALS

<u>METAL</u>	<u>MELTING POINT, F</u>
Tungsten	6,170
Rhenium	5,740
Tantalum	5,425
Osmium	4,900
Molybdenum	4,760
Iridium	4,450
Columbium	4,380
Boron	4,200
Chromium	3,430
Zirconium	3,380
Titanium	3,272
Hafnium	3,100

The investigation for better high temperature metals stems from two main considerations. One is the temperature limitation of the alloys that we are now using. For the most part, they do not retain desirable properties above 1650°F. The second consideration is the shortage that we are now experiencing in the alloying elements. This has shown the need for refractory

metals of a much less critical nature, however, successful attempts are being made in using alloys which have less of the critical alloying element. The real relief, though, must come from new alloy systems and the refractory metals that will maintain their desirable properties.

Molybdenum has long been of interest to designers particularly in the alloying of steels for resistance to certain chemicals. Also, it is used to a very great extent in the electronic industry in the manufacture of tubes. Here it is used in the making of grids, supports, plates, channels, caps, sleeves, rods, spring contacts, and similar parts. Lamp designers for years have been interested in molybdenum. They have used considerable quantities of molybdenum wire as supports for filaments, lead-in wires, and mandrel wire on which tungsten filaments are wound. World War II, with its enormous demand for electronic tubes and electronic equipment, required that the production of molybdenum be increased many fold. Not only this but the shapes and sizes of parts became much more complicated and varied. This also brought about better methods of shaping and working the metal. The production rate at Westinghouse alone increased 1500% of the pre-war figure.

Molybdenum disulphide has been attracting attention as a lubricant, however, such special uses would become insignificant, if the full structural potentialities of molybdenum were to be attained, especially in view of the abundance of the ore.

The United States is producing more than 85% of the world's supply of molybdenum, coming from the chief ore, molybdenite (MoS_2). The principal producers are the Climax Molybdenum Company, The Molybdenum Corporation of America, and The Kennecott Copper Corporation. In 1917 the Climax Company began

active work of the famous molybdenite deposits in Climax, Colorado in 1917. However, it has been since 1924 that they have been in production at this location. The Kennecott Copper Corporation began producing molybdenum in 1939. This, however, was as a by-product of their copper mining in Utah and New Mexico, which accounts for about 50% of our present molybdenum production. The mines of the Molybdenum Corporation of America are located in Questa, New Mexico.

In 1945, the reserves of molybdenum were estimated at 400 million tons. While this metal is now considered to be short and is under allocation, one may expect the demands to be met.

(15)

In addition to having a melting point above the temperature of the intended use, a successful high-temperature metal must possess a stable surface, adequately inactive to its environment, that is, it must not react at too high a rate with the ambient atmosphere, and it must not evaporate too fast. From the vapor pressure, it can be shown that molybdenum evaporates at a low rate below about 3000°F. Nevertheless, since its vapor pressure is too high for it to serve as an incandescent lamp filament, it is evident that this property should not be ignored when long service and high dimensional stability are required.

As a matter of fact, molybdenum does have poor surface stability in air at high temperatures due to a high rate of oxidation. This is its most troublesome property. The oxide, MoO_3 , forms and vaporizes at an appreciable rate above 1400°F. even when the atmosphere contains but a few per cent of oxygen. Unfortunately, the rate of oxidation is very much higher than for metals whose oxides are practically nonvolatile up to 3500°F. ^{and} remaining on

the surface to retard further reaction. For example, at 1800°F. in air flowing slowly, the surface of molybdenum recedes at the rate of 0.02 to 0.05 in. per hour. This rate of loss of metal is intolerable for most uses. Improvement of surface stability represents the most important and, at the same time, the most difficult problem that must be solved before the metal is widely used in heat engines. Several ideas are being developed; each gives hope of meeting the requirements of some of the high-temperature applications; none is free from serious objections.

