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1

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METHOD OF FORMING A PROTECTIVE COATING ON A MOLYBDENUM-BASE ARTICLE

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This application is a continuation in part application based on applicant's copending application, Serial No. 234,465, filed June 29, 1951, in which a dip method of applying protective coating is claimed.

The present invention relates to molybdenum-base alloys having oxidation resisting coatings effective at elevated temperatures and to methods of forming such coatings.

Because of its hardness and strength at elevated temperatures, molybdenum has long been regarded a promising metal for structural members which are subject to stress at high temperatures, i. e., in the range of 1500° F. to 3000° F. or even higher, and considerable work has been done in an attempt to utilize it for such purposes. Thus far, however, its use has been restricted because of the fact that molybdenum oxidizes readily if exposed to an oxidizing atmosphere at temperatures above about 700° F. At temperatures above 1200° F., the oxide volatilizes to such an extent that progressive oxidation continues indefinitely at a rapid rate.

Many oxidation resistant coatings for molybdenum have been studied in an attempt to solve the problem, but with indifferent success. One coating which has provided substantial protection against oxidation is a coating of molybdenum disilicide. However, it is extremely difficult to form an adherent coating of molybdenum disilicide on molybdenum; and, prior to the present invention, the only method of producing such coatings, namely vapor deposition, required heating the molybdenum article to be coated to a temperature in excess of 2550° F. Not only was this prior process costly, but it produced very thin coatings. Moreover, it is subject to the serious defect that it required heating the molybdenum article to a temperature above the recrystallization temperature of molybdenum, with the result that it seriously impaired the strength and toughness of the molybdenum. The recrystallization temperature of molybdenum and molybdenum-base alloys varies somewhat with the composition and mechanical treatment to which the metal has been subject, but is in the general range of 1650° F. to 2800° F., and in most cases can be considered above 2000° F.

The problem of forming an adequate protective coating on molybdenum is aggravated by the fact that a continuous protective film is essential. Even microscopic pin-point openings or cracks will permit progressive oxidation of the underlying molybdenum at temperatures above 1200° F., since the volatile oxide may escape through such openings.

Accordingly, it is the general object of this invention to provide novel coatings and improved methods of forming coatings which are effective to protect molybdenum-base alloys from oxidation at elevated temperatures. More particularly, it is the object to provide protective coatings which are effective at temperatures in the order of 1500° F. to 2000° F., although coatings beneficial at lower temperatures and at even higher temperatures may

2

be produced in accordance with the principles of the invention.

Another object of the invention is to provide methods of forming oxidation resistant coatings on molybdenum-base alloys at temperatures below the recrystallization temperature of the molybdenum-base alloys.

Other objects and advantages of the invention will become apparent from the following specification and claims.

The expression "molybdenum-base alloys," as used herein, means any alloy of molybdenum which contains at least 50% molybdenum and which oxidizes readily at elevated temperatures and includes commercially pure molybdenum.

The drawing contains a single figure representing a flow chart illustrating a mode of practising the principles of the present invention.

In accordance with the present invention, protective coatings are formed by spraying the article with molten or semimolten metal to form the protective coating. While several types of coatings have proven successful, all of the best results have been achieved with coatings containing both aluminum and silicon. Neither aluminum nor silicon alone when similarly applied provides comparable results as a coating material.

Molybdenum is a third essential constituent of the coating and may be applied with the aluminum and silicon. However, it is not necessary to apply molybdenum with the other essential constituents since molybdenum may be incorporated in the coating by diffusion between a preliminary coating and the base metal, and that is the preferred procedure.

In addition to the above mentioned essential elements, one or more of the elements chromium, iron and nickel have beneficial effects and may be present, but are not essential.

Since molybdenum need not be applied with the other coating elements and yet is an essential and substantial but uncertain portion of the final coating (estimated 25% to 45%), the preferred amounts of the other elements are best defined in terms of their relative proportions rather than their percentages in the final coating. Actually, the relative proportions of aluminum and silicon are not critical. Beneficial results have been obtained with as little as one part of silicon for each twenty parts of the aluminum, regardless of whether or not aluminum and silicon are the sole added elements. At the other extreme, beneficial results are obtained when the silicon is present in an amount as high as 180 parts for each 20 parts of aluminum. One or more of the elements chromium, iron and nickel may be added to the coating in a total amount that may range from zero to an amount four times the total of aluminum and silicon.

When none of the elements chromium, iron and nickel are present, the preferred ratio of silicon and aluminum in sprayed coatings is from 20 to 80 parts of silicon to each 20 parts of aluminum. This more restricted range is preferred over the coatings containing more aluminum because, while the high aluminum coatings provide useful protection against oxidation, the more restricted range of coatings have a higher melting point and are, therefore, harder at temperatures in the order of 1800° F. Moreover, since aluminum has a high thermal coefficient of expansion, it is preferred to use it in the more limited quantities.

In the sprayed coatings containing one or more of the elements chromium, iron and nickel, the best results have been obtained when the total of those elements was from one-half to twice the total of aluminum and silicon.

In all cases the final coatings consist essentially of aluminum, silicon and molybdenum or aluminum, silicon, molybdenum and one or more of the elements chro-