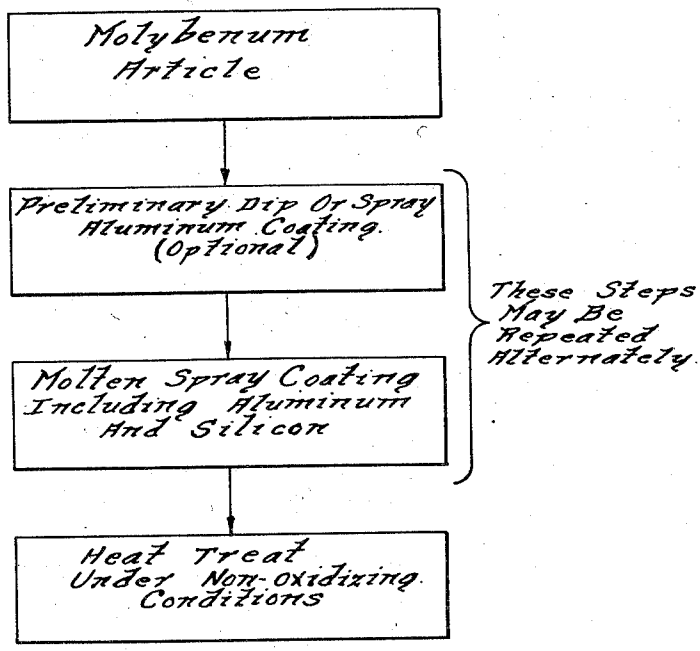
April 9, 1957 N. L. DEUBLE 2,788,290

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

Filed Sept. 17, 1954



INVENTOR.
Norman L. Deuble.
BY
Harness, Dickey & Pierce
ATTORNEYS.

United States Patent Office 2,788,290 Patented Apr. 9, 1957

2,788,290

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

Norman L. Deuble, Orange, N. J., assignor to Climax Molybdenum Company, New York, N. Y., a corporation of Delaware

Application September 17, 1954, Serial No. 456,885

7 Claims. (Cl. 117—65)

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

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-

mium, iron and nickel. Minor quantities of other metals may be present without impairing the performance of the coating or changing its character.

When the coating is applied by spraying, the coated article must be heat-treated at at least 1400° F., and preferably at a temperature within the range of 1600° F. to 2000° F. under conditions which are substantially nonoxidizing for a period sufficient to consolidate the coating and cause it to bond firmly to the base metal. The heat treatment should be continued for at least one-half hour and preferably for a longer period. Excellent results have been obtained with two hour treatments at 2000° F. in dry hydrogen. Longer periods of treatment are of no benefit but have no detrimental effect. During this heat treatment, the necessary diffusion between the base metal and the coating occurs. Thus, in all cases, the final coating contains molybdenum and, in some cases, deliberate additions of molybdenum in the coating are made, as will appear more fully hereinafter. The diffusion of molybdenum into the coating, and vice versa, not only changes the character of the coating but produces a firm bond between the coating and base metal.

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 spray method of application hereinafter described has a number of advantages. Thus, the spraying can be carried out at room temperature on articles of any size or shape without elaborate or expensive equipment. In addition, it may be used to coat only the molybdenum parts of assembled composite structures or to repair small areas in which a previous protective coating has failed. In the latter connection, oxidation tests of the coatings described herein usually show that coating failures occur at cracks which form in the coating and hence at only one spot which spreads progressively. If that spot is recoated, the remainder of the coating frequently provides further protection for a substantial period.

Ordinary commercial guns for metal spraying are used to apply the coatings. These guns are of two types: one employing a powdered metal supply and the other a metal wire supply. Both types are applicable, depending upon the nature of the metal used in the coating. A high degree of care is required to insure a uniform coating over all portions of the article.

A single sprayed coating of an alloy of 95% aluminum and 5% silicon to a depth of about .015 inch, when heat-treated in dry hydrogen for one-half hour at 1700° F., formed a uniformly adherent coating approximately .005 to .010 inch thick. This coating protected a pure molybdenum article for 768 hours at 1700° F. in ordinary atmosphere. The coating as sprayed is partially fused, porous and somewhat irregular. During the heat treatment of the sprayed aluminum-silicon alloy, it is fused and consolidated and diffusion between the base metal and the coating forms an adherent bond and a higher melting-point coating. Other forms of nonoxidizing heat treating methods may be employed. For example, the coated article can be heated in vacuum, an inert gas atmosphere or in neutral molten metal or salt baths.

