Dec. 14, 1954 A. KORBELAK 2,697,130

PROTECTION OF METAL AGAINST OXIDATION

Filed Dec. 30, 1950

Fig. 1.

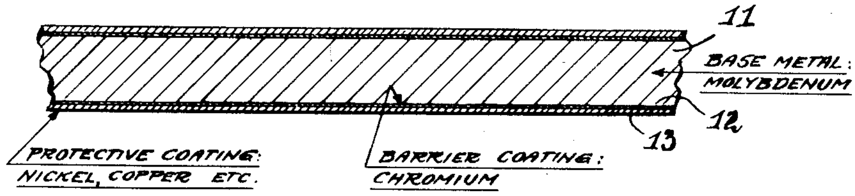

Fig. 2.

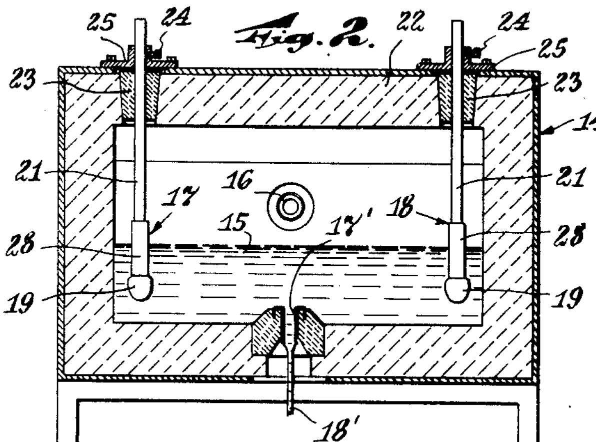

Fig. 3.

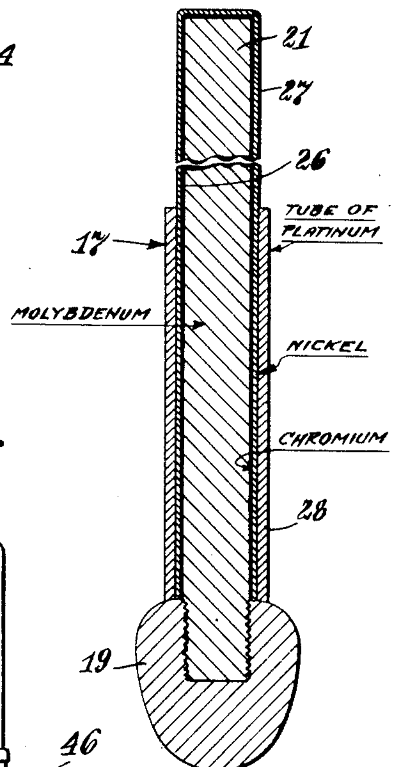

Fig. 4.

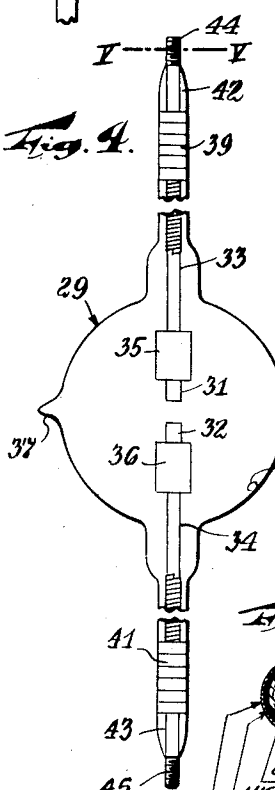

Fig. 6.

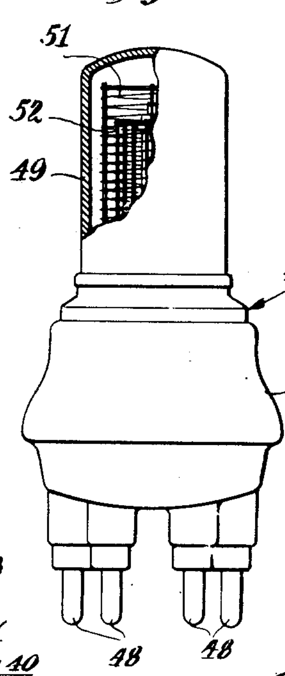

Fig. 5.

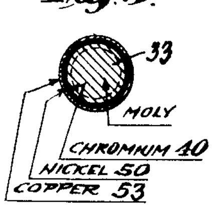

Fig. 7.

