June 5, 1951

J. H. RAMAGE
METHOD OF COATING REFRACTORY
READILY-OXIDIZABLE METALS
Filed Oct. 2, 1944

2,555,372

Fig. 1.

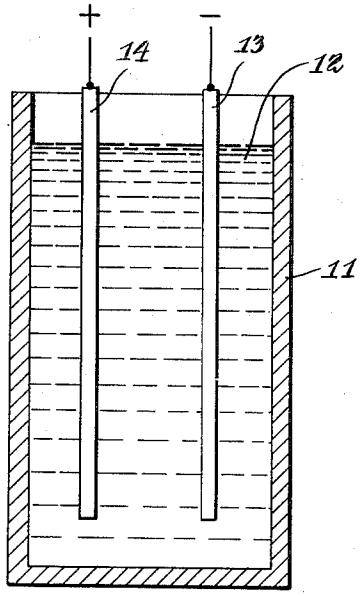


Fig. 2.

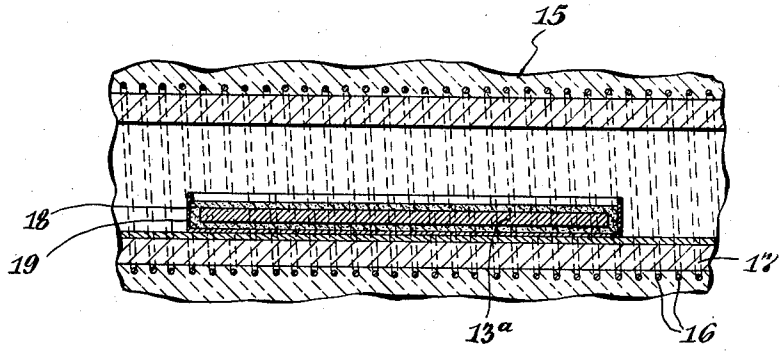
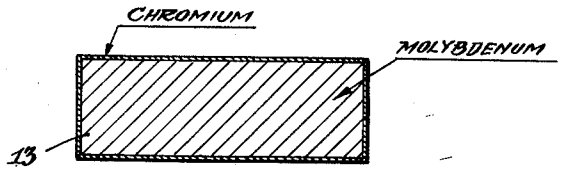


Fig. 3.



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Patented June 5, 1951

2,555,372

UNITED STATES PATENT OFFICE

2,555,372

METHOD OF COATING REFRACTORY READILY OXIDIZABLE METALS

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Application October 2, 1944, Serial No. 556,810

3 Claims. (Cl. 204—38)

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This invention relates to readily-oxidizable refractory metals protected against oxidation, and methods for accomplishing such a result.

The principal object of my invention, generally considered, is to produce articles constructed of refractory but readily-oxidizable metals, in which oxidation thereof is prevented by a coating or plating of chromium.

Another object of my invention is to protect articles which are constructed of refractory, but readily-oxidizable metal such as molybdenum, tungsten, tantalum, zirconium, thorium, uranium and other similar metals and alloys thereof, by electroplating with chromium and then heat-treating in a hydrogen atmosphere at a temperature sufficient to cause the plating to form a chromium-molybdenum eutectic or such between the chromium and metal on which it is plated, which provides for firm adherence between the chromium and the refractory metal, whereby the latter is protected from oxidation up to 1500° C., and possibly as high as the melting point of the chromium-refractory-metal eutectic, that is, about 1725° C. if the refractory metal is molybdenum.

A further object of my invention is to protect such metals and alloys as above mentioned by chromizing the surfaces thereof, that is, packing them in powdered chromium or a mixture of powdered chromium and chromic oxide, and heating for several hours in hydrogen at a temperature of about 1100° C.

Still further objects of my invention are articles of refractory readily-oxidizable metals, the surfaces of which are protected against oxidation by firmly adherent coatings of chromium.

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

Referring to the drawing:

Fig. 1 is a vertical sectional view of a plating bath which may be used for coating articles with chromium.

Fig. 2 is a vertical sectional view of a furnace in which articles so plated may be heat-treated, or in which articles may be chromized.

Fig. 3 is a transverse sectional view of an article of molybdenum coated or plated with chromium.

There are a number of metals such as molybdenum, tungsten, tantalum, zirconium, thorium, uranium, and other similar metals and alloys thereof, and particularly molybdenum, which have very good and useful properties as to strength, hardness, and relatively-high melting points, but which are susceptible to oxidation at

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moderately high temperatures. Molybdenum, for example, starts to oxidize at about 400° C. and at about 700° C. the oxide is volatile, so that at any temperature above that mentioned, it not only oxidizes when exposed to an oxidizing atmosphere, but the oxide formed volatilizes away very quickly and at an increasing rate as the temperature is increased.

