

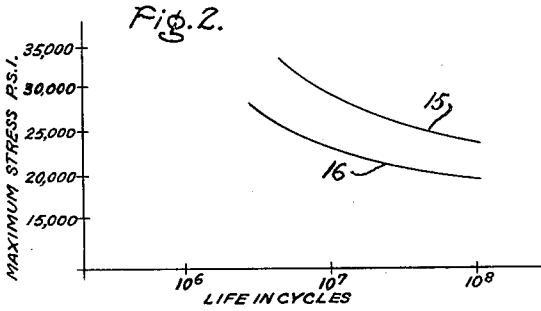
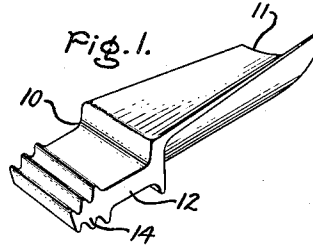
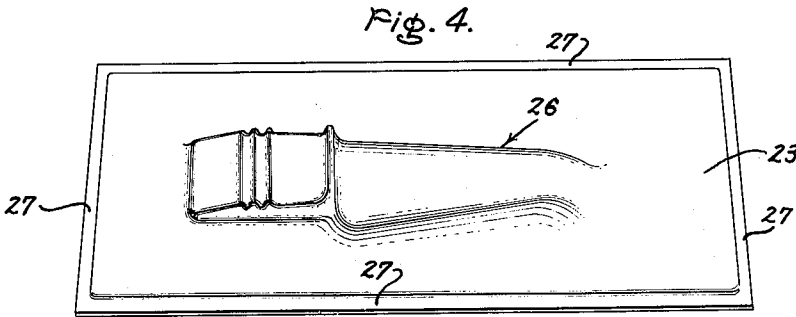
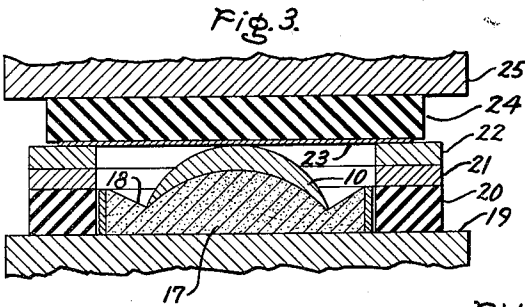
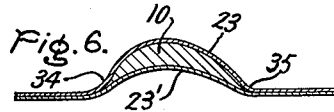
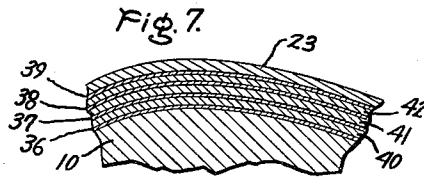
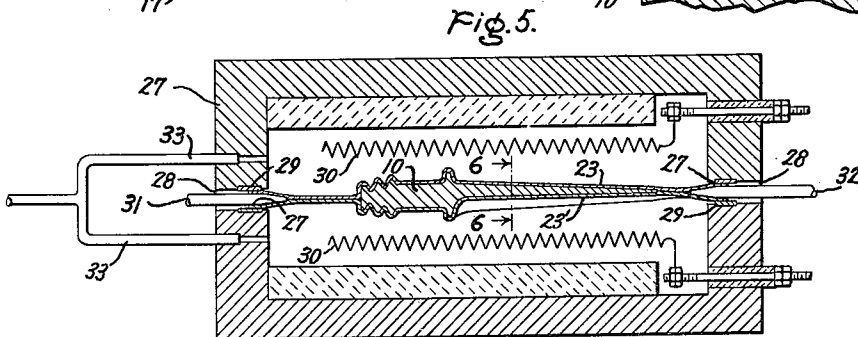
July 25, 1961

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2,993,264

PROTECTIVE COATING FOR MOLYBDENUM

Filed Dec. 23, 1955



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2,993,264

PROTECTIVE COATING FOR MOLYBDENUM

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Filed Dec. 23, 1955, Ser. No. 554,999

4 Claims. (Cl. 29—183.5)

This invention relates to the provision of protective coatings for structural components composed of molybdenum and molybdenum base alloys and more particularly to coatings for articles of molybdenum and molybdenum-rich alloys which function to resist oxidation, to prevent oxidation of the molybdenum article, and which are resistant to attrition by abrasion and erosion.

