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METHOD OF FORMING PROTECTIVE COATINGS FOR MOLYBDENUM AND MOLYBDENUM-BASE ALLOYS

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The present invention relates to a method of forming protective coatings for molybdenum and molybdenum-base alloys.

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 pinpoint 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 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 1800° F., although coatings beneficial at lower temperatures and at even higher temperatures may 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.

Another object of the invention is to provide novel methods of forming an adherent coating containing aluminum and silicon on a molybdenum-base alloy at temperatures below the recrystallization temperature of the underlying alloy.

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.

In accordance with the present invention, protective coatings are formed by dipping the molybdenum-base article in a molten, low-melting-point alloy of aluminum. 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.

Alloys of aluminum and silicon within the range specified have melting points below 1200° F. and, therefore, must contain other ingredients which raise the melting point to a substantial degree if protection at temperatures above 1500° F. is desired. On the other hand, if the coating is to be applied by dipping in a molten bath, it is preferred that the bath, itself, have a low melting point to avoid heating the molybdenum article above the recrystallization temperature. This difficulty is overcome in accordance with the present invention by the fact that there is diffusion between the molybdenum in the base article and the metals of the coating which produces not only a good bond but also a coating containing molybdenum which raises the melting point of the coating and enhances its capacity to provide oxidation resistance. To produce these results while the article is immersed in the bath, the temperature of the molten bath should preferably be held at 1350° F. or above.

The principles of the invention and of the several coatings and methods of application may be more fully understood from the following specific examples.

The article is dipped in a molten alloy of silicon and aluminum. The temperature of the molten alloy is not critical except that high temperatures facilitate diffusion between the molybdenum and the initial coating; and the temperature is preferably maintained below the recrystallization temperature of the article to be coated. Satisfactory results have been obtained at temperatures in the order of 1350° F. to 2000° F., but a temperature in the order of 1600° F. is preferred. The molten bath may be held in a graphite crucible and should be protected from the atmosphere by any suitable expedient in order to avoid oxide or scum. The simplest method of avoiding oxidation of the bath is to provide the bath with a floating cover of flux, such as a mixture of 73% sodium chloride and 27% sodium fluoride. The article is left suspended in the molten bath for a period of time sufficient to permit the desired degree of diffusion between the molybdenum and the coating. Immersion for periods of from 15 to 30 minutes has given satisfactory results. Increases in the time of immersion increase the thickness of the coating and, in general, thicker coatings provide greater protection against oxidation.

Satisfactory results have been achieved with the above described dip method, using as the molten coating bath an alloy comprising 88% aluminum and 12% silicon. Immersion for 30 minutes at 1600° F. in that alloy produced a smooth, adherent coating approximately .002 inch thick. It had sufficient ductility to protect a pure molybdenum article against oxidation during a limited amount of forging at 2600° F. and also prevented oxi-