INVENTOR
ALEXANDER KORBELAK

BY

ATTORNEY

United States Patent Office

2,697,130

Patented Dec. 14, 1954

1

2,697,130

PROTECTION OF METAL AGAINST OXIDATION

Alexander Korbelak, Bloomfield, N. J., assignor to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

Application December 30, 1950, Serial No. 203,704

7 Claims. (Cl. 174—50.61)

This invention relates to the protection of refractory metals readily-oxidizable at high temperatures, against such oxidation, the improvement of the bond strength, and the avoidance of absorption of the protecting coating by the metal itself.

The principal object of my invention, generally considered, is to use a chromium "strike" or "flash" film, or thin coating electroplated directly on articles of refractory metal, the oxide of which forms and volatilizes at relatively low temperatures, or to electroplate a chromium strike or flash coating on such articles, to obtain maximum bond strength for other metal electroplated thereover, and prevent absorption of such other metal, such as platinum and metal of the nickel group, by the refractory metal when finally electroplated over said film.

Another object of my invention is to protect against oxidation at high temperatures, articles constructed of refractory metals and alloys thereof, the oxides of which form and volatilize at relatively low temperatures, comprising electroplating such articles in a bath, incidentally of low efficiency, where hydrogen which develops during electroplating acts as a reducing medium, to clean-up light surface oxides, and where the crystals of the electrodeposit act as a continuation of the crystals of a base metal, in order to supply a high bond strength with the base metal for subsequent application of an electroplating of a final metal coating thereon.

A further object of my invention is to provide on molybdenum a duplex coating of such a character that it is not only protected against oxidation at high temperatures, but there is a good bond provided between the molybdenum and the coating, the coating immediately adhering to the molybdenum serving also to prevent diffusion of the outer coating into the molybdenum.

A still further object of my invention is to provide a coating for protecting molybdenum and metal of similar character, insofar as their high temperature oxidation characteristics are concerned, and heat treat to improve the adherence thereof so that blistering will not occur if abruptly heated to as high as 1000° C. and higher.

An additional object of my invention is to provide articles of molybdenum and other refractory metal having high-temperature oxidation characteristics similar thereto, protected by a plating of nickel or the like, the bond therewith being improved by an intermediate film material such as chromium having a coefficient of expansion intermediate that of the article and the coating, thereby giving the effect of a step seal and eliminating peeling of the coating.

Other objects and advantages of the invention will become apparent as the description proceeds.

Referring to the drawing:

Figure 1 is a sectional view of an article, the surface of which is protected against oxidation at high temperatures in accordance with my invention.

Figure 2 is a fragmentary transverse sectional view of a glass melting furnace having electrodes embodying my invention.

Figure 3 is an enlarged fragmentary axial sectional view of one of the electrodes of Figure 2.

Figure 4 is a fragmentary elevational view of another embodiment of my invention.

Figure 5 is an enlarged transverse sectional view on the line V—V of Figure 4.

Figure 6 is an elevational view, with a part in section, of another embodiment of my invention.

Figure 7 is a sectional view, on an enlarged scale, of the grid wire of the embodiment of Figure 6.

2

Although molybdenum, as a metal, melts at a temperature no lower than 2600° C. when in a reducing atmosphere, and does not boil until 3700° C. in such an atmosphere, its oxidizing characteristics are such that, if not protected, an oxide begins to form at a temperature as low as 450° C. At about 700° C., this oxide sublimes therefrom as heavy white fumes, exposing fresh surfaces. Thus, the metal cannot be used at all above a temperature of 700° C. if not protected against oxidation, as in a short while it would waste away. Although this metal has high strength and rigidity at temperatures as high as 1000° C., that is, it is better than commonly-used refractory metals, it thus cannot be used in oxidizing atmospheres unless adequately protected.

To be of any permanent value, an electrodeposited coating must adhere closely to the base metal. Such adherence depends primarily upon an intimate contact between the plated layer and the underlying metal. This means the absence of any grease, oxide, gas, or other foreign material. Stainless steel and similar chromium-nickel alloys can be plated with a smooth uniform deposit. However, unless a special pre-plating technique is used, such a plating may be stripped off as a continuous sheet or foil. Molybdenum, tungsten, and similar metal, are also very difficult to plate with a firmly adhering coating. I have developed a technique whereby molybdenum, tungsten, and alloys of similar character, such as molybdenum-base alloys and tungsten-base alloys, and high tungsten and high molybdenum alloy steels, may be plated with nickel and the plating then diffused by a high-temperature heat treatment in hydrogen. This gives a good bond but requires heat-treating facilities.

