COATING MOLYBDENUM WITH PURE GOLD

Filed Jan. 8, 1964

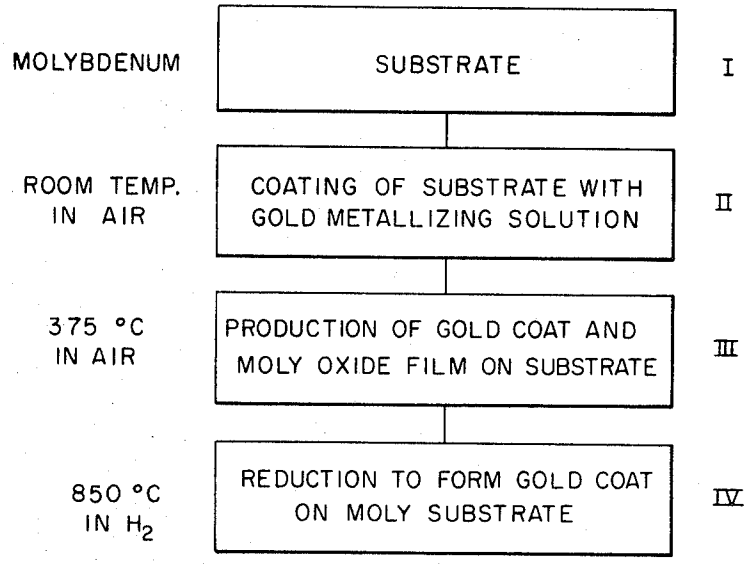



FIG. 1

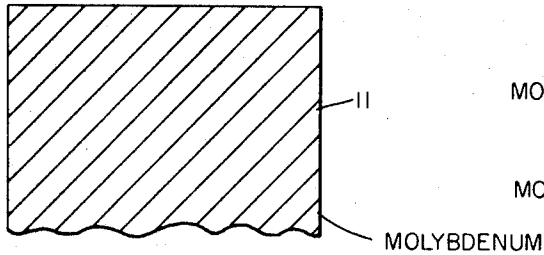



FIG. 2

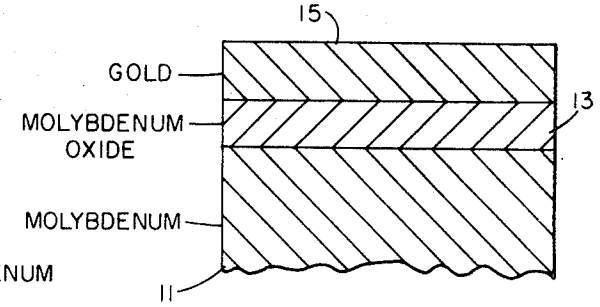



FIG. 3

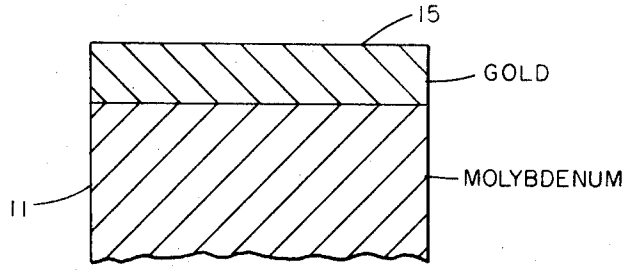



FIG. 4

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United States Patent Office 3,741,735
Patented June 26, 1973



3,741,735

# COATING MOLYBDENUM WITH PURE GOLD

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Filed Jan. 8, 1964, Ser. No. 336,605
Int. Cl. C23c 13/02
U.S. Cl. 29—198 6 Claims

## ABSTRACT OF THE DISCLOSURE

The invention is directed to a method of bonding gold to a molybdenum substrate by means of an intermediate layer of molybdenum oxide. The intermediate layer is formed during the plating of the gold and may be subsequently reduced to pure molybdenum to form a direct bond.

This invention relates to the method of coating molybdenum with gold and more particularly to the coating of molybdenum with gold to form a low emissivity shield. The invention described herein was made in the course of, or under, a contract with the United States Atomic Energy Commission.

In many electrical and space applications low emissivity shields are required. In thermoelectric convertors, for example, such as shown in FIG. 2 of U.S. application S.N. 279,344, it has often been desirable to provide a low emissivity shield for the hot junction thereof. It has been discovered that gold plated coatings on a smooth molybdenum substrate provides low emissivity but when the gold has been applied directly to the molybdenum with conventional methods, a poor bond has resulted and the gold coating has been easily stripped off.