Molybdenum and alloys of which molybdenum is the principal constituent are known to have high strength at elevated temperatures, and except for the fact that these materials are subject to drastic corrosion or oxidation when exposed to oxidizing atmospheres at temperatures over 1400° F., would be excellent as a structural material for the fabrication of components subjected to high temperature and high stress in gas turbine applications. It has been proposed that such components as gas turbine buckets, blades and the like might be successfully fabricated from molybdenum and molybdenum-rich alloys if the external surfaces exposed to oxidation could be provided with a protective coating to exclude the oxidizing atmosphere.

Many different coating materials have been applied to molybdenum articles in an attempt to prevent this high temperature oxidation, but while it has been found a relatively easy matter to provide a stable, continuous coating which will exclude oxygen for long periods of time under static conditions, when the molybdenum article is flexed or otherwise subjected to oscillatory loads to produce reverse bending, these previously known coatings have been effective for only brief periods of time.

A principal object of my invention is the provision of stable, adherent coatings for articles made from molybdenum and molybdenum-rich alloys which resist oxidation and penetration of oxidizing atmospheres for long periods of time at elevated temperatures. An additional object of my invention is the provision of composite articles of molybdenum and of molybdenum-rich alloys which are capable of withstanding oscillatory loading in oxidizing atmospheres at temperatures in excess of 1500° F. for extended periods of time. A still further object of my invention is to provide a method and apparatus for cladding molybdenum and molybdenum-rich articles in order to increase their resistance to oxidation, abrasion and erosion.

Briefly stated, in accordance with one aspect of my invention I provide a molybdenum or molybdenum-rich alloy article having a plurality of electrodeposited, alternately disposed layers of chromium and nickel which may advantageously be enclosed in a preformed sheet metal jacket and a method and apparatus for preparing such an article.

My invention will be better understood from the following description taken in conjunction with the accompanying drawing, and its scope will be pointed out in the appended claims.

In the drawing,

FIG. 1 is a perspective view of a typical gas turbine bucket;

FIG. 2 is a graphical illustration of fatigue properties of electroplated articles;

FIG. 3 is a transverse, cross-sectional view of drawing apparatus by which sheet metal may be preformed for turbine bucket jackets;

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FIG. 4 is a perspective of a preformed sheet metal jacket element;

FIG. 5 is a longitudinal cross-section of apparatus for applying preformed sheet metal jacket elements to a turbine bucket;

FIG. 6 is a cross-sectional view of a jacketed bucket prior to trimming taken along line 6—6 of FIG. 5; and

FIG. 7 is a fragmentary sectional view of an embodiment of my invention.

As shown in FIG. 1, the typical gas turbine bucket 10 comprises a blade or air foil portion 11, a shank 12 and dovetail portion 13. In operation in a gas turbine, the bucket 10 is usually affixed and retained in the periphery of a rotatable disk-like element by the dovetail and shank portions which engage a mating slot in the disk. The disk and bucket are rotated at high rates of speed at high temperatures, of the order of 1400° F. and above, while surrounded by an oxidizing atmosphere. Extremely high stresses are developed at the dovetail and shank portions and higher stresses in the air foil section 11. Further, these stresses are complicated by vibrational loads imposed during rotation which tend to subject the air foil and associated structure to bending first in one direction and then in a reverse direction.

