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PROCESS OF COATING MOLYBDENUM

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Molybdenum Article

Cleaning (e.g. Sandblast)

Al-Si Alloy (e.g. .015" thick coating
Al/Si = 88/12)

Coating

Oxidation

Vacuum Heat Treating

Pressure 10 Microns Hg Abs. or less
Time 1/2 hour
Temp. 2000 F

Molybdenum Article

+ Oxidation Resistant Coating

Coating .007"-.010" Thick
Coating contains MoSi_x+Al_2O_3+SiO_2+
Al/Si = 63/12 alloy of Mo, Si and Al

FIG. 1

FIG. 2

(Magnification 500x)

FIG. 3

(Magnification 500x)

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PROCESS OF COATING MOLYBDENUM


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This invention relates to the preparation of oxidation resistant coatings and more particularly to oxidation resistant coatings for molybdenum surfaces.

A number of industrial concerns and governmental agencies in the United States and abroad have been striving for many years to manufacture metal articles having high strength and high oxidation resistance under conditions of operation at elevated temperatures. In recent years much emphasis has been placed on the construction of nozzles for jets and rockets and blades for turbojets and turbo superchargers. For these applications it is highly desirable that the metal article, in addition to its refractory characteristics, be as light in weight as possible and also be machinable.

As a result of the extensive research work mentioned above, it is the general consensus of opinion that molybdenum and alloys thereof show much promise. However, the oxidation resistance of molybdenum is extremely poor since the oxide of molybdenum (MoO₃), which is formed at elevated temperatures, is volatile at the temperatures under consideration. Some improvement of the oxidation resistance of molybdenum has been obtained by the use of alloying elements, and certain protective coatings have been developed recently. Of these the most promising protective coating is molybdenum disilicide. However, the prior art processes for preparing such molybdenum disilicide coatings involve long expensive treatments at extremely high temperatures. Additionally these high temperatures must be uniform over the surface of the article being treated. Recently, the United States Bureau of Standards has made considerable strides in developing ceramic coatings which have been applied to molybdenum. While these surfaces are satisfactory for short exposure when they are properly applied, it is absolutely essential that they be completely free of pin holes. Such coatings are also subject to destruction by heat shock. The manufacture of ceramic and metacryl coatings, which are completely impervious, is extremely difficult, particularly for complicated surface shapes. It appears that the requirement for absolute perfection of such coatings will prevent their wide scale use in industrial and military applications when applied to molybdenum surfaces.

It is apparent from the above that, as of the present date, no completely satisfactory protective coatings have been developed for molybdenum articles. Accordingly, it is a principal object of the present invention to provide improved coatings which are capable of protecting molybdenum surfaces over a long period of time even though these surfaces are heated to high temperatures (on the order of 3000° F. and above) under oxidizing conditions.

Another object of the invention is to provide protective surfaces on molybdenum articles which permit rapid heating cycles and repeated shock cooling of the coating without appreciably decreasing the oxidation resistance of the coating.

Still another object of the invention is to provide processes of the above type which are rapid, cheap, and readily adaptable to articles of numerous sizes and shapes. Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and the relation of components and 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 the fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a flow sheet illustrating one preferred series of steps embodying the present invention; and

Figs. 2 and 3 are diagrammatic, schematic sketches showing greatly enlarged sectional views of the surface coatings and the interface between these coatings and the molybdenum surface.

In general the invention involves the application of an aluminum-silicon alloy to a molybdenum surface which it is desired to protect against oxidation. The molybdenum surface may be one formed of molybdenum or an alloy which is high in molybdenum. Equally it may be a molybdenum coating applied to other metals, such as a low alloy steel, or to some other material, such as carbon, a refractory, or the like. This aluminum-silicon coating is preferably applied to the molybdenum by metal spraying techniques, and may be applied as an aluminum-silicon alloy. The thus applied aluminum-silicon alloy coating is then oxidized slightly so as to form a high surface-tension film on this coating. Thereafter the coating is heated to a temperature on the order of above 2000° F. In the absence of air for a sufficient time to form a molybdenum silicide interface between the molybdenum surface and the aluminum-silicon alloy coating. In a preferred embodiment of the invention this heating is achieved under a vacuum of less than about 1 mm. Hg abs., and is continued for a time of about one hour.