In the spray method, high-melting-point metals such as molybdenum and chromium may be applied in the coating directly. Coatings containing those metals as well as iron and nickel have given excellent results. They may be coated in alternate layers with aluminum or aluminum-silicon alloys. In all such cases, however, the first layer applied to the molybdenum-base metal should contain aluminum. Examples of multiple-layer coatings include the following:

1. A pure molybdenum sheet was first spray-coated with aluminum to a depth of about .002 inch with a wire feed gun. This was followed by spraying an alloy consisting of 37% molybdenum, 32% silicon and 30% nickel to a thickness of about .002 inch. A second layer of .002 inch aluminum, a second layer of .002 inch of the same molybdenum-silicon-nickel alloy and a third layer of .002 inch aluminum were then applied in succession. The molybdenum-silicon-nickel alloy was crushed to a powder and sprayed in a powder spray gun. The multiple layer coating was heat treated in dry hydrogen at 2000° F. for 4 hours. One specimen of the resulting coating protected against oxidation for 315 hours at 1700° F. During the test of this coating, the temperature rose to 2200° F. for about 30 minutes as the result of a defective controller. Another sample with the same coating failed at one corner after 87 hours because of defective spray technique. The oxidized corner was repaired by spraying and retreating the same type of coating and the test resumed. Failure of the repaired sample occurred after 674 hours total at another spot on the original coating. In this coating, the nickel serves to reduce the melting temperature of the molybdenum-silicon-nickel alloy and thus facilitates the spraying operation. Nickel also appears to be advantageous from the standpoint of oxidation resistance.

2. A pure molybdenum sheet was first spray-coated with aluminum to a thickness of about .0025 inch and then with ferro-silicon (57.54% silicon and balance iron) to a depth of about .005 inch. A final coating of .0025 inch aluminum was then applied. The coating was heat treated in dry hydrogen for 4 hours at 2000° F. It gave oxidation protection for 662 hours in ordinary atmosphere at 1700° F.

3. A pure molybdenum sheet was first spray-coated with aluminum to a thickness of about .002 inch and then with a mixture of 33% aluminum powder and 67% of a powdered alloy of chromium, molybdenum and silicon (chromium 31%, molybdenum 31%, silicon 33%) to a thickness of about .005 inch. A final coating of aluminum .002 inch thick was then applied. The coating was heat treated in dry hydrogen at 2000° F. for 4 hours. It gave oxidation protection at 1700° F. for 1030 hours plus 21 additional hours at 2000° F. In this coating, the aluminum powder in the intermediate coating reduces the melting point of the sprayed material and thus facilitates spraying.

4. A coating identical to that of Example 3, except that it was heat treated at 1710° F. for one-half hour, gave oxidation protection at 1700° F. for 786 hours.

5. A pure molybdenum sheet was first spray-coated with aluminum to a thickness of about .002 inch and then with a silicon-aluminum alloy containing 70% silicon and 30% aluminum to a thickness of .004 inch. A final coating of aluminum .002 inch thick was then applied. After heat treatment in dry hydrogen for one-half hour at 1710° F., the resulting coating gave oxidation protection for 682 hours at 1700° F.

The difference in the results achieved with Examples 3 and 4 above, is not believed to be due to the difference in the diffusion heat treatments. Other data indicate that a treatment for one-half hour at 1700° F. is entirely adequate. It should be noted that the powdered chromium-molybdenum-silicon alloy, as applied in Example 3 above, was combined with aluminum in order to reduce the freezing point of the resulting sprayed metal and thus facilitate its adherence to the relatively cool, coated workpiece.

If desired, the aluminum layers in each of the above multiple-layer coatings may be applied by dipping in molten aluminum at temperatures in the order of 1600° F. to 1700° F. instead of by spraying and the intermediate layers which have higher melting points may be sprayed as above described. Moreover, the aluminum layers may contain from 5% to 15% silicon.

In addition to the above, specimens of single layer sprayed coatings .010 inch thick and having the following compositions, as sprayed, gave oxidation protection for more than 500 hours in moving air at 1700° F. or

more (the tests were discontinued after 500 hours without coating failure).