I have found that through the use of a chromium "strike" or "flash" coating (by which I mean one not over .00002" thick), or thin film, applied by electroplating, an improved adherence is obtainable. Through such a technique other protective metals which do not form volatile oxides, particularly platinum, and those of the "nickel group" comprising nickel, cobalt, and iron, may be electroplated over the chromium "flash" with such good bonding that the base metal may actually be sheared without failure of the bond between the plated layer and said base metal. Although, in theory, a nickel "strike" or "flash" coating should work about the same as chromium, due to the evolution of hydrogen of the cathode during plating, yet such a nickel "strike" coating proves to be inferior to even a regularly-deposited nickel coating.

A series of molybdenum strips were plated as test specimens to demonstrate the superior adherence imparted by my special process, as follows:

Test specimen:
- #1—Nickel plated directly onto molybdenum.
- #2—Copper plated directly onto molybdenum.
- #3—Nickel strike plus nickel plate on molybdenum.
- #4—Nickel strike plus copper plate on molybdenum.
- #5—Chromium strike plus nickel plate on molybdenum.
- #6—Chromium strike plus copper plate on molybdenum.

Specimens #2, #3 and #4 all showed blistering and signs of very poor adherences immediately upon taken out of the plating bath. Specimen #1 looked good when first taken out of the bath, but upon the bend test the coating was easily stripped or peeled from the molybdenum. Specimens #5 and #6 looked good and did not show signs of failure upon bending. It was actually found that the plated coating stood up without peeling, even upon shearing of the molybdenum.

It has, therefore, been found that a chromium "strike" or "flash" coating on the refractory metals molybdenum and, tungsten, and alloys with high percentages of such metals, the oxides of which form and volatilize at relatively low temperatures, gives maximum bond strength and permits the subsequent electroplating of other metals thereon. Although I specify chromium as the initial coating or strike, yet theoretically any plating bath of low efficiency, that is, where hydrogen acts as a reducing medium to clean up light surface oxides, and where the crystals of the electrodeposit act as a continuation of crystals of the refractory metal base, the same high bond strength should be obtained. However, this has not been found true of some other metals, including nickel.

I have found such a method useful in preventing or delaying oxidation of such refractory metals which have low temperatures of oxidation of parts exposed to high temperatures during use, such as those for gas turbines, rocket liners, ram jets, etc. Such a protection of molybdenum and other metal having similar refractory and oxidation characteristics, should not be confused with the protection of parts formed of iron or steel. It is well known that ferrous material of that character does not form volatile oxides, nor is it difficult to produce firmly adhering electroplating thereon, as in the case of metals having the characteristics under consideration.

Prior to my invention, chromium, nickel, platinum and other metal coatings had been applied to molybdenum in various ways, such as by electroplating, spraying or dipping, but with very poor results. In the case of chromium, even a slight crack in the coating caused failures within a few hours and exposed the base metal to high temperature oxidation. No chromium coating process is known which results in a plate thicker than .00002 inch and which is free of stress and cracks, or free of stress or cracks. See "Chromium Plating" by Dr. George Dubpernell, beginning on p. 589, vol. 80, "Transactions of the Electrochemical Society," 1941, and particularly pages 606–7.

In the cases of nickel, platinum and other members of the nickel and platinum groups, the affinity of these metals for molybdenum is such that the protection lasts only until the coating is absorbed. For instance, a three mil. (.003") plate of nickel lasted only three hours before volatization began in accordance with an actual experiment. The same thickness of nickel on a preliminary plate of chromium of about .0001" in thickness lasted for 24 hours. With a 5 mil. nickel plate on the same thickness of chromium plating, the test piece lasted 400 hours at 1000° C. without other protection against oxidation.

The foregoing tests show that such a preliminary coating of chromium acts not only to form a bond between the base metal and the final electroplating, but also prevents the rapid absorption of the final plating, of nickel or the like, by the molybdenum or the like. The chromium having a coefficient of expansion about midway between those of molybdenum and nickel, seems to behave in much the same manner as the intermediate glass in a graded glass seal.

