Patented Apr. 6, 1954

2,674,542

UNITED STATES PATENT OFFICE

2,674,542

METHOD FOR PRODUCING HARD SURFACED TITANIUM

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No Drawing. Application February 6, 1951, Serial No. 209,703

3 Claims. (Cl. 117—22)

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This invention relate to a method for forming a hard external surface layer upon articles of titanium and to the articles thus produced.

Titanium metal has recently become available in ductile massive form, such as ingots, sheets, rods, etc., suitable for fabrication to produce a variety of articles formerly made of steel. One of the many advantages of titanium is its relatively light weight. It may be alloyed with small amounts of other metals to improve certain physical properties, such as tensile strength, but so far as I am aware no satisfactory method has been available for imparting great hardness to its surface comparable to the hardness of the surface of case hardened steel.

The present invention contemplates a method for forming a hard surface layer upon articles of titanium or titanium containing small amounts of the usual alloying elements. I have discovered that certain titanium or zirconium alloys, such as the eutectic alloy of titanium and copper in molten condition, readily wet and spread over the surface of titanium. Alloys of titanium or zirconium with cobalt or nickel or silver and either with or without copper act in a similar manner. Consequently, such alloys in molten condition may be employed as a carrier for applying and spreading finely divided particles of a hard metal compound upon the surface of articles of titanium. The carrier alloy may then be caused to serve as a binder for holding the hard particles together in the form of a hard external surface layer. Thus, after the molten carrier alloy containing the hard particles has been applied to a selected portion of the surface of the titanium article, the article may be heated to cause a component of the carrier alloy to diffuse selectively into the body of the titanium article thereby reducing the amount of such component in the carrier alloy and causing the hard particles to be drawn close together by capillary action. The resulting hard surface layer will consist of the finely divided particles of the metal compound coated and held together by a minimum amount of the alloy binder, the body of the titanium article being separated from the hard external surface layer by a joining layer of an alloy of titanium and the diffused component.

As illustrative of hard metal compounds which may be employed in the practice of the invention, I may mention tungsten carbide, titanium carbide, chromium carbide, tantalum carbide, zirconium carbide, the nitrides of the corresponding metals, etc. It will be apparent that a variety of other hard materials may be employed, the only requirements being that they possess the desired hardness, are thermally stable under the conditions employed in the practice of the invention

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and are capable of being effectively wetted by the carrier alloy employed. These hard materials are employed preferably in a very finely divided condition, for example passing a 325 mesh screen or a 400 mesh screen, but particles of the order of a coarse powder may be employed where smoothness of the exterior surface of the final article is not important.

The carrier alloy may be preformed but, preferably, is formed in situ by reacting its finely divided components. Thus, a finely divided powder containing the thermally stable finely divided hard particles together with finely divided titanium metal or titanum hydride, or zirconium metal or zirconium hydride and finely divided copper, cobalt, nickel, silver or mixtures thereof, may be applied to the surface of the titanium article and the article heated in an inert atmosphere, such as vacuum or argon, until the carrier alloy is formed and becomes molten and spreads over the selected surface of the article. If titanium hydride or zirconium hydride is employed, it is decomposed with evolution of hydrogen which serves to reduce certain oxides which may be present, such as copper oxide or nickel oxide.

In the practice of the invention, the finely divided particles of the hard metal compound and the finely divided components of the carrier alloy are intimately mixed in desired proportions. I apply a desired amount of this mixture to the selected portion of the surface of the titanium article, preferably, in the form of a paint-like mass using a suitable liquid, such as ethyl alcohol or methyl alcohol, as a vehicle which may contain a small amount of a soluble adhesive, such as ethyl cellosolve, which is volatile at moderately high temperature. The article then is placed in a suitable furnace and heated in an inert atmosphere, such as vacuum or a monatomic gas such as helium or argon, to a temperature slightly above the melting temperature of the carrier alloy until the latter becomes molten and spreads over the selected surface of the article. The required temperature will vary with the composition of the carrier alloy. The melting temperature of the eutectic alloy of titanium and copper is 872° C. and when this is the carrier alloy the temperature used may be 900° C. to 1000° C. When the carrier alloy is essentially titanium and cobalt or nickel with or without copper, a higher temperature, such as about 1100° C., usually is required. In any case, the temperature should not be high enough to melt or deform the titanium article.

