Patented June 20, 1950 2,512,455

UNITED STATES PATENT OFFICE

2,512,455

COPPER-TITANIUM COATING AND BONDING PROCESS

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No Drawing. Application December 31, 1945, Serial No. 638,586

4 Claims. (Cl. 113—112)

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The present invention relates to an improvement on the process described and claimed in my U. S. Patent 2,351,798 of June 20, 1944.

The process of said prior patent has been proven to be highly useful when it is desired to form extremely thin layers of the alloy of copper and titanium (or containing copper and titanium) upon the surface. However, the said process is less satisfactory when it is desired to form a relatively thick layer of copper titanium alloy on the surface, because while an alloy containing about 72% of copper and 28% of titanium melts at a relatively low temperature, successive additions of titanium to this alloy very greatly raise the melting point of said alloy, until a condition is reached in which the copper titanium alloy contains much over 30% of titanium, in which event the said alloy would have a higher melting point than copper alone. In the specific example in said prior patent (page 2, first column, beginning line 22) the top of the copper article to be treated had an area of 100 square inches, and the amount of titanium hydride applied to this 100 square inches was 1 ounce. An ounce of fine powder uniformly spread over 100 square inches of surface area will only produce a very thin layer or film of material. The amount of metallic titanium produced by the reduction of 1 ounce of titanium hydride can readily and rapidly wholly alloy with the copper surface, to produce the low-melting point alloy. However, if much larger quantities of this titanium hydrid were spread upon this 100 square inches, only the contacting particles of the titanium could so alloy with the copper in the surface of the article, and the rest of the titanium, as produced, would combine with this low-melting point alloy containing about 28 or 30 parts of titanium to 70 to 72 parts of copper, thereby producing a titanium rich alloy which would have a much higher melting point than 878° C., the temperature given for conducting a coating operation in said patent.

Where it is desired to form a thicker coating of the copper titanium alloy upon the said base, it is advisable to modify the process, using a mixture of metallic copper and titanium hydride, both in a very finely divided state, so that as the titanium hydride becomes decomposed by the heat, forming elementary titanium, this titanium will combine with the finely powdered copper also present, to give the low melting alloy of copper and titanium from all of the titanium hydride so added. In this manner it is readily possible to form a thick coating of the low melting

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point eutectic alloy, spread entirely over the surface of the copper article, or over any desired portion thereof.

In the modification as above described i. e. for producing a relatively thick coating layer, I preferably use titanium hydride and metallic copper both in a very finely pulverized condition, for example, passing a 325 mesh screen or a 400 mesh screen. I preferably apply the said mixture of titanium hydride and copper to the surface to be coated, in the form of a thin paste, using a suitable liquid such as ethyl alcohol as a vehicle. The said paste becomes a dry coating before the metal article has been heated to a high temperature, due to the evaporation of the alcohol, and the process is preferably carried out by placing the article of copper or copper rich alloy or other article such as iron or steel coated with copper or copper rich alloy, and carrying the surface coating of paste of titanium hydride and metallic copper and vehicle into a muffle, closing up the said muffle hermetically, and filling with hydrogen or argon or drawing a high vacuum in said muffle. Then the muffle and contents are heated, as in the prior patent, to a temperature above the decomposing temperature of the titanium hydride, namely, about 872° C., and preferably to a temperature around 900 to 1000° C. The temperature, of course, should not be high enough to melt or deform the copper article or the copper alloy article and for most purposes a temperature of around 900 to 925° C. in the metal article itself, is satisfactory. This condition is maintained for a short time such as 15 to 30 minutes, during which time the titanium hydride becomes decomposed, the hydrogen evolved being of value in reducing any copper oxide which may be present, and the low melting alloy of copper and titanium will completely flow over the desired portion of the surface of the copper alloy article or copper article. The muffle and contents are preferably then allowed to cool substantially, while still under vacuum, to prevent oxidation of the surface coating. Such copper titanium alloy may alloy to some extent with the copper or copper alloy of the article itself, forming a very intimate bond therewith.

It will be understood that instead of the use of a vacuum, it would be possible to employ a neutral atmosphere or a reducing atmosphere such as hydrogen. A suitable neutral atmosphere would be argon.

The coating produced on the article is of a silvery appearance, is very hard, resisting abra-

sion and is also somewhat resistant to corrosion by strong acid.

In a modification, of the process in which still harder surfaces are desired, I may mix with the titanium hydride powder, a powdered tungsten carbide or titanium carbide, these being mixed with the whole of the titanium hydride or with the top portion only. If the desired layer including copper titanium alloys with the addition of the carbide, is to be relatively thick (i. e. if substantially more than one ounce of the titanium hydride is to be spread upon an area of 100 square inches of surface of the copper surface), I also use metallic copper in the said mixture or mixtures. These mixtures are coated upon the copper article or copper surface article in the same manner as above described, namely, the fine powders are mixed with alcohol or similar vehicle. The heating operation can be conducted as described above.

In this manner there is produced a coating of the low melting copper titanium alloy, on the surface of the copper article, which coating also contains, intimately mixed therewith or intimately mixed with the surface portions thereof, minute particles of titanium carbide or tungsten carbide. Such articles have an extremely hard surface, resistant to abrasion, resistant to corrosion even by strong acids.

In another modification I use metallic chromium, metallic nickel together with titanium hydride, and (unless a very thin coating is desired) copper powder.

The materials were all in the form of very fine powders, passing a 350 mesh screen, and the material was wetted with alcohol to form a thin paste, applied in the above manner to the copper surface, which was then heat treated in the manner above described. The particular advantage of this mixture is that it produces a surface which is strongly resistant to corrosion by acid.