In order to provide a more tenacious coating the use of nickel "striking" on the molybdenum before gold plating or the use of gold alloys has been tried but these systems have not provided the same advantageous low emissivity properties as the pure unalloyed, gold coatings. The lowness of the emissivity is also limited if the gold is alloyed with or diffused into the substrate. Additionally, it has been advantageous to provide a simple and efficient method for forming this coating.

It is an object of this invention, therefore, to provide an improved coating method and product;

It is also an object of this invention to provide an improved method for providing an unalloyed gold coating on a molybdenum substrate;

It is also an object of this invention to provide a substrate, and a substantially unalloyed coating with a tenacious bond on the substrate;

It is another object of this invention to provide a low emissivity shield for a thermoelectric convertor.

It has been discovered, in accordance with this invention, that the plating of pure gold on molybdenum can be accomplished by producing a porous molybdenum oxide film on a molybdenum substrate while depositing pure gold on the oxide, and converting this oxide back to molybdenum. With the proper selection of temperatures and ambient gases as described in more detail hereinafter, the required tenacious bond and low emissivity coating and shield are easily and simply obtained.

Various other objects and advantages will appear from the following description of several embodiments of this invention, and the novel features will be particularly pointed out hereinafter in connection with the appended claims.

In the figures:

FIG. 1 is a flow sheet illustrating the steps embodying the method of this invention;

FIGS. 2, 3 and 4 are diagrammatic, schematic sketches showing greatly enlarged sectional views of the surface coatings and the interfaces between these coatings according to the steps of the flow sheet of FIG. 1.



Referring now to FIG. 2, a substrate **11** is shown for receiving a pure gold coat to form a low emissivity shield. This substrate **11** advantageously comprises a coating on an electrical or space device such as the above mentioned hot junction of a thermoelectric convertor and to this end conventional coating may be employed to apply the molybdenum. For example, a vapour phase system may be used. Equally, however, a smooth, unitary, solid substrate may be used.

Referring now to FIG. 3, a porous molybdenum oxide film **13** is formed on the molybdenum substrate **11**. To this end a yellow $MoO_3$ film is formed on substrate **11** in about thirty minutes at a little above 300° C. in air and a film **13**, which is a mixture of yellow $MoO_3$ and violet $MoO_2$, forms on substrate **11** in about fifteen minutes at 375° C. in air.

A pure gold coating can also be formed on the substrate **11**. One advantageous method of application is to paint a metallizing solution of gold on the substrate **11** and to heat the painted substrate in air. Advantageously, this solution is an organic metallizing gold solution and in providing this solution it is advantageous to dissolve pure gold in aqua regia to form a gold chloride, to evaporate this solution to dryness and to mix the resultant compound with oil of lavender until the proper consistency for painting is achieved. This organic solution decomposes to form a gold deposit upon heating and a brand of this organic gold solution that is successful for this purpose is the Hanovia brand liquid bright gold solution for heat reflection made by the Engelhard Industries, Inc., East Newark, N.J.

Should the pure gold be deposited from the organic gold solution simultaneously with the forming of the oxide film **13** in an air ambient, it has been discovered that a pure gold deposit **15** will be formed and adhere tenaciously to the oxide film **13**. The film **13**, in turn, adheres tenaciously to the substrate **11**. Should the oxide film **13** then be reduced in hydrogen at about 850° C. for five minutes the gold coat **15** will become tenaciously and directly attached to the pure molybdenum substrate **11** produced by the reduction of the oxide film **13** as illustrated by the product shown in FIG. 4.

The system of this invention has the advantage that the gold coating retains the surface characteristics of the moly substrate, so that if a smooth surface is started with, the gold will have a mirror smooth surface. Moreover, the gold cannot be separated from the moly substrate by mechanical means as illustrated by actual tests in which thin moly sheets plated with the gold have repeatedly been bent back and forth in many different ways until the moly sheet has been broken. In this case there was no sign that the gold had parted from the moly. Additionally, the gold has been scraped with a steel tool without any peeling of the gold from the substrate.

