Sept. 1, 1953 J. W. GARRISON ET AL 2,650,903

PROTECTION OF MOLYBDENUM AGAINST OXIDATION

Filed July 5, 1947

Fig. 1.

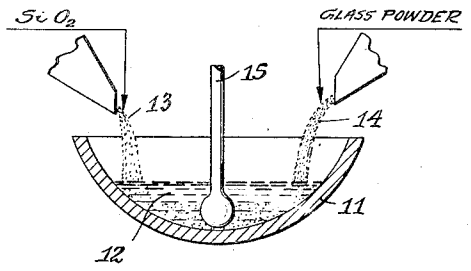


Fig. 2.

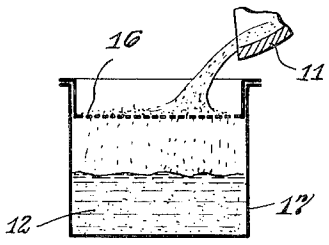


Fig. 3.

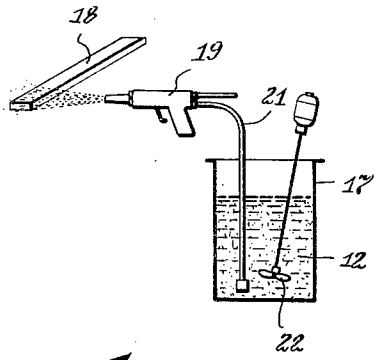


Fig. 4.

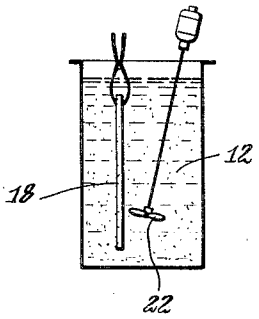


Fig. 5.

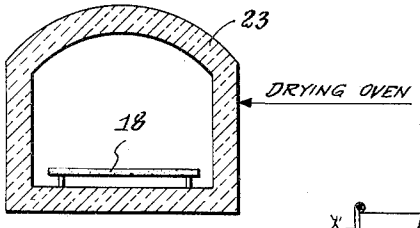


Fig. 6.

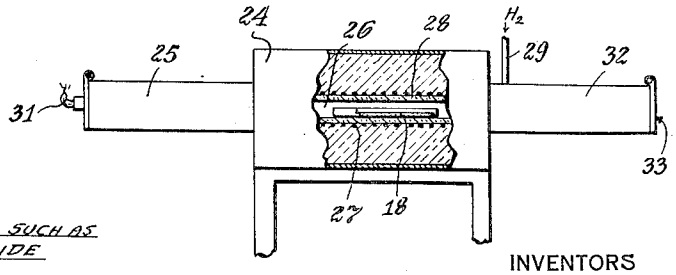
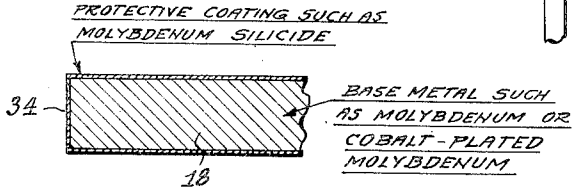


Fig. 7.



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PROTECTION OF MOLYBDENUM AGAINST OXIDATION

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9 Claims. (Cl. 204—38)

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This invention relates to the manufacture of articles of molybdenum and alloys consisting mainly of molybdenum protected against oxidation by a surface coating.

The principal object of our invention, generally considered, is the application to articles formed of molybdenum and alloys in which molybdenum is the main constituent, either with or without a preliminary coating of cobalt, of a uniform silica-type coating, that is, one consisting largely of silica, fired thereon at a temperature above 1300° C.

Another object of our invention is to apply a uniform silica-type coating to molybdenum or an alloy thereof, either with or without preliminary plating of cobalt thereon, and then fire to cause the coating to fuse on the surface as a uniform non-porous film.

A further object of our invention is to protect articles of molybdenum or alloys thereof by making a slip of silica and glass in an alcoholic medium, screening, and spraying or dipping to apply said slip to the articles which are then dried and fired to cause fusion of the coating material, whereby non-porous uniform protective coatings are caused to firmly adhere to the articles.

A still further object of our invention is to protect molybdenum and alloys thereof by a silica-type coating superimposed on a coating of molybdenum silicide, thereby at the same time increasing the hardness approximately 20 points on the Rockwell "B" scale and greatly decreasing oxidation, while having a coating which volatizes little, if any, at temperatures up to about 1000° C.

Other objects and advantages of the invention will become apparent as the description proceeds.

Referring to the drawing:

Figure 1 is a diagrammatic sectional view, partly in elevation and partly in vertical section, showing apparatus used in the process of making the slip for protecting molybdenum articles.

Figure 2 is a diagrammatic sectional view showing apparatus used in the process of screening the slip to remove coarse particles prior to application to the article to be protected.

Figure 3 is a diagrammatic view of apparatus including a container for the slip, means for stirring a slip therein, and a spray gun for applying said slip to the article to be protected.