One method of protection is known as cladding, in which another more oxidation resistant metal is welded to the surface of molybdenum by rolling. This process has been investigated and improved by Bruckart, Whalen, Jaffee, and Genser. From their work, it can be said that cladding is feasible with nickel or with an alloy of 90% platinum, 10% rhodium. In creep tests on molybdenum clad with 15% its thickness with "A" nickel on each side, the minimum creep rate at 1800°F. and 5000-psi. stress was 0.0001% per hr. The obvious limitations of inconel and nickel clad is the relatively low melting points of the surface metal, and of the platinum alloy is its high cost and scarcity. Even so, cladding will meet some high-temperature requirements.

A second method of surface protection is by the vapor-phase deposition of silicon. This method has been developed to a very promising stage by Beidler, Powell, Campbell, and Yntema. They report that a silicon coating 0.025 mm. thick completely protects the underlying molybdenum for 4000 hr. in air at 1000°C. (1830°F.) and for 30 hr. at 1700°C. (3100°F.). The principal limitations of this protection method are (a) the coating may fall when plastic strain occurs, and (b) the coating must be perfect in its

coverage, a small flaw permitting loss of molybdenum over a relatively large area.

This method of protection, while still being improved, has had notable success. The Pansteel Metallurgical Corporation has recently announced the availability of molybdenum bar, rod, wire, and tubing with siliconized coatings.

The third method of protection involves a ceramic coating. This method, too, probably will be suitable for certain applications but has not yet shown as much promise as the two methods just mentioned.

The fourth method of protecting molybdenum against oxidation is by electroplating. Some success has been reported, but this method also has been inadequately investigated.

The last method involves the alloying of molybdenum with an element or elements which suppress the formation of the volatile MoO_3 . This method has only recently been investigated and has achieved, so far, the least success. However, it has been only superficially surveyed. An important advantage which an oxidation resistant alloy would have over coated molybdenum is the capacity for self-healing in the event of damage to the surface. Those oxidation resistant alloys which have so far been developed are brittle and consequently difficult to fabricate.

One of the most difficult operations to perform in working with molybdenum is to braze it to other members. There are very few metals which will wet sufficiently to join the metal. This problem may be overcome by electroplating the area to be brazed with nickel, which is very easily wet by most solders.

Another problem encountered in the use of molybdenum in the electronic

industry is its surface resistance in high frequency applications. This has become particularly important in recent years because of the research that is going into higher wattage magnetrons and other transmitting tubes in the ultrahigh-frequency range. Silver plated molybdenum becomes a very important material for these applications.

Because of the many uses which are developing for plated molybdenum, a method was needed, particularly for use in electron tubes, by which adherent deposits could be obtained. Until very recently, there was no procedure available that could be performed by the ordinary plating installation to obtain satisfactorily adherent deposits. Therefore, it was felt that the need for work in this field is of immediate importance.

PURPOSE

There are two primary purposes for this investigation: first, there was an attempt made to find which of the existing methods used in the plating of adherent deposits on molybdenum gave the most satisfactory results; second, there was an attempt made to devise a method by which adherent deposits may be made on molybdenum, preferably by using only chemicals and techniques that would be available in the average plating installation.

11. One stainless steel methanol tank, 16" X 12" X 12", with hinged cover.

12. Nickel, stainless steel, platinum, iron, and lead electrodes.

There were many other smaller miscellaneous items, such as, a reversing switch, thermostatic hot plates, stainless steel beakers, microscope, etc., that were used.

Any of the items previously listed may be replaced by other standard equipment that will perform the same function.

