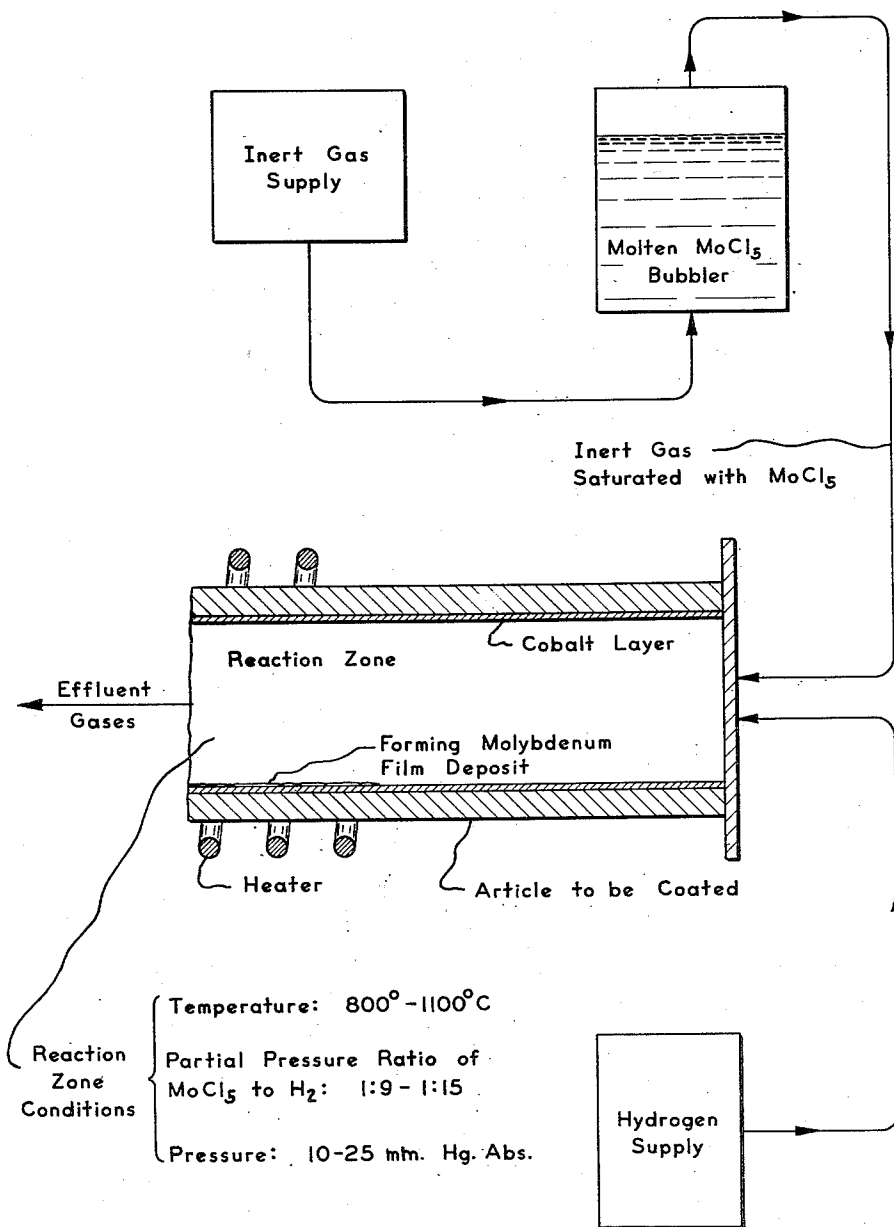


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P. L. RAYMOND
METHOD OF PRODUCING AN ADHERENT MOLYBDENUM COATING
ON A METAL SUBSTRATE
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INVENTOR.
PAUL L. RAYMOND
BY
Oliver W. Hoopes
ATTORNEY

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METHOD OF PRODUCING AN ADHERENT MOLYBDENUM COATING ON A METAL SUBSTRATE

Paul L. Raymond, Natick, Mass., assignor to National Research Corporation, Cambridge, Mass., a corporation of Massachusetts

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4 Claims. (Cl. 117—71)

This invention relates to coating and in particular to the coating of metal substrates with molybdenum.

One object of the present invention is to produce adherent coatings of molybdenum on metal substrates.

Another object of the invention is to provide uniform, adherent molybdenum coatings on the interior surfaces of hollow objects.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

The numerous applications to which molybdenum-coated articles may be adapted are dependent to a great extent on the adherence of the molybdenum to the metal substrate, as fully explained in copending application Serial No. 380,846, filed September 17, 1953, now Patent 2,783,164. The above invention is, therefore, directed to a process for coating metal substrates, and in particular the interior surfaces of hollow objects, with a uniform, adherent deposit of molybdenum. This may be accomplished by forming a suitable diffusion bond between the metal substrate and the molybdenum, eliminating powdery material deposits on the metal surfaces which are about to be coated, and precisely controlling the reducible molybdenum compound-hydrogen ratio.

In the present invention, a uniform, adherent coating of molybdenum may be obtained on a metal substrate, particularly steel, by coating the metal substrate, prior to depositing molybdenum thereon, with a layer of cobalt or nickel which is capable of forming a diffusion bond with both the metal substrate and the molybdenum. A coating of molybdenum is then deposited on the thin cobalt or nickel layer by reducing a molybdenum compound with hydrogen at a temperature between about 800° C. and 1100° C. In a preferred embodiment of the invention, this is accomplished by bubbling an inert gas, such as argon or helium, through a bath of molten molybdenum pentachloride and diluting the resultant vapors to the desired concentration with a separate stream of heated hydrogen.