Now referring to the drawing in detail, there is shown in Figure 1 an article such, for example, as a plate 11 formed of molybdenum or other metal having similar oxidation characteristics, such as tungsten or molybdenum-tungsten alloy. The surface of this article is first coated with a strike film or barrier coating 12 of chromium. Such a film, to perform the desired function, should be only about .00002" in thickness so as to be free of stress and cracks or free of stress or cracks. On this film, is in turn, plated the real protective coating, such as electroplated nickel 13 or metal of the same group. This may be as thick as desired in accordance with the service intended, examples being from .003" to .004" in thickness. That is, it may be 150 or more times the thickness of the "strike" coating 12, which serves to bond it to the base metal 11, as well as preventing it from diffusing into said base metal when highly heated. Although such an article may be used without further treatment, it is desirable to heat it sufficiently so that the electroplating coating is further consolidated upon the article, whereupon the formation of blisters is avoided if the article is subsequently quickly heated to temperatures as high as 1000° C.

Referring now to the embodiment of my invention illustrated in Figures 2 and 3, there is shown a glass furnace 14 containing a quantity of glass 15 which may be initially melted by an oil burner 16. The furnace is in the form of a closed chamber and the pressure created above the surface of the molten glass tends to assist gravity and cause said glass to flow through the aperture or outlet orifice 17' in the form of a stream 18' to apparatus using such molten glass, reference being made to the Richardson et al. Patent No. 2,116,450, dated May 3, 1938.

After the glass has become molten, it may be kept in that state by passing electric current therethrough between electrodes 17 and 18 from a source of power (not shown).

Each electrode preferably comprises, as shown in Figure 3, an enlarged head 19 threadably or otherwise secured to a rod 21, desirably formed of high melting point metal, such as molybdenum or tungsten. Each rod 21 has its outer end passed through a sealing plug 23 in the upper wall 22 of the furnace, being held at the desired elevation by means of a set screw 24 threadably connected to a supporting bracket 25. In order to protect the rods 21 against undesired oxidation, I applied a "strike" plating of chromium thereto, as indicated at 26, and plated thereover a thicker coating of nickel or the like 27, as in the embodiment of Figure 1. Also, as in said first embodiment, the chromium coating is desirably only about .00002 inch thick, while the nickel plating may be considerably thicker, say about .004 inch thick.

In order to protect the nickel plating from the corrosive and dissolving action of the molten glass 15, I desirably apply over the lower part of each rod 21, a tube 28 of platinum of such a size that it will only fit thereover when the rod is considerably colder than the platinum. After hot applying the platinum tube 28, and both elements later reaching the same temperature, the tube of platinum is shrunk onto said plated rod 21. Each tube of platinum, when in place on its rod, extends down below the normal level of the molten glass 15, preferably to the top of the head 19, so that all of the nickel is protected against solution in the glass, and the glass at the same time is protected from discoloration by nickel being dissolved therein.

The combined chromium and nickel plating above the top of the platinum tube prevents the rod from undesired oxidation, not only in the furnace 14, but also in the air above the top wall 22 of the furnace.

Referring now to the embodiment of my invention illustrated in Figures 4 and 5, there is shown a high-pressure gaseous discharge lamp 29, comprising an envelope formed of material such as quartz and capable of withstanding high operating temperatures. A pair of oppositely-disposed refractory metal electrodes 31 and 32, formed of tungsten or the like, are secured to the leading in and supporting conductors 33 and 34, respectively, by refractory metal fastening collars 35 and 36. Each collar may be secured to its leading-in conductor and electrode in a suitable manner, as by a threaded connection, set screws, or by welding.

As is customary in the art, following exhaust of the lamp at the tip 37, it is filled with a small quantity of inert gas, such as neon, argon, or mixture thereof, at a pressure of about 50 mm. to facilitate the initiation of a discharge, and a small quantity of vaporizable material, such as mercury 38 is inserted. Said vaporizable material supports the discharge once the lamp reaches stabilized operating temperature ranging from about 500° C. to 700° C., at which time it is completely vaporized and at a pressure ranging between 5 and 10 atmospheres. Such a lamp thus provides a high-intensity light source and may have a power input of 7.5 kw. For this reason, the leading-in and supporting conductors necessarily carry comparatively high current and accordingly are of relatively large cross-section area.

The leading-in conductors of such a lamp may thus be approximately 1/4" in diameter and formed of molybdenum or tungsten. For the purpose of forming an hermetic seal between each leading-in conductor and the quartz envelope, the seal is first formed as a preliminary assembly, including graded seals 39 and 41 which are finally shrunk over the leads 33 and 34 and connected to the outer ends thereof by means of glass beads 42 and 43, having a coefficient of expansion approximating that of the leads 33 and 34, as described in the Freeman et al. application, Serial No. 109,902, filed August 12, 1949.