SOLUTIONS

(17)

(1) Nickel Plating Bath

(a) Make up

Nickel sulfate - 44 oz/gal

Nickel chloride - 4 oz/gal

Boric acid - 4 oz/gal

Non-Pitter, as needed

Carbon filtered and electrolytically purified

(b) Solution Operation

Nickel - 11 oz/gal

Chloride - 1.2 oz/gal

Boric acid - 4 oz/gal

ph - 1.8

Temperature - 45 to 55°C

Cathode current density, 20-60 amp/ft.²

(17)

(2) Chromium Plating Bath

(a) Make up

Chromic acid - 34 oz/gal

Sulfuric acid - .30 oz/gal

(b) Operation

Chromic acid, 33.5-36.5 oz/gal

Sulfuric acid, .335-.365 oz/gal

CrO₃/SO₄ ration 100 ± 5

Temperature - 45 to 70°C

Cathode current density, 100-400 amp/ft.²

(3) Copper High Speed Plating Bath (DuPont)

(a) Make up

Coppralyte plating salts, potassium - 24 oz/gal

Potassium hydroxide - 5.6 oz/gal

Addition agent RH774 - 8cc/gal

(b) Solution Operation

Copper - 5.6 oz/gal

Free KCN - .5 oz/gal

Potassium hydroxide - 5.6 oz/gal

Addition agent RH774 - 8cc/gal

Temperature - 80 to 85°C

Current density, 10-60 amp/ft.²

(3)

(4) Acid Copper Plating Bath

(a) Make up

Copper sulfate - 32 oz/gal

Sulfuric acid - 6 oz/gal

Molasses - 1 pint/100 gal

(b) Operation

Copper - 8.1 oz/gal

Sulfuric acid - 6 oz/gal

Temperature - room

Cathode current density, 20-60 amp/ft.²

(5) Platinum Plating Bath⁽¹⁷⁾

Water - 1 liter

Ammonium phosphate (secondary) 20 grams

Sodium phosphate (secondary) 100 grams

Platinic chloride - 4 grams

Current density - 9 amp/ft.²

Temperature - 70 to 90°C

(6) Penn Salt Cleaner #35

Concentration, 6-8 oz/gal

Temperature - 200 to 212°F

Time for immersion, 1-10 minutes

(7) Nitric Acid, Technical, 42° Be, (70%)

(8) Hydrochloric Acid, Technical, 20° Be, (31.4%)

" " C. P., (37.8%)

(9) Sulfuric Acid, Technical, 66° Be (93.2%)

(10) Hydrofluoric Acid, Technical, (52%)

(11) Ammonium Hydroxide, C.P., NH₃ (29.1%)

(12) Phosphoric Acid, Technical, (85%)

(13) All solid chemicals were either of C. P. or plating grade.

(14) Nickel Strike or Activation

Nickel chloride - 32 oz/gal

HCL - 500 cc/gal

6 volts - one minute - room temperature

(15) Indium Plating

This was purchased as a commercial cyanide bath.

TREATMENT SCHEDULES

The treatments in this list of schedules are presented under three headings; namely, treatments which gave no adherence, treatments which gave questionable adherence, and treatments which gave satisfactory adherence of electroplated films on molybdenum.

In order to prevent much repetition, the following steps are understood to hold for all the molybdenum samples that were treated. The purpose of these four steps is to obtain a surface which is free of dirt and grease.

- (a) Degrease in clean trichloroethylene at room temperature
by dipping
- (b) Dry
- (c) Immerse in soak cleaner, and agitate part. (Pean Salt E-35,
190°F, 8 oz/gal) or equivalent soak cleaner
- (d) Rinse in cold running water

The rinsing in cold running water was done by allowing tap water from the city water line to overflow from a five gallon ceramic crock. A rapid flow was maintained at all times to insure against contaminating the samples in the rinse water. This condition was also maintained in the rinsing steps listed under the treatments.

It will be noted that in many trials there is a step in which an ammonium hydroxide rinse is used. This was at room temperature and was only controlled to the extent of keeping an ammonia odor coming from the rinse.

In the electrolytic etching steps that are given, the current densities

were varied from about 10 amp/ft.² to 300 amps/ft.², unless otherwise stated. The time of these etches varied from about one minute to five minutes. Also, unless otherwise stated they are at room temperature which on most days was about 80°F.

When the molybdenum came from the etching steps in the trials it was transferred to the next steps as quickly as possible, not allowing the film of solutions to dry on the strip. When going into the nickel or other plating baths, electrical contact was made before the part was immersed in the solution, however, this was not always found essential but was thought to be good practice.