Coating No. 6:	Parts
Aluminum	20
Silicon	76
Chromium	104

Coating No. 7:	Parts
Aluminum	20
Silicon	33.5
Chromium	46.5

Coating No. 8:	Parts
Aluminum	20
Silicon	8.4
Chromium	11.6

Coating No. 9:	Parts
Aluminum	20
Silicon	6.8
Chromium	6.6
Molybdenum	6.6

Coating No. 10:	Parts
Aluminum	20
Silicon	90
Iron	90

Coating No. 11:	Parts
Aluminum	20
Silicon	40
Iron	40

Coating No. 12:	Parts
Aluminum	20
Silicon	10
Iron	10

Coating No. 13:	Parts
Aluminum	20
Silicon	5

Coating No. 14:	Parts
Aluminum	20
Silicon	10

Coating No. 15:	Parts
Aluminum	20
Silicon	20

Coating No. 16:	Parts
Aluminum	20
Silicon	26.5
Nickel	53.5

Coating No. 17:	Parts
Aluminum	20
Silicon	6.6
Nickel	13.4

Coating No. 18:	Parts
Aluminum	20
Silicon	8
Iron	6.8
Copper	3.2
Magnesium	2.0

Coating No. 19:	Parts
Aluminum	20
Silicon	74
Chromium	72
Iron	34

Coating No. 20:	Parts
Aluminum	20
Silicon	33
Chromium	32
Iron	15

Coating No. 21:	Parts
Aluminum	20
Silicon	8
Chromium	8
Iron	4

Specimens of coatings Nos. 6, 7, 8 and 10 also gave protection for more than 100 hours at 2000° F. The tests of coatings Nos. 7, 8, 16, 17, 18, 19, 20 and 21 were conducted at 1800° F. Each of the above listed single layer sprayed coatings Nos. 6–21 inclusive was heat treated in dry hydrogen for two hours at 2000° F. to consolidate the coating and cause a diffusion of molybdenum throughout the coating layer.

In all of the oxidation tests, the test specimens were heated in an electric furnace through which air was circulated. The temperature was maintained at 1700° F., unless otherwise stated above, and the specimens were removed twice in each 24 hours and allowed to cool to 75° F. for close visual inspection. At the first sign of any oxidation on any specimen, the test of that specimen was stopped. The total hours given above are those at the time of failure of the specimens, except in the case of coatings Nos. 6–21 inclusive, which did not fail. This method of testing also evaluates the capacity of the coatings to withstand repeated changes in temperature. This is an important matter since many other types of coatings which gave some protection at 1700° F. disintegrated when first cooled from 1700° F. to room temperature and were worthless thereafter. Since all the failures in the satisfactory coatings appeared to result from microscopic cracks in the coating, it is believed that the repeated heating and cooling and the difference in the thermal coefficients of expansion of the coating and molybdenum combined to form the cracks which induced failure in the tests.

One reason for the apparent increased effectiveness of some of the multiple-layer sprayed coatings as compared with the dip and single-layer sprayed coatings noted above may lie in the greater thickness of the former. In addition, the uniformity of the sprayed layers varied somewhat and, consequently, the oxidation resistance life at 1700° F. given above for specimens Nos. 1–5 inclusive does not necessarily represent the optimum for each type of coating. Test results indicate that the spraying technique is an important factor in the effective life of the coating.

The actual percentage of each element in the coating is difficult to ascertain, partly because of the diffusion which occurs between the coating and the molybdenum in the base metal. Available data suggest that the composition of the final coating may be different at different depths, but that point has not been fully investigated. In some cases after diffusion treatment, the outer surface may have a thin, porous layer of oxides which is easily scraped off and evidently offers little, if any, protection against oxidation. Thus, the protective effect of the coating is not impaired by grinding off the outer surface of the diffused coating, including all of the porous oxide. It is assumed that the protective effect results from the formation of a very thin, dense, adherent oxide film on the underlying main body of the coating which appears to contain little, if any, oxide and is very hard. The outer two to three thousandths of an inch of the coatings of Examples 2 and 5, above, analyzed approximately 36% molybdenum.

The results achieved with the coatings of the present invention are not fully understood and are difficult to explain, particularly in view of the fact that coatings formed by applying aluminum or silicon alone will not protect molybdenum against oxidation at 1700° F. It is believed, however, that the coating contains a complex compound of molybdenum, aluminum and silicon, and probably a number of such compounds which provide the desired protection. There does not appear to be any significant progressive oxidation of the coating since an analysis of the outer portion of one of the coatings showed 1.3% oxygen prior to testing and only 3.2% oxygen after 500 hours in ordinary air at 1700° F.