When molybdenum buckets were fabricated, attempts were made to protect them from oxidation by the electrodeposition of nickel thereon. First, great difficulty was experienced in providing an electrodeposited coating of nickel upon molybdenum or molybdenum-base alloys which would adhere thereto when heated. After means had been found to provide adherent electrodeposited nickel films upon molybdenum and molybdenum-rich alloys, I then found that these coatings were not stable at elevated temperatures when subjected to reverse bending loads, or, as commonly referred to, "fatigue loading conditions." I discovered that under this type of loading rapid intergranular failure occurred at the grain boundaries of the nickel coating, resulting in cracks forming at the nickel grain boundaries through which oxygen was able to pass and attack the molybdenum substrate. I further discovered that merely increasing the thickness of the nickel coating did not produce an increase in time of oxidation resistance commensurate with the increase in coating thickness. It has been proposed that a protective coating having greater resistance to penetration be formed by depositing a chromium film upon the molybdenum surface, followed by an electrodeposited nickel film thereon and followed by a final electrodeposited chromium film thereover, a slow heat treatment cycle following the nickel deposition and a second slow heat treatment cycle following the final chromium deposition. This type of coating has been shown to have greater resistance to penetration than a coating consisting essentially of nickel. I have discovered, however, that a coating consisting of a plurality or multiplicity of layers of nickel interspersed by chromium layers produces a resistance to penetration far greater than that which would be expected.

In particular, I have discovered that a molybdenum or molybdenum-rich alloy article provided with a coating having an aggregate thickness of from about 0.005 to 0.010 inch, consisting of a film of chromium less than 0.001 inch thick, preferably about 0.0005 inch thick, electrodeposited upon the molybdenum alloy, followed by a plurality of layers of electrodeposited nickel alternated with layers of electrodeposited chromium has outstanding resistance to fatigue failure. The layers of nickel are each preferably about 0.0006 to 0.0008 inch thick, while the intervening layers of chromium, including a final layer of chromium covering the last nickel layer, are each about 0.0002 to 0.0003 inch thick. The thickness of the

several coatings should be regulated so that the chemical composition of the electrodeposited coating ranges between about 65 to 80 percent by weight nickel, the balance being substantially chromium. In practice, it is preferred that the article be subjected to a short time duration, $\frac{1}{4}$ to $\frac{1}{2}$ hour, anneal at about 1800° F. in a hydrogen atmosphere after each chromium layer has been applied, and to a 4 to 6 hour anneal at about 1800° F. in a hydrogen atmosphere after each nickel layer has been applied. Upon microscopic examination, the coating layers are found to have been modified by diffusion during heat treatment to form a plurality of alternating layers of nickel-rich nickel-chromium alloy and nickel.

In order to compare the effectiveness of the multiple nickel layer coating of my invention with a coating consisting of a nickel layer interposed between a pair of chromium layers, a plurality of fatigue test specimens were prepared from forged bars of a commercial alloy containing 0.3 percent columbium, balance substantially all molybdenum. Each fatigue test specimen was prepared from a round bar of this material $8\frac{3}{4}$ inches long having a diameter of 0.625 inch. A pair of opposed cylindrical surface each having a 5 inch radius was machined in the central portion of each of the bars, the minimum distance between the opposed surfaces being about 0.343 inch.

One group of the test bars was then plated in the following manner. The surfaces of the molybdenum alloy bars were cleaned anodically at 12 volts for 1 minute in an aqueous solution of sulfuric acid at room temperature followed by rinsing in water, ammonium hydroxide, and finally distilled water. The bars were then placed while still wet in a conventional chromium plating solution in which the concentration of CrO_3 was maintained between 275 and 325 grams per liter. The bath temperature was held between 65 and 70° C. and the cathode current density adjusted to 1.5 amperes p.s.i. After a layer of chromium at least 0.0003 inch thick had been applied in this manner, the bars were removed from the plating bath. The chromium plated specimens were then thoroughly washed and placed directly in a conventional acid-nickel strike bath for 5 minutes at a cathode current density of 100 milliamperes per square centimeter. The specimens were then transferred directly without rinsing to a conventional "Watt's-type" nickel plating solution where plating was continued for 5 minutes. At the end of this time the specimens were rinsed and dried and heat treated for 15 minutes in a hydrogen atmosphere from about 1700° to 1850° F., preferably 1800° F.

Following heat treatment, the specimens were electropolished in a phosphoric acid-sulfuric acid solution, rinsed, returned to the nickel strike bath for 5 minutes and again transferred directly to the Watt's solution, where electroplating of nickel was continued until about 0.003 inch total thickness of nickel was attained. Following the nickel plating step, the specimens were heat treated for at least 15 minutes at about 1800° F., in a hydrogen atmosphere. This heat treatment was followed by cleaning the specimens by electropolishing in the phosphoric acid-sulfuric acid solution for a few seconds, followed by rinsing in distilled water. A final chromium plated film about 0.0003 inch thick was applied over the nickel layer by utilizing the same bath and procedure recited for the first chromium coating and the resulting specimen heat treated for at least 15 minutes at 1800° F. in a hydrogen atmosphere.