The adherence of the plating on the samples was tested by bending the strips of molybdenum until they ruptured. If the electroplating did not peel, another sample would then be fired in line hydrogen at 900°C for 15 minutes. If the plating withstood these two tests, they were considered to have an adherence which was satisfactory.

When a stainless steel electrode was used in the trials, it was of type 304.

The treatment, after coming from the plating bath, was to simply rinse in hot and cold running water and dry.

Treatments Which Gave No Adherence

The following treatment schedules were not sufficient to give satisfactory adherence of electroplated films on molybdenum:

Trial 1:

(a) Pass alternating current through a molybdenum sample in the presence of 52% hydrofluoric acid from one to five minutes. Current density 20 to 300 amps/ft.², platinum electrode.

- (b) Rinse in cold running water
- (c) Nickel plate

Trial 2:

- (a) Same as trial 1
- (b) Rinse in dilute NH_4OH
- (c) Rinse in cold running water
- (d) Nickel plate

Trial 3:

- (a) Etch anodically in varying strengths of KOH and NaOH solutions at current densities from 10 to 300 amp/ft.² (alternating current also used)
- (b) Rinse in cold running water
- (c) Nickel plate

Trial 4:

- (a) Same as trial 3
- (b) Rinse in dilute NH_4OH
- (c) Rinse in cold running water
- (d) Nickel plate

Trial 5:

- (a) Anodic and cathodic etching in 210 g/liter CrO_3 solution. Current densities from 10 to 300 amp/ft.²
- (b) Rinse in cold running water
- (c) Nickel plate

Trial 6:

- (a) Etch anodically and cathodically in 52% hydrofluoric acid at current densities from 10 to 300 amp/ft.²
- (b) Rinse in cold running water

(c) Nickel plate

Trial 7:

- (a) Same as trial 6
- (b) Rinse in dilute NH_4OH
- (c) Rinse in cold running water
- (d) Nickel plate

Trial 8:

- (a) Anodic etch in 70% H_2SO_4 at current densities from 10 to 300 amp/ft.²
- (b) Rinse in cold running water
- (c) Nickel plate

Trial 9:

- (a) Same as trial 8
- (b) Rinse in dilute NH_4OH
- (c) Rinse in cold running water
- (d) Nickel plate

Trial 10:

- (a) Etch with alternating current in 90% H_2SO_4 , platinum electrode
- (b) Rinse in cold running water
- (c) Copper plate in cyanide bath

Trial 11:

- (a) Etch anodically and cathodically in hot 50% H_2SO_4 , platinum electrode
- (b) Rinse
- (c) Nickel plate

Trial 12:

- (a) Same as trial 11, but used iron electrode

Trial 13:

- (a) Anodic etch in 90% H_2SO_4 , stainless steel electrode
- (b) Rinse in cold running water
- (c) Rinse in dilute NH_4OH
- (d) Rinse in cold running water
- (e) Cathodic etch in same 90% H_2SO_4 , stainless steel electrode
- (f) Rinse in cold running water
- (g) Copper plate, cyanide bath, and in acid copper bath

Trial 14:

- (a) to (d) same as trial 13, except H_2SO_4 was 50% and also tried nickel plating and also tried platinum electrode

Trial 15:

- (a) Etch in solution of 3 parts H_2O , 2 parts H_2SO_4 , and 1 part HNO_3
- (b) Rinse in cold running water
- (c) Rinse in dilute NH_4OH
- (d) Rinse in cold running water
- (e) Cathodic etch in 50% H_2SO_4 , platinum electrode
- (f) Nickel plate

Trial 16:

- (a) to (g) same as trial 13 except 75% H_2SO_4 and platinum electrode was used. Alkaline cleaner was substituted for NH_4OH for one run also.