Figure 4 is a view similar to Figure 3, but showing apparatus which may be used for applying the slip to the article to be protected by means of dipping.

Figure 5 is a transverse sectional view of an

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oven which may be used for drying the slip on the article to be protected prior to fusing it in place.

Figure 6 is an elevational view, partly in vertical section, showing a furnace which may be used for fusing the dried slip on the metal article to be protected.

Figure 7 is a transverse sectional view of an article formed of molybdenum or alloy thereof, either with or without a plating of cobalt, and protected by a silica-type coating.

For several years, various attempts have been made to apply protective coatings to molybdenum and alloys consisting mainly of molybdenum, for the purpose of resisting high temperature oxidation. Such treatment as chromizing, chromium plating, nitriding, calorizing, nickel plating, platinum plating, and others have been tried without success. Attempts to form surface coatings such as borate, borosilicate, and various other types were made. Some evidence of resistance to heavy volatilization of molybdenum oxide above 750° C. was shown by a silica-type coating formed by packing a piece of molybdenum in a mixture of silicon and silica and treating at 1000° C. in dry hydrogen, as determined by us.

Since at approximately 1300° C., silicon and hydrogen form hydrogen silicide which is reactive, a protective coating of molybdenum silicide, a stable compound, is formed by such a treatment of molybdenum with a silica-type or high silica glass coating thereon.

This invention, therefore, relates to the application of such a coating and the subsequent firing thereof to provide a non-porous uniform coating protective against oxidation for molybdenum, and similar material such as alloys consisting mainly of that metal.

Referring to the drawing in detail, like parts being designated by like reference characters, there is shown a container 11 holding a quantity of alcohol 12, which may be of the methyl type, and into which is being added a quantity of silica 13 and a quantity of glass powder 14. The purpose of mixing silica with glass is to increase the silica content of the glass mixture, in order to provide material which is very viscous when hot. A metal article coated with such material will not have the coating disturbed or blown therefrom, even when heated to a temperature high enough to melt said coating. A desirable formula for the mixture being made, as shown in Figure 1, is in the following proportions, parts by weight, SiO_2, 58.6; Al_2O_3, 20.6; BaO, 9.6; ZnO,

0.5; CaO, 6.5; MgO, 1.9; Na_2O, 3.0; and K_2O, 1.6.

102.3 parts by weight or pounds of glass of the foregoing composition is desirably made by agitating the following ingredients in a pony mixer, or other device for thoroughly incorporating them, then placing in small sand crucibles and holding in a pot furnace at about 1350° C. until melted. A desirable raw batch formula is as follows:

	Parts by weight or pounds
Silica, SiO_2	58.6
Aluminum hydroxide, $Al(OH)_3$	39.5
Barium carbonate, $BaCO_3$	12.5
Calcium carbonate, $CaCO_3$	11.7
Magnesium carbonate, $MgCO_3$	4.5
Zinc oxide, ZnO	0.5
Sodium carbonate, Na_2CO_3	5.2
Potassium carbonate, K_2CO_3	2.5

After cooling, the glass is ground and silica added. A preferred ratio between the glass, powdered silica, and alcohol is 100 grams glass powder, 20 grams powdered silica, and 150 cc. of alcohol. A glass melt is made and, after cooling and grinding, the desired additional silica added to make the desired final composition, in order to facilitate melting the glass. If all the desired silica were in the original mix, a very high temperature would be required for melting it. The final mixture, containing between 16 and 17% or about 16.7% of alumina, is agitated, as by means of a stirring rod **15**, and milled for preferably about 24 hours in order to insure that the materials are very finely divided and thoroughly mixed.

After the formation of the slip, the same is desirably passed through a 325 mesh screen **16**, as indicated in Figure 2, in order to remove any coarse particles, the screened slip being collected in receptacle **17**. The slip is then applied to an article **18** of molybdenum or molybdenum alloy, as by means of a spray gun **19** fed through tube **21** from the slip **12**, while the same is desirably stirred by means of a power-driven impeller **22**. As an alternative, the slip **12** may be applied to the article **18** by dipping the latter therein, while said slip is being stirred as by power-driven impeller **22**, as in Fig. 4.

Instead of applying the slip directly to the molybdenum surface of the article **18**, the latter is desirably coated first with a film of cobalt, as by means of electroplating. A desirable formula for the electroplating bath is:

	Grams
$CoSO_4 \cdot 7H_2O$	504
NaCl	17
H_3BO_3	45
Water to make 1 liter	

The operating conditions for electrodepositing cobalt from such a bath on molybdenum or molybdenum alloy articles, are as follows:

Temperature	20–30° C.
Current density	30–164 amps./ft.^{2}
Anode	99% cobalt.
Time	30 sec.

After application of the silica-type coating to the plain or cobalt-plated molybdenum article, as above described, the article is either permitted to dry naturally or placed in a drying oven **23**, as shown in Figure 5, for that purpose.

