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SIMULTANEOUS BRAZING AND CORROSION PROTECTING REFRACTORY METALS

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The present invention relates to the coating and brazing of shaped objects of refractory metals so as to render the objects resistant to corrosion at high temperatures.

In the recent past the various alloys of steel have satisfied most structural needs. However, with the advent of rockets and missiles the temperatures involved that will have to be sustained by the metal structural members and parts has increased several fold.

The strength of a metal is directly related to its melting point. Therefore, the refractory metals would be a preferred material of construction in the rocket and missile field because of their high melting points. Refractory metals considered most promising are molybdenum (M.P. 2620° C.), tantalum (M.P.2996±50° C.) and tungsten (M.P. 3370° C.).

As with most materials, one will find that in order to take advantage of certain properties, one will have to compensate for other properties of the material.

These materials are subject to drastic corrosion or oxidation when exposed to oxidizing atmospheres at temperatures over 1400° F. It has been suggested that components for rocket and missile applications could be fabricated from these refractory metals if the external surfaces exposed to oxidation could be provided with a protective coating to exclude the oxidizing atmosphere.

Many different coatings have been applied to these metal articles in an attempt to prevent this high temperature oxidation. One in wide use is the silicide coating. Such a coating may be produced by vapor depositing a thin layer of silicon onto the hot surface of the transition metal or it can be formed by being painted or sprayed on, or by the sintered method. While such a coating has very good protective value at elevated temperatures, its brittleness may result in cracking when struck or deformed. In order to be of value, any protective coating must completely cover the surface. Any defects, such as a crack or pinhole makes the coating useless since the base metal will erode by oxidation at the point of defect.

Other suggested methods of protection for these refractory metals are the application of ceramic coatings and cladding. These latter methods are for limited application and have not found any general use.

Accordingly, it is an object of the present invention to provide a method of protectively coating refractory metals.

Another object is to provide a means of bonding together shaped objects of refractory metals.

Still another object of the invention is to provide a method of simultaneously protectively coating and bonding together shaped articles of refractory metals.

Yet another object is the provision of a novel corrosion resistant, brazing alloy for coating surfaces.

Other objects and many of the attendant advantages will be readily appreciated as the same becomes better understood by reference to the following description of the invention.

The refractory metal to be coated and/or brazed is first prepared for electroplating by suitable known methods. It is then plated with nickel followed by an electroplate of rhodium.

The plated metal object is then heated in a protective vacuum atmosphere to about 2500° F. The protective atmosphere can also be hydrogen or cracked ammonia gas. The binary coating melts and fuses to the base refractory metal. The result is a high temperature corrosion and oxidation resistant integrally bonded coating. The integral bond is a result of the nickel simultaneously forming solid solution alloys with the refractory metal and rhodium electroplate. The solid solution forms most readily when tantalium is the base metal being coated.

If desired, these coated refractory articles can be joined by placing them in close proximity or wiring them together and then heating to about 2500° F. in vacuum or other protective atmosphere. The adjoining electroplates will then fuse together resulting in the refractory metal shapes being brazed together. This process will coat and protect intricate and complex shapes as readily as simple configurations. The coated and brazed articles of this invention have been tested to 2800° F. in a dynamic oxidizing atmosphere and have shown excellent resistance to oxidation or corrosion.

The following is a more detailed description of an embodiment of the present invention. The refractory metal article to be protected in this example tantalum, is first degreased by being immersed in a suitable solvent such as acetone or carbon tetrachloride.

The tantalum article is then cleaned mechanically by abrasive means such as emery paper, steel wool, etc.

Then, the article is cleaned chemically by etching in an appropriate acid such as a solution of sulfuric acid (95%), nitric acid (4.5%), hydrofluoric acid (.5%) containing 18.8 grams per liter of chromic oxide.

The tantalum article is then placed directly in a conventional acid-nickel strike bath for several minutes at a cathode current density of 100 milliamperes per square centimeter. The specimen is then transferred directly without rinsing to a conventional "Watt's-type" nickel plating solution where plating is continued at .5 to 2 amperes per square decimeter to a thickness of about .0001 inch to .001 inch depending on desired final results.

The nickel coated tantalum specimen is then removed from this bath, rinsed and placed in a rhodium plating bath where rhodium is deposited at a current density of 7 amperes per square decimeter to a thickness of .0001 inch or less, again depending on desired final results. The coated article is removed and heat treated and/or brazed as previously described.

The several solutions used are conventional and the composition thereof may be varied within the skill of the plating art. The solutions used in the example herein for the nickel bath consisted of an aqueous solution containing about 240 grams per liter of $NiSO_4 \cdot 6H_2O$, about 45 grams per liter of $NiCl_2 \cdot 6H_2O$ and 30 grams per liter of H_3BO_3, the remainder being water. The rhodium bath consisted of 162 grams per liter of the phosphate or sulfate of rhodium with an excess of acid of either sulfuric or phosphoric acids.

It should be understood that the foregoing disclosure relates only to a preferred embodiment of the invention and that numerous modifications may be made therein without departing from the spirit and the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A composite article including a base of a refractory metal selected from the group consisting of tungsten, tantalum and molybdenum having a multiple layer metal surface coating fused to said base to provide high-temperature oxidation and corrosion resistance, said surface comprising rhodium integrally bonded to said base metal by solid solution alloys of base metal, nickel and rhodium, said integrally bonded surface being characterized by alloyed strata resulting from a plating of said base with thin coatings of nickel and rhodium and subjection of

said article to heat treatment at about 2500° F. whereby a fused integrally bonded surface is obtained on said base.

2. The method of protecting refractory metal selected from the group consisting of tungsten, tantalum and molybdenum articles against oxidation and corrosion at high temperatures including the steps of cleaning said metal articles, electroplating nickel thereon of a thickness of from about .0001 to .001 inch, thereafter electroplating rhodium up to about .0001 inch in thickness on the nickel surface, and heat-treating said plated article in a protective non-reactive environment at about 2500° F. whereby solid solution alloys of nickel with the refractory metal and rhodium are formed, thereby integrally bonding an oxidation and corrosion resistant coating on said refractory metal article.

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