The importance and existence of the oxide film is illustrated by tests of several .010 inch thick moly strips which were painted with the gold solution and air fired for 30 minutes. The moly did not oxidize below 300° C. and although the gold compound decomposed, the gold film was easily scratched off by a finger nail. Also, although the gold film did not crack when the moly strip was bent to a 1/64 inch radius the gold film did crack when the moly strip, represented for example by substrate **11** in FIG. 2, was repeatedly bent back and forth.

In tests to determine the optimum air and hydrogen firing temperature and times, for the production and reduction of the required oxide coating, the air firing was advantageously above 300° C. for the best gold compound

deposition and oxide formation. Temperatures that were lower gave very slow deposition and insufficient or no oxidation while higher temperatures up to 375° C. produced fast deposition e.g. in 15 minutes, good oxide formation as indicated by yellow and violet colored moly oxides, and excellent gold bonding. Five minutes at 850° C. in a hydrogen atmosphere gave excellent reduction of the oxide and corresponding good gold tenacity.

Referring to FIG. 1, a typical procedure used in preparing an example of the shield of this invention is as follows:

A molybdenum substrate was employed illustrated by Step I. A strip .010" thick was coated with an organic gold metallizing solution by painting it on the substrate as illustrated by Step II. Hanovia brand liquid bright gold #8146, no flux, was successfully painted on for this step but dipping and spraying of the same are also successful for this step. The moly substrate was cleaned before painting. Organic solvents or degreasers and a dry cloth are suitable. A suitable camel hair brush may be used to apply a thin coat sufficient so that the brush marks flow out. Etching and sand blasting of the surface were neither required or advantageous.

The coated moly was fired in air to decompose the organic gold solution and to deposit a continuous gold film **15** on top of an oxide film **13** on the substrate **11** as illustrated by Step III. This air firing employed a time cycle and temperature which formed a mixture of yellow $MoO_3$ and violet $MoO_2$ oxides in the film **13** and at the same time the gold was deposited, as illustrated by Step III. The furnace temperature was 375° C. and the firing time was 15 minutes. Satisfactory results, however, have also been obtained with other times and temperatures such as 260° C. for two hours. In general the time temperature cycles for the oxide formation on the molybdenum may be determined visually by observing the development of a thin molybdenum oxide film on the uncoated surface of the molybdenum during air firing.

The described air firing produces a gold coat and an oxide film each about 0.1 micron thick, and the painting and air firing steps may be repeated as many times as required to build up the desired gold thickness. For this example, there were three gold paintings and firings on one .001 inch thick moly strip. At this stage, the gold film has a slight bronze tint and a strong tenacity to the moly oxide and the oxide has a strong tenacity to the moly substrate.

The coated and air fired parts were next fired in a hydrogen atmosphere at a temperature and time cycle which reduces the yellow and violet moly oxides to moly as illustrated by Step IV. To this end a temperature of 850° C. for five minutes reduces the oxide. The gold then has a bright yellow gold color and excellent tenacity to the substrate. Also, the gold has a smooth, mirror surface with an emissivity of about .04 at room temperature. Equally satisfactory results have also been obtained at 800° C. for time intervals from 10 or 20 minutes and this as well as the reduction at higher temperature may be determined visually. The lower acceptable limit, however, appears to be 600° C. and below this temperature the bond of the gold to the moly is less strong than the 800° C. samples.

The dryness of the hydrogen was investigated and satisfactory results were obtained with hydrogen furnace atmosphere moisture contents ranging from —4° F. to —40° F. dew points.

The high temperature stability of the product was also tested and several examples have had good stability in life tests in a vacuum at 550° C. for over 1200 hours.

In accordance with another embodiment, thick gold films to 0.1 mil thick are obtained by electroplating gold on gold after the gold application steps of FIG. 1 are completed. These additional coats were applied on top of one or more of the thin gold films described after the reduction Step IV without any surface preparation. These thicker plated coatings, whether sintered or not, however, possess all of the exceptional bonding properties of the coats provided from the gold metallizing solution.

As far as could be determined, and in accordance with theory, there was no alloying or diffusion between the gold and moly in the process of this invention. It is important that nothing alloy with the gold as it would increase the low emissivity values. For this reason moly is advantageous as the substrate since it does not alloy with the gold. In theory, the gold molecules are mechanically intermixed and locked into the moly surface. This is also true with the porous molybdenum oxide film on the surface of the molybdenum. The simultaneous formation of the gold coat and oxide film materials gives an excellent interlocking bond but to further improve the bond between the gold and the molybdenum, the molybdenum oxide is converted back to molybdenum, which is stronger than the oxide, by firing the material in a reducing atmosphere at a sufficiently high temperature.