After drying, the coated article is passed through a hydrogen retort furnace **24**, as illustrated in Figure 6, said article being slightly preheated in the front entrance chamber **25**, and then passed on to the insulated retort **26**, where it is heated as by means of a resistance coil **27** of molybdenum or tungsten around an inner refractory tube **28**, while hydrogen is passed thereinto as through pipe **29** and escapes as indicated at **31**. After heating to fuse the coating at a temperature above 1300° C. to effect a reduction of some of the silica in the coating to form hydrogen silicide which, in turn, reacts with the surface of the molybdenum to form a coating of molybdenum silicide under the glass coating, the article is passed through the cooling chamber **32** and finally withdrawn at the exit **33**.

Figure 7 is a cross-sectional view showing a base metal, such as molybdenum or cobalt-plated molybdenum having a protective silica-type coating **34**, which may include molybdenum silicide if the fusion temperature in hydrogen is above 1300° C.

A study of coatings applied to articles in the manner above described shows that an apparently non-crystalline outer coating about .004'' thick is formed on the surface of the article. Such a photomicrograph, at a magnification of 75, indicates that while there is a definite line of demarcation shown, between the coating and the molybdenum, beyond this line there is a penetration zone approximately .008'' in depth having a structure similar to that of an intermetallic compound.

The coating increases the hardness of the article 20 points on the Rockwell "B" scale over the normal hardness of the molybdenum itself. This increase in surface hardness is expected to improve the resistance to abrasion of the coated material as compared with the uncoated metal.

Tests on coated samples show little if any evidence of volatilization of the coating at temperatures up to about 1000° C. It is therefore believed that the invention will have considerable use in connection with operations where it is desired to employ articles of molybdenum or alloys thereof having approximately the characteristics of molybdenum.

Although preferred embodiments of our invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

We claim:

1. The method of protecting articles of molybdenum and alloys thereof consisting mainly of molybdenum against oxidation, comprising forming a slip in alcohol of finely divided glass and silica, applying a coating of said slip to the surface of the metal to be protected, drying, and fusing said slip on said surface in a hydrogen atmosphere at a temperature above 1300° C. and high enough to generate hydrogen silicide and cause it to react with the surface of said article.

2. The method of protecting articles of molybdenum and alloys thereof consisting mainly of molybdenum against oxidation, comprising placing said article in a solution of a salt of cobalt, electroplating cobalt from said solution on said article, making a slip of finely-divided silica and glass, applying a coating of said slip to the plated article, drying, and fusing said coating thereon in a hydrogen atmosphere at a temperature above 1300° C. and high enough to generate hydrogen silicide and cause it to react with the surface of said article.

3. The method of protecting articles of molybdenum and alloys thereof consisting mainly of molybdenum against oxidation, comprising mak-

ing a slip of finely divided viscous glass in an alcoholic medium, applying said slip to such an article, drying, and heating in hydrogen to a temperature above 1300° C. to fuse said slip on said article, and cause the evolution of hydrogen silicide and its reaction with the surface of said article, thereby providing a uniform non-porous coating of molybdenum silicide thereon.

4. The method of protecting articles of molybdenum and alloys thereof consisting mainly of molybdenum against oxidation, comprising placing said article in a solution of a salt of cobalt, electroplating cobalt from said solution on said article, making a slip of finely-divided silica and glass with a relatively-high alumina content, applying a coating of said slip to the plated article, drying, and fusing said coating thereon in a hydrogen-including atmosphere at a temperature above 1300° C.

5. The method of protecting articles of molybdenum and alloys thereof consisting mainly of molybdenum against oxidation, comprising making a slip of finely divided high silica glass, containing between about 16% and 17% of alumina, in an alcoholic medium, applying said slip to such an article, drying, and heating in hydrogen to a temperature above 1300° C. to fuse said slip on said article, and cause the evolution of hydrogen silicide and its reaction with the surface of said article, thereby providing a uniform non-porous coating of molybdenum silicide thereon.

6. The method of protecting against oxidation articles of molybdenum and alloys thereof consisting mainly of molybdenum, comprising forming a slip of finely divided glass and silica, applying a coating of said slip to the surface of the article to be protected, drying, and fusing said slip on said surface in a hydrogen atmosphere at a temperature above 1300° C., in order to generate hydrogen silicide and cause it to react with the surface of said article.

7. The method of protecting against oxidation articles of molybdenum and alloys thereof consisting mainly of molybdenum, comprising electroplating cobalt on such articles, making a slip of finely-divided high-silica glass, applying a coating of said slip to the plated article, drying

and fusing said coating thereon in a hydrogen atmosphere at a temperature above 1300° C., to form hydrogen silicide and cause it to react with the surface of said article.

8. The method of protecting against oxidation articles of molybdenum and alloys thereof consisting mainly of molybdenum, comprising making a slip of finely divided glass, applying said slip to said articles, drying and heating in hydrogen to a temperature above 1300° C. to fuse said glass on said articles and effect the evolution of hydrogen silicide and its reaction with the surface of said articles.

9. The method of protecting against oxidation articles of cobalt-plated molybdenum and alloys thereof consisting mainly of molybdenum, comprising applying a coating to such plated articles of finely-divided high-silica glass suspended in a liquid, drying, and fusing said coating thereon in a hydrogen-including atmosphere at a temperature above 1300° C.

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