The product of this treatment comprises several layers; the base layer is the original molybdenum surface. At the interface between this molybdenum surface and the applied aluminum-silicon coating, there is formed a layer which predominates in a molybdenum silicon compound, this compound being, it is believed, molybdenum disilicide. The fact that this molybdenum disilicide layer forms at the relatively low temperature of 2000° F. is believed to be due to the mutual solubility of the silicon and molybdenum in the aluminum. The reaction between the molybdenum and the silicon is thus a liquid phase reaction rather than a solid diffusion reaction. Most of the remainder of the coating predominates in an alloy of molybdenum, silicon and aluminum. The outer surface of the coating predominates in oxides of aluminum and silicon.

Referring now to Fig. 1 there is illustrated one preferred series of steps for carrying out the above process. A molybdenum article is first cleaned, such as by grit blasting, sand blasting, or by being subjected to a chemical cleaning. To the thus cleaned molybdenum surface is then applied the coating containing aluminum and silicon. This coating is preferably applied by spraying, with an oxy-acetylene spray gun, an aluminum silicon alloy containing on the order of 88% aluminum and 12% silicon. In a preferred embodiment this aluminum-silicon coating is on the order of 0.10 to .015 inch thick, and is strongly adherent to the molybdenum surface. The thus coated molybdenum article is then subjected to a slight oxidation, such as by heating in air to a tempera-
ture on the order of 1200° F. for 30 minutes. However, it is preferred that this oxidation be achieved by chemical means since the results are more uniform.

Chemical oxidation which involves dipping the aluminum-silicon coated article into a bath containing about 4 oz. of sodium chromate (Na$_2$CrO$_4$) per gallon of water. The article is maintained in this solution for about ten minutes, the solution being kept preferably at a temperature on the order of 200° F. The article removed from this oxidation treatment contains a thin film of oxide on the surface thereof.

The article is then washed and dried, and subjected to a heat-treating operation in the absence of air. As mentioned previously this heating is preferably done in a vacuum on the order of less than 1 mm. Hg abs., for example a total pressure of about 10 microns Hg abs. During this heat treating the article is heated for about one-half hour at a temperature of about 2000° F. In this heating process the oxide film acts to hold the aluminum-silicon alloy on the surface of the article by effectively increasing its surface tension. This is due to the fact that the aluminum oxide is insoluble in the aluminum at the treating temperature and thus forms a tenacious "skin" over the molten aluminum. The aluminum and silicon form a ternary alloy with the molybdenum. The silicon and molybdenum, in this ternary alloy, form what is believed to be molybdenum disilicide at the interface between the aluminum-silicon coating and the molybdenum surface. This molybdenum disilicide interface has a thickness which is a function of time of treatment, and the treatment is preferably continued for a sufficient length of time (on the order of 1/2 hour) so that this interface is at least 0.5 mil in thickness. The total aluminum-silicon coating thickness, after heat treating, has decreased to about 0.005 to 0.010 inch thick, and analysis indicates that the range of aluminum to silicon is now about 63 to 12. This loss in thickness is partly attributable to interdiffusion between the silicon and molybdenum, and partly attributable to evaporation of about 10% of the amount of the aluminum at the high temperature and low pressure involved in the heat treatment.

A thin (20 mil) molybdenum article treated in accordance with the technique of Fig. 1 can be heated to a temperature in excess of 3000° F. under oxidizing conditions for 7-5 hours prior to destruction of the article. Additionally such an article can be rapidly heated to 3000° F. and shock-cooled many times without appreciably affecting its life.