A second group of test specimens were electroplated and heat treated according to my invention, namely, by first applying a chromium layer of about 0.0005 inch thickness followed by a preliminary nickel film, heat treated, electropolished, plated with nickel to about 0.0007 inch thickness, heat treated, electropolished, plated with a second film of chromium about 0.0003 inch thick, given a preliminary nickel plate, heat treated, electro-

polished, plated to form a second nickel film of about 0.0007 inch thickness, heat treated, electropolished, plated with a third film of chromium about 0.0003 inch thick, given a preliminary nickel plate, heat treated, electropolished, plated to form a third nickel film about 0.0007 inch thick, heat treated, electropolished, plated with a fourth film of chromium about 0.0003 inch thick and heat treated. In preparing the surfaces of these specimens for plating, heat treatment, cleaning of plated surfaces, and plating, the same procedures and solutions used in the preparation of the first group of specimens were employed.

The several solutions used are quite conventional and the compositions thereof may be varied considerably within the scale of the plating art. However, the chromium plating bath actually used consisted of an aqueous solution containing from about 275 to 325 grams per liter CrO_3 and sufficient sulfuric acid so that the ratio of CrO_3 to sulfate ions was maintained at about 100 to 1. The acid nickel sulfate strike bath contained about 450 grams per liter of nickel sulfate, about 50 grams per liter concentrated sulfuric acid, and the balance water. The "Watt's" solution contained about 280 to 300 grams per liter nickel sulfate, 30 grams per liter nickel chloride, 40 grams per liter toric acid, and the balance water. The electropolishing solution containing about 20 percent by volume concentrated sulfuric acid, balance concentrated phosphoric acid.

It may be seen from the foregoing that the first group of specimens were provided with a plated coating consisting of a 0.0003 inch thickness layer of chromium, a 0.003 inch thick layer of nickel thereon, and a final 0.0003 inch thick layer of chromium. The second group of specimens were provided with a multiple layer coating consisting of a 0.0005 inch thick layer of chromium followed by a 0.0007 inch thick layer of nickel, a 0.0003 inch thick layer of chromium, a 0.0007 inch thick layer of nickel, a 0.0003 inch thick layer of chromium, a 0.0007 inch thick layer of nickel, and a 0.0003 inch thick layer of chromium.

These specimens were then tested for resistance to fatigue loading at elevated temperatures in an air atmosphere in the conventional manner, and representative results of these tests are reproduced in the following table:

Cr-Ni-Cr PLATED SPECIMENS

Temp., ° F.	Stress (p.s.i.)	Life (cycles $\times 10^{-5}$)
1,650-----	35,000	0.95
	30,000	2.99
	25,000	102.5
1,800-----	25,000	5.1
	20,000	57.0

MULTIPLE LAYER PLATED SPECIMENS

1,650-----	35,000	19.2
	30,000	101.0
	30,000	8.5
1,800-----	25,000	46.3

¹ Test terminated, specimen unbroken.

In the foregoing table, specimens from the first group are identified as "Cr-Ni-Cr Plated Specimens," while the specimens from the second group are identified as "Multiple Layer Plated Specimens." It will be immediately apparent that the test bars coated according to my invention were able to withstand high temperature fatigue loads for much longer times than the chromium-nickel-chromium plated comparison specimens. For example, at 1650° F. the limiting stress for over 1 million cycles is about 25,000 p.s.i. for the chromium-nickel-chromium coated bars, while it is about 30,000 p.s.i. for the multiple layer plated bars of my invention.

A graphical comparison of the 1800° F. fatigue behavior is illustrated by the characteristic curves shown

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in FIG. 2 in which curve 15 shows the fatigue strength of the test bars comprising my invention and the curve 16 shows the fatigue strength of the chromium-nickel-chromium test bars. It should be noted that the ordinate axis of the graph is a linear scale, while the abscissa axis of the graph is composed of recurrent cycles of logarithmic scales.