In order to prevent undesirable oxidation of these leads 33 and 34 during the shrinking operation and connection with the beads 42 and 43, as well as to insure a better union, said leads are desirably first coated with a chromium "strike" plating 40 and then with a nickel plating 50, as in the preceding embodiment. This is done after the leads 33 and 34 are not only formed but provided with threads 44 and 45 at their ends, if such threads are to be used, for connection to conductors leading to a source of power (not shown). This means that the heating, necessary to effect such a union between the leads and the beads, does not reduce the outer diameter of the threaded ends of said leads by oxidation and vaporization, as would otherwise occur. After the operation of sealing the leads to the beads, the end portions if threaded, or which project beyond the beads, are advantageously copper plated as indicated at **53**, to insure good electrical contact between them and the conductors from the power supply.

Referring now to the embodiment of my invention illustrated in Figures 6 and 7, there is shown an electron discharge device **46**, of the type designated as a triode, with a glass or other ceramic bowl or envelope portion **47**. The portion **47** also constitutes the base of the device and for which purpose it may be equipped with appropriate prongs **48**, projecting from the bottom thereof, for the conduction of power to the electrodes within the envelope. At the upper rim of the bowl **47**, there is sealed a metallic cylindrical dome-like anode portion **49** which, with the bowl **47**, constitutes a closed and evacuated envelope. Said portion **49** is advantageously made of copper, thereby having the advantage of that metal for ease in shaping the anode and for the high electrical conductivity afforded thereby.

Disposed coaxially with the anode portion **49**, is a grid **51**, formed of wire such as shown in Figure 7. Within the grid and anode, is a cathode assembly **52**, shown as comprising a circular series of substantially parallel strands, thereby providing a filamentary cathode of considerable area for copious electron emission. As this filamentary cathode is extensive, and during operation heated to about 1800° C., it tends to heat the grid and cause undesired thermionic emission therefrom. It is, therefore, desired to use my invention in forming the grid wire, which may be of molybdenum or tungsten, with first a "strike" plating of chromium **54** and then a plating of platinum **55** thereover, said platinum being effective for repressing the emission, and the chromium serving, as in the preceding embodiments, to form a barrier layer preventing interdiffusion of the coating and metal of the wire, as well as to effectively unite the inner surface of said platinum to the outer surface of the base which, in this case, is a wire of molybdenum. Also, as in the preceding embodiment, the chromium coating need only be very thin, about .00002" in thickness, while the platinum coating may be considerably thicker like the nickel coating was in the preceding embodiment.

Although preferred embodiments of my invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims. For example, although I specify .00002" as the preferred thickness of the chromium plating, subsequent improvements in the plating art may change the optimum thickness.

I claim:

1. In a discharge device, lead-in conductors formed of a metal selected from the group consisting of molybdenum and tungsten, a film of plated chromium, about .00002" thick thereon, said film having nickel plated thereon, united to the envelope of said device by a graded seal, terminating bead of glass, and copper plated on that portion of said lead external of said bead.

2. The method of protecting against oxidation at high temperatures, articles constructed of metal of the group consisting of molybdenum, tungsten, molybdenum-base alloys and tungsten-base alloys, the oxides of which form and volatilize at relatively low temperatures, comprising electroplating such articles with a film of chromium about .00002" in thickness, and then electroplating metal of that section of group VIII of the periodic table consisting of platinum and metals of the nickel group on said film.

3. An article composed of metal of the group consisting of molybdenum, tungsten, molybdenum-base alloys and tungsten-base alloys, the oxides of which form and volatilize at relatively low temperatures, a film of plated chromium about .00002" thick, thereon, and said film having plated thereon metal of that section of group VIII of the periodic table consisting of platinum and metals of the nickel group.

4. An article composed of molybdenum, a film of plated chromium about .00002" thick thereon, and said film having plated thereon a thicker coating of nickel.

5. An article composed of molybdenum, a film of plated chromium about .00002" thick thereon, and said film having platinum plated thereon.

6. An article composed of tungsten, a film of plated chromium about .00002" thick thereon, and said film having plated thereon a thicker coating of nickel.

7. An article composed of tungsten, a film of plated chromium about .00002" thick thereon, and said film having platinum plated thereon.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,314,603	Mott	Sept. 2, 1919
1,578,254	Bennett	Mar. 30, 1926
1,759,099	Dake	May 20, 1930
1,840,130	Rashevsky	Jan. 5, 1932
2,244,267	Slayter et al.	June 3, 1941
2,446,277	Gordon	Aug. 3, 1948
2,497,111	Williams	Feb. 14, 1950
2,555,372	Ramage	June 5, 1951