An important feature of the coatings lies in the fact that they not only protect molybdenum against oxida-

tion but the aluminum actually reduces any molybdenum oxides which may have formed during or before the coating operation, forming alumina which apparently remains in the coating. Thus, it is not necessary to deoxidize the surface of the molybdenum article before applying the coating. However, visible oxide films are preferably removed. This can be done by immersion in a bath of 90% KOH plus 10% $NaNO_2$ at 750° F. followed by a wash in cold water or by grit-blasting the surface. Grit-blasting is preferred, since it provides a roughened surface.

All proportions given herein are proportions by weight.

What is claimed is:

1. The method of forming a protective coating on a molybdenum-base alloy article which includes spray-coating the surface of the article with a powder-fed metal spray gun and supplying to said spray gun for the formation of said coating a mixture of the powders of different metals, one of said metals being predominantly aluminum and the other being an alloy containing a substantial quantity of silicon and metal from the group consisting of chromium, iron and nickel, the proportions of total aluminum and silicon being from one to one hundred and eighty parts of silicon for each twenty parts of aluminum, and the total of metal from said group ranging from one-half to twice the total of aluminum and silicon, and holding the coated article at an elevated temperature under non-oxidizing conditions to cause a diffusion of molybdenum throughout a major portion of the thickness of the coating.

2. The method of forming a protective coating on a molybdenum-base article which consists in spraying metal on the surface of the article, said metal containing aluminum and silicon in the proportions of from one to one hundred and eighty parts of silicon for each twenty parts of aluminum, and thereafter heating said coated article under substantially non-oxidizing conditions at a temperature in excess of about 1400° F. to consolidate the coating, cause diffusion of molybdenum throughout the major portion of the thickness of the coating, and bond it to the article.

3. The method of forming a protective coating on a molybdenum-base article which consists in spraying metal on the surface of the article, said metal containing aluminum and silicon in the proportions of from one to one hundred and eighty parts of silicon for each twenty parts of aluminum, said metal also containing molybdenum, and thereafter heating said coated article under substantially nonoxidizing conditions at a temperature in excess of about 1400° F. to consolidate the coating and bond it to the article.

4. The method of forming a protective coating on a molybdenum-base article which consists in spraying metal on the surface of the article, said metal containing aluminum and silicon in the proportions of one to one hundred and eighty parts of silicon for each twenty parts of aluminum, the remainder of said sprayed metal consisting essentially of metal from the group consisting of chromium, iron and nickel in an amount ranging from one-half to twice the total amount of aluminum and silicon, and thereafter holding said coated article under substantially non-oxidizing conditions at an elevated temperature to cause consolidation of the coating and diffusion of molybdenum throughout a major portion of the thickness of the coating.

5. The method of forming a protective coating on a molybdenum-base article which comprises applying to the surface of the article a metal layer which is predominantly aluminum and thereafter spraying a second metal layer on the surface of the article, said second metal layer containing aluminum and metal from the group consisting of chromium, iron and nickel, at least one of said metal layers also containing silicon, the total silicon in both layers being at least one part for each part of the total aluminum in both layers, and thereafter holding said coated article under substantially nonoxidizing conditions at an elevated temperature to cause consolidation of the coating and diffusion of molybdenum throughout a major portion of the thickness of the coating.

6. The method of forming a protective coating on a molybdenum-base article which consists in spraying metal on the surface of the article, said metal containing aluminum and silicon in the proportions of from one to four parts of silicon for each part of aluminum and thereafter heating said coated article under substantially nonoxidizing conditions at a temperature in excess of about 1400° F. to consolidate the coating, cause diffusion of molybdenum throughout the major portion of the thickness of the coating and bond it to the article.

7. The method of forming a protective coating on a molybdenum-base article which comprises spraying metal on the surface of the article, said metal containing aluminum and silicon in the proportions of from one to four parts of silicon for each one part of aluminum, the remainder of said sprayed metal consisting essentially of metal from the group consisting of chromium, iron and nickel, and thereafter holding said coated article under substantially nonoxidizing conditions at an elevated temperature to cause consolidation of the coating and diffusion of molybdenum throughout a major portion of the thickness of the coating.

References Cited in the file of this patent

UNITED STATES PATENTS

2,166,510	Whitfield	July 18, 1939
2,682,101	Whitfield	June 29, 1954
2,690,409	Wainer	Sept. 28, 1954