Microscopic examination of cross-sections of fatigue tested specimens of my invention revealed that while the nickel zones or layers of the coating still exhibited cracks at the grain boundaries, the nickel-chromium alloy zones acted to prevent these small cracks from growing longer and forming a single crack extending through the entire protective coating.

When gas turbine buckets were plated according to my invention and installed in an aircraft gas turbine, it was found that the stream of combustion gases passing over the buckets contained abrasive particles which abraded or eroded the protective coating excessively. Accordingly, I have provided the following apparatus for cladding turbine buckets and the like with sheet metal.

The apparatus shown in cross-section in FIG. 3 comprises a forming die in which a base or "punch" member 17 is provided with a contoured upper surface 18 adapted to receive and conform to one side of a turbine bucket 10. Punch member 17 rests upon a supporting platen 19 of a suitable press apparatus, a resilient pad 20 surrounds punch 17 and supports a spacer element 21 and a blank holder 22. A suitably dimensioned sheet of cladding metal 23 is supported upon blank holder 22 and a resilient or deformable die 24 constructed of rubber or the like is adapted to be pressed against the upper surfaces of bucket 10 and punch 17 by the upper platen 25.

When the platen 25 is urged toward platen 19, the sheet metal blank 23 is deformed or drawn about the upper contours of the bucket 10 and the exposed upper surfaces of punch 17 to form a sheet having substantially the exact configuration of one-half of bucket 10 embossed thereon, as shown in FIG. 4 at 26. Further, coaction between die 24 and blank holder 22 during the forming operation produces a rimlike flat margin 27 at the edges of the formed sheet having a useful function to be described subsequently.

It may be seen that by removing bucket 10 from punch 17 and removing spacer element 21 that a second sheet of cladding metal 23' not shown in FIG. 3 may be supported upon blank holder 22 and deformed or drawn over the contoured surface 18 of die 17 to produce an embossed surface thereon contoured to substantially the exact configuration of the other side of bucket 10.

These contoured sheets 23 and 23' may then be bonded to the surfaces of bucket 10 by means of the following apparatus. As was shown in FIG. 5 a pressure chamber 27 is provided having recess means 28 about its periphery to accommodate the edge portions 27 of contoured sheets 23 and 23'. Sheets 23 and 23' are assembled with a bucket 10 and edge portions 27 thereof are sealed in recesses 28 by means of resilient gasket elements or the like 29. As shown, the sheets 23 and 23' act as a diaphragm to separate the interior of pressure chamber 27 into two substantially equal volume closed compartments. Means are provided for heating the interior of the chamber and assembly 23, 23' and 10, such as, for example, electrical heating elements 30.

Means are provided at 31 for the introduction of hydrogen between sheets 23 and 23' and around bucket 10 and exiting at 32. Means 33 are also provided for introducing an inert gas such as argon into the interior of the chamber 27 at high but equal pressures to each of the two compartments thereof.

As a specific example of the operation of the apparatus of my invention, assume that contoured sheets 23 and 23' have been formed from 0.005 inch thick nickel sheet metal. The formed sheets 23 and 23' are assembled with

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bucket 10 as shown in FIG. 5 and hydrogen gas is passed through the interior of the assembly as it is heated to a temperature of about 2000° to 2400° F., preferably about 2200° F. After the assembly has reached the desired temperature, an inert gas, for example argon, is admitted to the two chambers until a pressure of about 600 p.s.i. or greater is attained therewithin. The flow of hydrogen is terminated and the temperature and chamber pressure are maintained for a time, of the order of ½ hour to 2 hours, sufficient to pressure weld the contoured sheets 23 and 23' to the bucket 10. The relationship of sheets 23 and 23' to bucket 10 is shown in FIG. 6. After cooling, the excess sheet metal is trimmed from the periphery of the clad bucket, for example, by cutting 23 and 23' at 34 and 35.