Trial 17:

- (a) Etched anodically in 75% H_2SO_4 , stainless steel electrode
- (b) Rinse in cold running water
- (c) Rinse in dilute NH_4OH

- (d) Rinse in cold running water
- (e) Rinse in boiling 50% KOH
- (f) Rinse in cold running water
- (g) Nickel plate

Trial 18:

- (a) Etch in solution of 50 parts HNO_3 and 50 parts HF
- (b) Rinse in cold running water
- (c) Rinse in dilute NH_4OH
- (d) Rinse in cold running water
- (e) Nickel plate

Trial 19:

- (a) Etch in solution of:
 - 1000 cc H_2O
 - 325 g $\text{K}_3\text{Fe}(\text{CN})_6$
 - 44.5 g NaOH
- (b) Rinse in cold running water
- (c) Nickel plate

Trial 20:

Same as trial 19 but use NH_4OH dip and rinse just before plating

Trial 21:

- (a) Anodic etch in solution of:
 - 1000 cc H_2O
 - 250 g KOH
 - .25 g CuSO_4
- (b) Rinse in dilute NH_4OH
- (c) Rinse in cold running water
- (d) Rinse in hot HCL (omitted for one run)

(e) Nickel plate

Trial 22:

- (a) Anodic etch in phosphoric acid, pure
- (b) Rinse in cold running water
- (c) Rinse in dilute NH_4OH
- (d) Rinse in cold running water
- (e) Cathodic etch in phosphoric acid, pure
- (f) Rinse in cold running water
- (g) Nickel plate

Trial 23:

- (a) Fire in dry H_2 atmosphere for 15 minutes at 950°C
- (b) Shove into cooler still in dry H_2 atmosphere
- (c) When at room temperature, take out and put directly in nickel bath

Trial 24:

- (a) Etch anodically in 20-40% KOH steel electrode, 9 amp/ft.²
- (b) Rinse in cold running water
- (c) Make molybdenum anodic in nickel bath, 3.6 amp/ft.²
- (d) Nickel plate 11 amp/ft.²

Trial 25:

- (a) Same as trial 15 except Wood's nickel strike was used

Trial 26:

- (a) Etch in oxalic acid solution with and without current
- (b) Rinse in cold running water
- (c) Nickel plate

Trial 27:

The following samples were treated in DuPont's sodium hydride

Descaling Process:

<u>Sample Number</u>	<u>Sodium Hydride Descaling</u>	<u>Plating</u>
1	None	Nickel
2	10 minutes	Nickel
3	20 minutes	Nickel
4	10 minutes	Nickel strike - Cu plate
5	10 minutes & 15 seconds 10% HCL at room temperature	Nickel
6	None (hot alkaline soak & cathodic HCL)	Nickel
7	None (hot alkaline soak)	Nickel strike & nickel
8	10 minutes	Copper strike

All samples were quenched in 10% ethyl alcohol, after the sodium hydride treatment. They were rinsed for 30 seconds in running water and then placed in the plating bath. In the event additional samples are treated, it would be desirable to quench 50% of them in water.

Trial 28:

(a) Etch in solution of:

3 parts H₂O

2 parts H₂SO₄

1 part HNO₃

(b) Rinse in cold running water

(c) Etch in hot solution of:

1 part HCL

1 part H₂O

(d) Rinse in cold running H₂O

(e) Dip in concentrated oxalic acid solution

- (f) Rinse in cold running water
- (g) Nickel plate, platinum plate

Treatments Which Gave Questionable Adherence

The following treatment schedules gave doubtful adherence on the samples of molybdenum which were plated:

Trial 1:

- (a) Etch for 5 minutes at 5 volts A.C. in 52% HF at 90°C, stainless steel electrode
- (b) Direct to nickel plating

Trial 2:

- (a) Etch anodically in 50% H₂SO₄, room temperature, platinum electrode, 2 amps/in.²
- (b) Rinse in cold running water
- (c) Rinse in dilute NH₄OH
- (d) Rinse in cold running water
- (e) Etch cathodically in same 50% H₂SO₄, room temperature, platinum electrode, 2 amp/in.²
- (f) Rinse in cold running water
- (g) Nickel plate

Trial 3:

- (a) Etch in solution of:
 - 3 parts H₂O
 - 2 parts H₂SO₄
 - 1 part HNO₃
- (b) Rinse in cold running water
- (c) Dip in hot 50% HCL
- (d) Rinse in cold running water

(o) Indium plate

Trial 4:

(a) to (g) same as trial 2 except pure phosphoric acid was used in place of the 50% H_2SO_4 . Nickel powder and then iron powder was dissolved in the phosphoric acid in small percentages.