The relative proportions by weight of the hard metal compound and the carrier alloy used will vary somewhat with the composition of each. The amount of carrier alloy should be sufficient

to wet and effectively coat the hard particles and provide a molten mass which spreads readily over the selected surface of the article and should be substantially in excess of one ounce for each 100 square inches of such surface. The amount of carrier alloy should be substantially in excess of the amount thereof required merely as a binder for the hard particles. In accordance with the invention, any desired portion of this excess is subsequently removed. One method for accomplishing this removal, but not my preferred method, is dissolution with a solvent therefor, such as an acid, which is non-solvent for the hard metal compound.

Another method for reducing the amount of carrier alloy directly associated with the hard metal particles in the surface layer of the treated article, and which is my presently preferred method, is to subject the article treated as previously described to a subsequent heat treatment in an inert atmosphere, such as vacuum or a monatomic gas, to cause at least one of the components of the carrier alloy to diffuse into the principal body of the article thereby forming a joining layer of an alloy of such component or components with the metal of that body separating that body and the hard external surface layer. In this manner, the amount of carrier alloy may be reduced any desired amount and its composition may be changed to that desired depending upon its initial composition. Thus, if the carrier alloy initially is an alloy of titanium, cobalt and copper, this subsequent heat treatment may be conducted to cause a substantial amount of the copper and a much smaller amount of the cobalt to diffuse into the body of the titanium article to leave an alloy associated with the hard metal particles and serving as a binder therefor which is essentially an alloy of titanium and cobalt. In such case, the joining layer separating the body of the article and the hard external surface layer is essentially an alloy of titanium and copper containing a small amount of cobalt.

The temperature used in this subsequent heat treatment may be above or below the melting temperature of the carrier alloy as will be understood by the art. When the temperature used is above the melting point of the carrier alloy, the hard metal particles tend to be drawn together more compactly by the force of the capillary action. At a temperature of this order the time of heat treatment to accomplish a satisfactory reduction in the amount of carrier alloy associated with hard metal particles usually ranges between about two to four hours for small articles but a longer or shorter period of heat treatment may be used when desired. A satisfactory reduction in the amount of carrier alloy associated with the hard metal particles is indicated by a substantial change in its melting temperature, such as a change of about 50° C. The period of time required to obtain a given desired result will vary indirectly with the temperature used.

The invention is further illustrated by the following specific example.

A finely divided mixture of titanium hydride and copper containing titanium and copper substantially in the proportion of the eutectic alloy of these metals was prepared. A second finely divided mixture of particles of tungsten carbide and 15 per cent by weight of cobalt was prepared. These two mixtures were intimately mixed in the proportions of equal parts by weight. This powder was stirred into sufficient ethyl alcohol to make a paint-like mass which was applied to

one of the flat surfaces of a wafer or disc of titanium metal about one inch in diameter and about one eighth of an inch thick and originally weighing 6.8 grams. The thus prepared wafer was placed in a small electrically heated furnace which was heated to about 200° C. while subjected to vacuum to remove air and moisture. The vacuum then was disconnected and argon was introduced into the furnace to establish a pressure slightly greater than atmospheric pressure and the temperature of the furnace was raised rapidly to 1100° C. After about 10 minutes, the carrier alloy of titanium, cobalt and copper containing the solid hard particles of tungsten carbide had become molten and wetted the entire flat surface of the wafer. The heating was continued for about one hour and fifty minutes and the furnace was allowed to cool to room temperature while filled with argon. The treated article was then removed and its flat surface was coated with a smooth silver like coating which could not be scratched with a file. The treated article weighed 7.5 grams.

I claim:

1. The method for forming a hard surface upon a selected portion of an article comprising essentially titanium which comprises applying to said portion a material capable of forming a molten alloy containing solid finely divided hard particles of a metal compound when heated to a temperature substantially below the melting temperature of said article, said alloy comprising titanium and a metal selected from the group consisting of copper, nickel, cobalt, silver and mixtures thereof, therafter heating said article in an inert atmosphere to cause a molten layer of said alloy containing said hard particles to spread over said selected portion, the amount of said molten alloy being substantially in excess of the amount required to coat said hard particles completely, thereafter heating the article above the melting temperature of said alloy but below the melting temperature of said article thereby causing said metal to diffuse from said layer into said article and draw said hard particles together more compactly by the force of capillary action, and then heating said article below the melting temperature of said article until a desired amount of said metal has diffused into said article, said hard particles of a metal compound being thermally stable at the temperature employed and being selected from the group consisting of metal carbides, metal nitrides and mixtures thereof.

2. The method as described by claim 1 wherein said metal comprises essentially copper and cobalt.

3. The method as described by claim 1 wherein said metal comprises essentially copper and nickel.

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