I have found a method to prevent this oxidation and volatilization and thus make it possible to utilize the high temperature properties of a metal such as molybdenum, even in an oxidizing atmosphere. My method consists in coating the surface of the molybdenum with chromium, either by plating and heat treating, or chromizing by heat treating the article while covered with powdered chromium or a mixture of powdered chromium and chromic oxide, as distinguished from using therewith a lower melting-point alloying metal or metals. The heat treating of the plated molybdenum is in hydrogen or other reducing or protective atmosphere, preferably at about 1100° C. for from about 15 minutes to ½ hour. However, the chromizing of molybdenum parts requires several hours in hydrogen or other reducing or protective atmosphere at about 1100° C.

I have found that molybdenum, so coated or plated with chromium in this manner, resisted oxidation and volatilization even in an oxidizing atmosphere up to about 1500° C. It is believed that such resistance extends up to the melting point of the chromium-molybdenum eutectic, that is, up to about 1725° C. The thickness of the coating in the instance referred to was about 1½ mils, but such thickness may be varied depending on the uses to which the article is to be put and the temperature to which it is to be subjected.

On heating, the chromium migrates into the molybdenum at such a rate that it will be absorbed completely in about 25 hours at 1630° C. It is conceivable, therefore, that the effectiveness of chromium as a protector may be impaired if the coated article is held at a temperature as high as 1630° C. for about 50 hours or more. However, I have found that operating as low as 1500° C., the chromium-plated molybdenum would still effectively resist oxidation for several thousand hours and at lower temperatures almost indefinitely. Although the surfaces do tarnish or darken a little, probably due to a superficial coating of some oxide of chromium, such coating adheres very tightly to the metal therebeneath and stops further oxidation.

Referring to the drawing, like parts being des-

ignated by like reference characters, a container 11 is shown in Fig. 1 holding an electroplating bath 12 of a chromium compound such as is used conventionally for chromium plating. The article to be plated, designated 13, is made the cathode and in this instance, is formed of molybdenum. The anode 14 may be made of chromium or carbon.

After electroplating the article 13, or as much thereof as desired, with chromium to the required thickness, the plated article is covered with powdered chromium or a mixture of at least 50% chromium powder and powdered chromic oxide, and transferred to an electric furnace 15 where it is heated in a hydrogen or other reducing or protective atmosphere, as by means of an electrical resistance element 16 surrounding a tube 17 of alumina, to about 1100° C. for from about 15 to 30 minutes.

As an alternative, an article 13a of molybdenum may be covered with powdered chromium 18, or a mixture of at least 50% of such powdered chromium and powdered chromic oxide, and placed in a boat 19 of alumina or other inert refractory material and subjected to heating in a hydrogen or other reducing atmosphere for several hours at about 1100° C. This causes chromium to be deposited on the surface of the molybdenum article, the thickness of the coating depending on the length and temperature of treatment.

From the foregoing, it will be seen that I have provided for the protection of molybdenum and other similar materials against oxidation, whereby such may be used in oxidizing atmospheres up to relatively high temperatures. Although specific methods for treating molybdenum only has been disclosed, it will be understood that similar methods may be used for applying protective coatings to molybdenum alloys, tungsten and alloys, and tantalum and alloys with equal facility. It is also believed that such coatings can be applied to other similar metals such as zirconium, thorium, uranium and other easily oxidizable but refractory metals and alloys thereof.

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. The term "hydrogen" or "hydrogen atmosphere" in said claims includes such in which hydrogen is a diluted active ingredient and the word "metal" includes alloys of metals.

I claim:

1. The method of protecting against oxidation at high temperatures, articles constructed of refractory but readily-oxidizable metals and alloys thereof comprising electroplating them with chromium, covering said plated articles with powdered chromium, and heating in hydrogen at a temperature of about 1100° C., to obtain a firmly-adherent coating of chromium thereon.

2. The method of protecting molybdenum articles against oxidation at high temperatures, comprising electroplating them with chromium, covering said plated articles with powdered chromium, and heating in hydrogen at a temperature of about 1100° C., to obtain a firmly-adherent coating of chromium thereon.

3. The method of protecting against oxidation at high temperatures, articles constructed of metal selected from the group consisting of molybdenum, tungsten, tantalum, zirconium, thorium, uranium, and refractory but readily oxidizable alloys thereof, comprising electroplating them with chromium, covering said plated articles with powdered chromium, and heating in hydrogen at a temperature of about 1100° C., to obtain a firmly-adherent coating of chromium thereon.

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