The partial pressure of molybdenum pentachloride in the molten state is much more constant than the partial pressure of the solid due to a more uniform temperature distribution throughout the liquid and a substantially constant surface area during the run, these factors producing a more even flow of vapor than was previously possible. This vapor is composed primarily of molybdenum pentachloride, although, due to disproportionation (and/or reduction if hydrogen is used as the carrier gas), small quantities of the lower chlorides are also present. These

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lower chlorides are particularly detrimental to the process in that they deposit on the walls of the article being coated and prevent the molybdenum from forming a strong, adherent bond with the cobalt or nickel layer. The formation of these undesired lower chlorides may be largely prevented by the use of argon as a carrier gas for the vapor.

Heretofore, the concentration of the molybdenum pentachloride was so erratic that effective control over the pentachloride vapor-hydrogen ratio, which is preferably about 1:10 on the basis of partial pressure ratio, was virtually impossible. It is definitely preferred that the ratio of MoCl_5 vapor to H_2 be equal to 1:10 or slightly less. A partial pressure ratio of 1:9 will cause incomplete reduction of the chlorides, resulting in the deposition of lower chlorides of molybdenum on the walls of the object being coated. A partial pressure ratio of 1:11 or higher will cause the operation to go at less than the maximum possible rate, the increase in ratio directly causing a decrease in the plating speed. The limiting ratios for the successful operation of the instant invention are 1:9 as a lower limit and 1:15 as a practical upper limit. However, in the present invention, addition of an inert gas, such as argon, as a carrier stabilizes the flow of pentachloride vapor to the point where the molybdenum pentachloride vapor-hydrogen vapor partial pressure ratio can be effectively controlled.

The invention is clearly set forth in the self-explanatory drawing and will be more fully described in the following example in connection with the plating of molybdenum on steel, it being understood that the example is illustrative and is not to be construed as limiting the invention in any way.

Example 1

A piece of steel pipe, thoroughly cleaned internally of all foreign substances, was coated with a layer of cobalt to a depth of about 0.0004 inch, employing the chemical reduction method described by Brenner and Riddell in the Journal of Research, National Bureau of Standards 39, 388 (1947). Although the cobalt coating produced by employing this method will contain traces of combined phosphides, they will in no way affect the adherence of the subsequent molybdenum coating. The steel pipe (internally coated with cobalt) was placed in a vacuum system and then heated to about 950° C. by means of an external heater, and a mixture of molybdenum chloride vapors, argon and hydrogen was passed through the pipe. This mixture was obtained by bubbling 0.2 liter per minute of argon through molten molybdenum pentachloride, the molten bath being maintained at a temperature of about 228° C., and then introducing into the vapor, after reduction of the pressure from 760 mm. to 17 mm., 9 liters per minute of heated (about 160° C.) hydrogen, the molybdenum chloride-hydrogen vapor partial pressure ratio being 1:10.

Hydrogen reduction of the molybdenum chloride took place in the heated portion, depositing thereon a coating of molybdenum. The heater was then moved in the opposite direction to the flow of hydrogen and molybdenum chloride vapors so as to heat a new portion of the cobalt-coated surface to be coated with molybdenum. Under these conditions, an adherent coating of molybdenum was deposited on the cobalt along the entire interior surface of the pipe. The cobalt, during this latter coating operation, diffused to a small extent into both the molybdenum and the steel of the pipe and prevented diffusion of carbon from the steel to the molybdenum.

The preferred metal substrates for the present invention are those which are capable of forming a satisfactory diffusion bond with cobalt or nickel. Suitable substrates may consist of steel, nickel, cobalt or other metals whose

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melting point is above the temperature at which diffusion of the bonding metal takes place.

The molybdenum is deposited over the nickel or cobalt layer and a diffusion bond between the molybdenum and said layer is formed. The molybdenum coating is preferably deposited by reducing the pentachloride of molybdenum with hydrogen. Suitable molybdenum deposits may be obtained when the pentachloride is reduced at a temperature between about 800° C. and 1100° C., preferably above about 900° C., and at a total pressure between about 10 and 25 mm. Hg abs. A preferred pressure range is 15 to 20 mm. Hg abs., the median pressure of 17.5 mm. Hg abs. being optimum.

It should also be mentioned that, although the cobalt or nickel in the intermediate bonding layer will diffuse to some extent into the metal substrate and molybdenum during the coating operations, it may occasionally be necessary to reheat the coated article so as to promote a further diffusion of said bonding layer. This additional treatment may be desirable only where the coated article requires an exceptionally adherent coating of molybdenum or where the surface is desired to be an alloy of the bonding metal and molybdenum.

The heating may be accomplished either by a gas burner, induction heating or resistance heating, the heating being over as large an area as possible so that the reaction can proceed more smoothly and rapidly.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a method of producing an adherent molybdenum

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coating on a metal substrate capable of forming a diffusion bond with a metal selected from the group consisting of cobalt and nickel wherein the process comprises coating a thin layer of the bonding metal on the metal substrate and depositing a coating of molybdenum on said thin layer by the hydrogen reduction of molybdenum chloride vapors, the improvement which comprises generating the molybdenum chloride vapors by bubbling an inert gas through a molten molybdenum pentachloride bath and thereafter reacting the resulting mixture of vapors with a stream of hydrogen.

2. The method of claim 1 wherein the molybdenum chloride vapor-hydrogen vapor partial pressure ratio is between 1:9 and 1:15.

3. The method of claim 1 wherein the molybdenum chloride vapor-hydrogen vapor partial pressure ratio is about 1:10.

4. The method of claim 1 wherein said molybdenum chloride vapors are reduced with hydrogen at a temperature between about 800° C. and 1100° C.

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