Unsuccessful attempts have been made to prepare and photograph microsections of this phenomenon. It is estimated that three air fired coats of gold give a gold film 0.3 micron thick and that the bonding zone is primarily developed during the deposition of the first coat. Therefore, the bonding interface layer thickness must be several magnitudes thinner.

This invention has the advantage of providing a low emissivity shield for thermoelectric convertors and the like. Additionally, this invention contemplates a method and article providing a gold coating that adheres tenaciously to a substrate. This substrate is advantageously molybdenum, in which case the moly forms an oxide simultaneously with the deposition of the pure gold from a metallizing solution and this oxide is reduced to form a tenacious, low emissivity, gold bond free from diffusion and alloying between the gold and moly.

As the foregoing relates to preferred embodiments of this invention and numerous modifications and alternations may be made therein without departing from the spirit and scope of the invention, it is intended that the appended claims define the scope of this invention.

I claim:

**1.** The method of bonding a gold coating to a molybdenum substrate, comprising joining said coating and substrate with an intermediate molybdenum oxide film therebetween by the steps of painting said substrate with a gold metallizing solution, and heating said painted substrate in an oxygen containing ambient to produce an oxidized film from said ambient on said substrate and a gold coat from said solution on said film.

**2.** The method of bonding a gold coating to a molybdenum substrate, comprising applying said gold to said molybdenum with a molybdenum oxide film formed during said gold application by the steps of painting said substrate with a gold metallizing solution in an oxygen containing ambient at room temperature, heating said painted substrate in air to produce a molybdenum oxide film from said ambient on said substrate and a gold coat on said film that is physically interlocked to said substrate through the intermediary of said molybdenum oxide film, and heating said gold coated oxide film and substrate in hydrogen chemically to change said oxide film to molybdenum and to transfer said physical interlocking of said gold coat and oxide film to a physical interlocking directly between said gold coat and said substrate.

**3.** The method of bonding a gold coating to a molybdenum substrate to produce a low emissivity shield, comprising joining a gold coating and molybdenum substrate with a molybdenum oxide film therebetween by painting said substrate with a gold metallizing solution and heating said painted substrate in air from 300° C. to 375° C. to produce a molybdenum oxide film from said air on said substrate and to deposit said gold on said film and physically to intermix and lock said gold in the porous film at the interface of said film and said gold and substantially reducing said film to form a direct bond between the

substrate and said gold coating by heating said gold coated film and substrate in hydrogen chemically to change said oxide film to pure molybdenum whereby said gold and said molybdenum substrate are mechanically intermixed and locked at their interface.

4. The method of bonding a gold coating to a molybdenum substrate, comprising the steps in which an organic gold metallizing solution is painted on the substrate in air and heated in air to 375° C. for 15 minutes to deposit and join the gold from said solution to a molybdenum oxide film comprising $MoO_3$ and $MoO_2$ on the substrate.

5. The low emissivity shield produced by the method of claim 3.

6. The method of bonding a gold coating to a molybdenum substrate, comprising simultaneously forming at between 300° C. and 375° C. from a gold containing metallizing solution a gold coat below .3 micron in thickness and a pure, porous, molybdenum oxide film having a thickness of about 0.1 micron interposed between said gold coat and a smooth molybdenum substrate, said oxide film giving a mechanical, interlocking bond between said substrate and said coat, converting said film to pure substrate at 850° C. in hydrogen so as to maintain said mechanical bond while said film thickness is strengthened, and said gold has a mirror smooth surface and is prevented from alloying with said substrate, and adding gold to said coat by electroplating whereby said coat is increased in thickness and said gold is strongly bonded to said substrate.




**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,816,066 | 12/1957 | Russell | 204—40 X |
| 3,147,547 | 9/1964 | Kuebrich et al. | 204—35 X |

OTHER REFERENCES

AD–158412, "Oxidation Resistant Coating for Molybdenum," Jan. 8, 1958, pp. 1–20, publ. by AEC (Nuclear Science Abstracts 13:5554).

NP–6546, "Investigation of High Temperature Resistant Materials," 1957, pp. 1–20, publ. by AEC (Nuclear Science Abstracts 12:4832).



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U.S. Cl. X.R.

29—199; 117—71 M, 130 R, 217; 204—29, 35 R, 37 R, 38 R, 40