Treatments To Obtain Satisfactory Adherence

In addition to the procedures listed in the conclusions, the following variations also gave very adherent nickel deposits on molybdenum:

Trial 1:

- (a) Etch a piece of stainless steel, such as type 304, anodically in 70% H_2SO_4 until solution turns light green
- (b) Then, etch molybdenum anodically in solution at room temperature, 2 amp/in.², for one minute using stainless steel electrode
- (c) Rinse in cold running water
- (d) Rinse in dilute NH_4OH
- (e) Treat cathodically in same H_2SO_4 for one minute, 2 amp/in.² at room temperature, use stainless steel electrode
- (f) Rinse in cold running water
- (g) Nickel plate immediately

Trial 2:

Same as trial 1 except in place of step (b) the molybdenum was etched in a solution of:

3 parts H_2O

2 parts H_2SO_4

1 part HNO_3

Trial 3:

Same as trial 1 except in place of step (b) the molybdenum

was etched anodically in a 40% KOH solution under the same conditions as part (b).

Trial 4:

Same as trial 1 except 80% H_2SO_4 was used.

Trial 5:

Same as trial 1 except 80% H_2SO_4 was used, and instead of electrolyzing a stainless steel electrode, a gram of manganese powder was added to the solution and a platinum electrode was used.

Trial 6:

Same as trial 1 except nickel electrode was used instead of the stainless steel.

DISCUSSION

First of all, one should consider the following excerpt from work done by George L. Clark, George Pish, and Leonard E. Weeg. (c)

"In order to investigate the interfacial structure and bonding of electrodeposited metals, without stripping the plating from the base metal, a stepwise method of deposition was adopted, giving, on the same specimen, coatings varying from 2 to 55×10^{-6} in. in thickness. The platings were examined by X-ray and electron-diffraction methods, and the results correlated with measurements of optical reflectivity. In general, three types of bonding of the plating to the base metal were demonstrated. In the first, the deposited metal forms its own characteristic lattice from the start of deposition, and clings mechanically to faults and irregularities in the base-metal surface. In the second type, the first-deposited atoms enter into solid solution with the base metal, the solid solution acting as a transition layer between normal base metal and normal deposited metal, which appears as a separate phase beyond a limiting thickness. Thirdly, the first few layers of deposited metal may extend the lattice type and dimensions of the base metal, subsequent layers reverting to the normal structure for the deposited metal."

From the aforementioned investigation, it can safely be stated that very little possibility exists in applying the first type of adhesion and obtaining pore-free coatings, consequently, much work would be done in an attempt to apply the second and third type of adhesion. For the second method, a thorough investigation of metals that are soluble in molybdenum is necessary. Of these, only the ones which are readily platable should be considered. For the third type of adhesion, the following material from "Crystal Growth" by

(4)

Buckley should be considered. This is from the work on Electrodeposited Metal Crystals.

"At times, the new grain growth is simply an extension from already existing surface grains. This takes place with greatest facility when the surface is newly etched, when there are no colloids or contaminating impurities to adsorb on the surface, and when there is slow growth, as by small current densities and an approximate identity in pattern and spacing of the two lattice planes (when the base and deposit are different). The "tolerance" in the latter case is similar to that found in epitaxis, or parallel-growth formation, so that the base-metal parameter should not be more than $2\frac{1}{2}\%$ smaller or $12\frac{1}{2}\%$ greater than the depositing metal. At times, continuation of growth from the underlying grains is not so strictly orientated. In fact, with two metals possessing different structures, absolute continuity is ruled out but a parallel orientation on similar lines to the Widmånstatten structure is then found when the conditions for epitaxis hold good."