While one preferred series of steps has been illustrated above in connection with the discussion of Fig. 1, it should be apparent that numerous modifications thereof may be practiced without departing from the scope of the invention. For example, the aluminum and silicon may be applied separately to the molybdenum surface, although the coating with an aluminum-silicon alloy is particularly easy to achieve with present metal-spray guns. The relative proportions of aluminum to silicon in the coating are not particularly critical although it is preferred that there be an excess of aluminum over the silicon. As mentioned before, the oxidation treatment may be achieved by heating under oxidizing conditions and, if desired, this oxidation may take place as the initial step in the heat treating operation. For example, the heat treating furnace may be initially charged with the article at about 1200° F. for about 30 minutes, the air may be removed from the heat treating furnace and the furnace may be kept evacuated during the remainder of the heat treating. Equally other chemical oxidation agents such as sulfates, phosphates, and nitrates may be employed. Alternatively the aluminum may be anodized by usual techniques.

Referring now to Figs. 2 and 3 there are shown greatly enlarged, diagrammatic, sectional views of the coatings achieved by practicing the present invention. These illustrations are based on photomicrographs made at magnifications of about 500×. Fig. 2 shows the molybdenum surface 10 to which has been applied an aluminum-silicon alloy coating 12. In Fig. 3 the coating 12 is illustrated with a layer 14 of an aluminum-silicon alloy coating 16 which predominates in an alloy of molybdenum, silicon and aluminum. On top of this alloy layer 16 there exists a layer 18 which predominates in aluminum oxide and silicon oxide.

As mentioned previously in the specification, the invention is considerably broader than the protection of pure molybdenum articles against oxidation. It may be practiced, with equally beneficial results, for protecting molybdenum surfaces which are high in other alloying constituents. Also the molybdenum surface to be protected may in itself be only a thin coating applied to some other material. For example, a piece of porous carbon may be coated with molybdenum by utilizing metal spraying or other techniques, such as vapor phase reduction or decomposition of a molybdenum compound on the surface to be protected. The thus applied molybdenum layer may then be protected against oxidation by following the techniques described previously in the specification. A porous carbon article was spray-coated with molybdenum, then coated with aluminum-silicon alloy and treated in accordance with the Fig. 1 process. The article so protected was heated to 2600° F. for 52 minutes under oxidizing conditions. At the end of this time only a slight attack of the carbon article was evident. An unprotected carbon element, under similar conditions, was destroyed in 5 to 7 seconds.

In the preceding discussion of the invention considerable emphasis has been placed on the formation of the oxide film on the aluminum-silicon coating prior to the heat treating operation. This step is of extreme importance in treating larger shapes, particularly where the coated surface will not be horizontal during heat treatment. However, for very small shapes this oxidation step may be eliminated, this being most feasible when the coated surface can be maintained horizontal during heat treatment. Equally well, the heat treating molybdenum-silicon coating may be achieved by spraying the alloy or aluminum under oxidizing conditions. However, this method of oxidation is less preferred since it is not susceptible to precise control and may interfere with the formation of a continuous liquid film during subsequent heat treatment.

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

What is claimed is:

1. The process of increasing the oxidation resistance of a molybdenum surface which comprises applying to said surface an aluminum-silicon alloy coating, oxidizing said coating slightly, and heating said coating to a temperature of about 2000° F. in the absence of air for a sufficient time to form a molybdenum disilicide interface between said molybdenum surface and said coating, said aluminum-silicon alloy containing more than 50 percent aluminum.

2. The process of claim 1 wherein said oxidizing step is achieved by dipping said coated surface in an oxidizing bath.

3. The process of claim 1 wherein said molybdenum surface comprises a molybdenum coating applied to a solid material that can withstand a temperature of 2000° F., without losing its solid form.

4. The process of claim 3 wherein said solid material
is a metal comprising at least one element other than molybdenum.

5. The process of claim 3 wherein the solid material is comprised of carbon.

6. The process of increasing the oxidation resistance of a molybdenum surface which comprises applying to said surface an aluminum-silicon alloy coating, oxidizing said coating slightly and heating said coating to a temperature of about 2000° F. in a vacuum of less than 1 mm. Hg abs. for a sufficient time to form a molybdenum silicide interface between said molybdenum surface and said coating, said aluminum-silicon alloy containing more than 30 percent aluminum.

7. The process of claim 6 wherein the coating is applied by spraying and about 10% to 30% of the aluminum in said alloy coating is vaporized from said coating during said heating step.

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