While in the foregoing example the sheets 23 and 23' have been disclosed as being formed from 0.005 inch thick nickel sheet, it is obvious that thicker or thinner sheet may be successfully used or that sheet metal composed of nickel-base alloys or other deformable alloys having suitable corrosion and welding characteristics may be used. For example, 0.0035 inch thick sheet metal composed of about 80 percent nickel, 13 percent chromium, 6.5 percent iron and 0.20 percent copper has been successfully deformed and pressure welded to buckets by means of the foregoing apparatus. While molybdenum articles may be directly clad with sheet metal in this manner, it is desirable and preferred that molybdenum turbine buckets be protected from oxidation by the plated coating of my invention and that the plated coating be in turn protected from abrasion by the provision of sheet metal cladding thereover, pressure welded to the outer layer of the plated coating. In this manner, if there are any small openings in the sheet metal jacket, particularly where formed sheet 23 joins sheet 23', the underlying plated coating will prevent the drastic oxidation of the molybdenum or molybdenum-base alloy of the bucket. Such a preferred construction is illustrated in FIG. 7 in which bucket 10 is provided with electrodeposited layers of chromium 36, 37, 38 and 39, electrodeposited layers of nickel 40, 41 and 42 and a sheet metal jacket 23 pressure welded to chromium layer 39. Of course, the various plating operations, heat treatment of the plated layers, and the forming and pressure welding of the sheet metal jacket are preferably accomplished as recited previously.

It should be further noted that while the specific examples of my invention described previously have been restricted to a multiple-layer coating consisting of four layers of chromium and three layers of nickel, a greater number of alternating layers may be deposited if desired. For example, I have deposited a multiple-layer consisting of as many as seven layers of chromium separated by six alternate layers of nickel upon gas turbine buckets without adversely affecting the quality of the coating. Preferably at least four layers of chromium and three layers of nickel should be employed and the aggregate composition of this preferred coating and coatings consisting of a greater number of alternately disposed layers should consist of about 65 to 80 weight percent nickel, and the balance chromium.

From the foregoing, it may be readily seen that I have provided an oxidation resistant, electroplated coating for molybdenum and molybdenum-base alloys which is particularly resistant to failure at elevated temperatures and high fatigue loads. Further, I have provided a sheet metal jacket for protecting such a coating from abrasion, particularly where the coated article is a gas turbine bucket and have provided apparatus particularly adapted to forming and pressure welding the jacket elements to the plated article. While specific examples of my invention have been recited in the foregoing specification and shown in the drawing, it will be obvious to those skilled in the art that various changes and modifications may be made without departing from the invention, and it is intended to cover in the appended claims all such changes

and modifications that come within the true spirit and scope of the invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A composite article including a body consisting substantially of molybdenum and a multiple layer coating substantially covering the surface of said body to provide improved resistance against high temperature oxidation of said body when it is subjected to cyclic stresses, said multiple layer coating comprising a first chromium layer deposited on said body as a continuous film covering substantially the entire surface thereof, and a plurality of nickel layers of from 0.0006 to 0.0008 inch thick alternating with a plurality of chromium layers of from 0.0002 to 0.0003 inch thick, said layers being present as continuous films covering said first chromium layer and ending in an outermost layer of chromium, adjoining nickel and chromium layers forming alloys at the interfaces therebetween which improve the protective properties of said multiple layer coating.

2. A composite article as defined in claim 1 wherein the total thickness of said multiple layer coating is from 0.005 to 0.010 inch.

3. A composite article as defined in claim 1 wherein the thickness of said first chrome layer is from 0.001 to 0.0005 inch.

4. A composite article including a body consisting substantially of molybdenum and a multiple layer coating

substantially covering the surface of said body to provide improved resistance against high temperature oxidation of said body when it is subjected to cyclic stresses, said multiple layer coating comprising a first chromium layer deposited on said body as a continuous film of from about 0.001 to 0.0005 inch thick covering substantially the entire surface thereof, a plurality of nickel layers of from 0.0006 to 0.0008 inch thick alternating with a plurality of chromium layers of from 0.0002 to 0.0003 inch thick, said layers being present as continuous films covering said first chromium layer and ending in an outermost layer of chromium, and a sheet metal jacket of a corrosion resistant material pressure welded to the outermost layer of the multiple layer coating to protect said article against abrasion.

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