If this information holds true, then for the third type of adhesion an investigation should be made of the minimum inter-atomic distances in all platable metals to see which fall within the limits stated above as compared to molybdenum.

Another item to which consideration should be given, is the pre-treatment of the molybdenum before plating. (13) In a N KCl solution the potential of molybdenum ranges from + .66 volts in the passive state to -.74 volts in the active state. Strongly oxidizing agents or strong bases will activate this metal. It is thought by many observers that the all-important step in the plating of molybdenum is to get it in an active state before plating.

By taking all of the above considerations into account, the following metals should be platable on molybdenum, and adhesion obtained.

- (1) Nickel
- (2) Chromium
- (3) Iron
- (4) Platinum
- (5) Tantalum
- (6) Tungsten
- (7) Vanadium

As may be seen in this investigation, adherent deposits of nickel and chromium were obtained directly on molybdenum after proper treatment of the surface.

For a proper pretreatment, one should consider the following statements by C. L. Mantell ⁽¹¹⁾ in his "Industrial Electrochemistry."

Electrolytic reduction may occur in the place of hydrogen evolution if the electrolyte contains readily reducible substances, when H⁺ ions are discharged at the cathode. Catalysts of the carrier type in the electrolyte at times have an important place in electrolytic oxidation and reduction. These are commonly metals which have multiple valence ions such as titanium, vanadium, cerium, manganese, and uranium salts. The carriers will be oxidized at the anode and reduced at the cathode and may, thus, be an intermediate reactor.

The previously mentioned principles seem to be of considerable importance in the preplating treatment of molybdenum. It may be noted that under the section of successful treatments, the best results were had when the parts were treated cathodically in concentrated sulfuric acid to which a metal carrier had been added. Nickel, manganese, and iron were used successfully in this investigation, however, it was found that good results could only be obtained in 70-95% sulfuric acid. When phosphoric, hydrochloric,

and hydrofluoric acid was used, only questionable adhesion of the plating was obtained. It is thought, if the conditions could be found, that even these acids may be made to give consistently good results. It was discovered that if 66° Be sulfuric acid was used, one did not need the metal carrier. It was thought that this method of treatment would be the best, since almost every plating installation would have available 66° Be sulfuric acid.

Since such excellent results were obtained with this cathodic treatment, it was thought that there would be a possibility of plating molybdenum directly with metals other than nickel. This was not substantiated, for in the attempts to plate silver, copper, gold, platinum, and indium adhesion was not obtained. One is not surprised at this, however, if the previously mentioned considerations for adhesion were studied. ^(1,8,16) Adhesion of only very thin films of platinum was obtained from a platinum chloride bath, but when any attempt was made to increase this thickness, there was always peeling.

The rinse in dilute ammonium hydroxide was found to be of utmost importance. Whenever this step was left out, adhesion of the plating was not obtained regardless of what electrolytic treatment was given to the molybdenum. The concentration in this case was not found to be critical. As long as the smell of ammonia came from the solution, it was found to work satisfactorily. This is probably due to the fact that most molybdenum oxides are soluble in ammonium hydroxide.

The acid treatment for rigid pieces of molybdenum was found to give adhesion of a sufficient quality for brazing. The plating was found to peel off flexible thin sheets using this treatment.

The method devised by A. Karbelak worked very well and excellent adhesion was obtained, however, there is the disadvantage that intricately

designed parts would require specially constructed plating racks. It was also found that the electrolytic treatment proposed by the author would not sufficiently treat parts that are shadowed, therefore, the plating would have to be done before forming. In each case, however, adhesion was found to be sufficient so that it would be permissible to plate the parts and then form them. If this approach would be impossible then one could resort to auxiliary anodes or cathodes as the case may be.

The big advantage for the method of spraying used by RCA is that as long as the part is not too complicated to spray, it can be plated. The big disadvantage in this case is the need for a hydrogen atmosphere furnace.