The further development of this process indicated that copper-titanium eutectic alloy can be successfully used for brazing or uniting together copper articles. In this case, the copper surfaces to be joined, or at least one of them, are painted with a mixture of titanium hydride and copper powder in the eutectic proportion so as to give a sufficient amount of this alloy. Then the articles are joined by laying one part upon the other and heated in an atmosphere of hydrogen until the powdered mixture between the surfaces to be joined is liquefied and wets both surfaces. If heating is continued then part of the titanium will diffuse from the molten layer into the solid copper. In other words, it ceases to be a eutectic alloy and it freezes there in spite of the fact that the temperature in the furnace remains constant. In other words, I place between copper surfaces a powdered mixture which forms a limited eutectic alloy. Then as titanium diffuses away from that molten layer into solid copper, the melting point of the molten layer rises. It freezes and thereby joins the two copper articles together. Clamps may be used to press the two articles together.

An important characteristic of welds made by the above process is that after making the weld and cooling the welded article, the article can be heated to a temperature much higher than the temperature at which the joining of the pieces was effected, without the pieces forming the joint dropping apart. The initial formation of the eutectic alloy from titanium hydrid and copper can be effected at about 872° C. It is my belief

that the molten eutectic alloy, at this stage, contains considerable free hydrogen, perhaps in solution which is squeezed out on cooling the joint. The formed joint, after cooling, can be heated even to near 1000° C., without refusion of the bond. This is sometimes an advantage.

Another step in this development was to take advantage of the property of titanium-copper eutectic alloy in wetting copper surfaces by dipping a copper article into a bath of copper-titanium eutectic alloy. When the copper article immersed, becomes heated to a temperature above the melting point of the eutectic alloy, that is in the order of 900° C. or thereabouts, it remains covered with a thin layer of copper-titanium alloy at the instant of withdrawing the article from the bath. In other words, the copper article can then be covered with a much harder surface layer of titanium-copper or titanium-copper containing other materials in suspension or solution.

For example, if copper wire is drawn through a molten bath of titanium-copper alloy held at 900° C. or thereabouts, it comes out covered with a protective layer of copper-titanium having much greater hardness and greater corrosion resistance than pure copper. In this way it is possible to produce copper cables and copper wires which will resist the oxidation at higher temperature or attack by acids, acid fumes, etc., much better than pure copper.

I give the following as illustrative of proportions that have been found to be very suitable for use in this invention, but I do not restrict the invention to these precise proportions and reserve the right to cover the use of proportions somewhat beyond these figures.

Titanium hydride	28 to 30
Metallic copper	70 to 72
Titanium carbide	
Tungsten carbide	
Metallic nickel	
Metallic chromium	

It is well known that commercial titanium hydride often contains some free titanium (metal). Such a commercial product is wholly satisfactory for use in the present invention.

In the above examples, I have used alcohol as the vehicle with which to form the paste. Other suitable vehicles are easily volatile liquids which do not leave carbon when they evaporate, e. g. water, carbon tetrachloride, etc.

It is to be understood that the heating referred to above can be applied in a suitable manner, e. g. the article with its coating agent applied (the composition of which can be varied as indicated above, depending upon the result to be accomplished) can be placed in a muffle or closable container, preferably in an atmosphere of hydrogen (or argon or in a vacuum) and heat can be applied. As examples of suitable heating methods, the passage of alternating or direct current through the article itself, modified resistance welding process, high frequency electric current, induction heating, atomic hydrogen torch and electric arc, being mentioned as suitable.

When using the electric arc, oxy-hydrogen torch, atomic hydrogen torch, etc., and wherever a stream of hydrogen is directed to the pulverulent titanium hydride, copper and/or other powdery materials it is advisable to also supply thereto an additional flux (e. g. calcined borax) or grease or paraffin. This will assist in preventing the hydrogen current from blowing the

powders away from the place where they are wanted.

I claim:

1. A process of producing a coating on a metal article, the surface portion at least of which is composed of a metal containing copper as a substantial component, which process comprises applying to at least a part of the surface of such article a coating of very finely divided material which contains metallic copper and titanium hydride, both in the form of fine powders, heating such article in the absence of substantial amounts of free oxygen, to a temperature above 872° C., but substantially below the melting point of pure copper, whereby the titanium hydride decomposes with liberation of hydrogen and a low-melting point alloy containing copper and titanium is formed, which alloy, while molten, flows over at least a portion of the surface of such article to coat the same, and thereafter cooling the said article to well below 872° C., while still under non-oxidizing conditions, whereby a coating of an alloy containing copper and titanium, of any desired thickness can be produced on said article.

2. A process as claimed in claim 1, in which the coating composition containing powdered titanium hydride and metallic copper, also contains a substance selected from the group consisting of titanium carbide and tungsten carbide.

3. A process for forming a thick metal layer consisting essentially of titanium and copper upon the surface of a metal article comprising copper at said surface which comprises applying upon said surface a finely divided powder consisting essentially of titanium hydride and copper, then heating the article in a non-oxidizing atmosphere to a temperature between about 872° C. and the melting point of copper to form a low melting alloy of copper and titanium upon said surface and cause said alloy in molten state to

spread over said surface, and thereafter cooling the article substantially while under a non-oxidizing atmosphere.

4. A process for joining preformed metal articles comprising essentially copper at the surfaces to be joined which comprises assembling said articles together with a finely divided powder between said surfaces consisting essentially of titanium hydride and copper in proportions to form a eutectic alloy of titanium and copper, heating the assembly in a non-oxidizing atmosphere to a temperature of about 872° C. to form a molten layer of a low melting point alloy between said surfaces and cause said molten layer to wet said surfaces, and continuing the heating substantially at said temperature until the molten layer freezes by change in composition due to diffusion to form a higher melting point alloy, and cooling.

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