CONCLUSIONS

The following are step by step procedures for obtaining adherent electroplated deposits on molybdenum:

(1) The following method, devised by the author, is satisfactory for plating round rigid pieces of molybdenum with nickel but not satisfactory for plating thin flexible sheet stock.

- (a) Degrease in trichlorethylene
- (b) Dry
- (c) Alkaline degrease, soak, 190°F (Penn Salt K-35 or equivalent)
- (d) Cold water rinse
- (e) Dip in solution of:
 - 3 parts water
 - 2 parts sulfuric acid
 - 1 part nitric acidat room temperature until part is gassing all over
- (f) Rinse in cold running water
- (g) Dip in hot (130° to 140°F) solution of one part hydrochloric acid to one part of water
- (h) Rinse in cold running water
- (i) Plate in low ph Watt's nickel bath
- (j) Rinse in hot and cold running water
- (k) Rinse in methanol
- (l) Dry in oven

(2) The following method, devised by the author, is satisfactory for plating of flexible sheet molybdenum with nickel:

- (a) Degrease in trichlorethylene
- (b) Dry
- (c) Alkaline degrease, soak 190°F (Penn Salt K-35 or equivalent)
- (d) Etch anodically in 66° Be sulfuric acid (95%) for one minute at 9 volts
- (e) Rinse in cold running water
- (f) Rinse in ammonium hydroxide solution (strength not important)
- (g) Treat cathodically for one minute at 9 to 10 volts in 66° Be sulfuric acid (95%), can use same acid as used in (d)
- (h) Rinse in cold running water
- (i) Plate in low ph Watt's nickel bath. It is preferable to make electrical contact before placing part in nickel bath.
- (j) Rinse in hot and cold running water
- (k) Rinse in methanol
- (l) Dry in oven

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(3) The following method, devised by A. Korbelak of Westinghouse, also gave very good results in the plating of flexible sheet molybdenum with nickel:

- (1) Clean the molybdenum free of heavy oxides, grease or other foreign soils and contaminating films by appropriate cleaning methods such as hydrogen baking, degreasing, etc.
- (2) Electroetch the molybdenum in a solution of sulfuric acid

(approximately 2 parts acid to 1 part water). Make the part anodic and treat for about 30 seconds at about 10 volts D.C.

- (3) Rinse the molybdenum thoroughly in clean running water to remove the blue moly oxide film formed in the electroetch
- (4) Complete the dissolution of the moly oxide film by a rinse in a hot (180-210°F) alkaline solution such as TSP, caustic soda, or any commercial electrocleaner
- (5) Rinse in water and neutralize in a mild 5-10% sulfuric acid solution
- (6) Rinse in water and transfer to a standard chromium plating solution
- (7) Chromium plate for 20-60 seconds at about 1 amp/in² at standard operating temperature
- (8) Rinse thoroughly in plenty of clean running water and transfer to a chloride nickel solution (2 lbs. of nickel chloride and 1 pint of HCl per gallon)
- (9) At room temperature, nickel strike over the chromium bond at about 25-50 amps/ft.² for 15-60 seconds or more
- (10) Any other plate may be put on over this nickel to any thickness using appropriate rinses, etc.

(4) The following method, used at RCA Victor, has been very successful in obtaining adherent electrodeposits on any type of molybdenum:

- (a) Degrease in trichlorethylene

(b) Spray or paint with the following:

95% nickel oxide powder plus 5% silver oxide powder
suspended in an equal volume of nitro-cellulose binder.

(The binder is made simply by dissolving nitro-cellulose
in a solvent until the proper viscosity for spraying or
painting is obtained).

(c) Fire at 950°C in line hydrogen atmosphere for 15 minutes

(d) Plate with any desired metal using appropriate processing

Of all the processes that were tried, only the ones previously
listed gave consistently good results. It was also found that the process-
ing steps listed may be changed somewhat without affecting the adherence
of the deposits, however, care should be exercised in doing this.

It may also be concluded that adherent deposits cannot be obtained
on molybdenum without special treatments.