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# REACTED COATING OF TITANIUM

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9 Claims. (Cl. 117—114)

The present invention is a division of my appplication Serial No. 251,979, filed October 18, 1951.

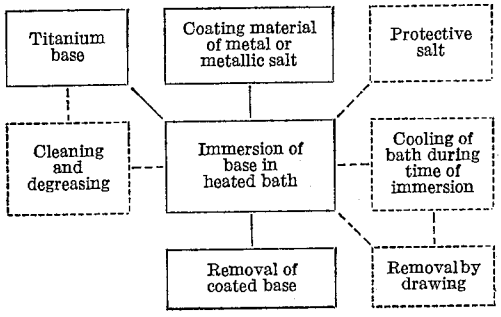
This invention relates to titanium and titanium base alloys, and contemplates materially enhancing the utility of these materials, particularly for high temperature service, by the use of coatings of other metals which bond themselves to the base metal by penetrating and alloying or combining therewith.

As structural materials, titanium and its alloys offer a unique combination of high tensile strength and low density, but their utilization for high temperature service has been handicapped by their susceptibility to corrosion by atmospheric gases under some service conditions. At elevated temperatures both oxygen and nitrogen migrate from the surface into the interior of bodies of titanium and titanium base alloys, embrittling the whole structure. Moreover, titanium cannot be soldered, and is difficult to draw, due to its tendency to "gall" or adhere strongly to drawing tools and dies.

The present invention comprises the discovery that coatings of aluminum, tin, copper, lead and other metals can be applied to a titanium base in such a way as to combine or alloy with the surface metal, thereby forming a permanently bonded protective and non-galling coating. A copper coating can be secured by dipping for from 5 to 35 seconds in fused cuprous chloride or an admixture thereof with other chlorides at a temperature of 650° C. to 700° C. Such coatings can be soldered. A lead coating which enables wire and deep drawing can be secured by immersing for a few minutes in a lead bath at 870° C. to 925° C., the bath being cooled to 350° C. to 650° C., before the coated titanium is removed. An adherent tin coating can be secured by immersing carefully cleaned titanium in molten tin at 780°–790° C. for one or two minutes.

The preferred coating metal is aluminum. The titanium body to be coated is first thoroughly cleaned, as by grit blasting, grinding or the like, degreased with carbon tetrachloride or the like, and is then immersed in a bath of molten aluminum, preferably at a temperature between about 725° C. and 900° C. At somewhat higher temperatures, say 1000° C., the molten aluminum attacks the titanium and forms a pasty sludge. A protective salt, such as potassium chloride, may be floated on the bath to minimize oxidation thereof.

A simplified flow diagram of the process is as follows, steps shown by dotted lines being alternatives in the step sequences shown by solid lines as indicated herein:






The time of immersion varies with the bath temperature. At 900° C., good coatings have been secured with times as short as 15 seconds and as long as 90 seconds, while at 725° C., the time range is from 1 to 8 minutes. A time of about 4 minutes is preferred. The coating secured by an immersion of 8 minutes is unnecessarily heavy, and some aluminum is lost by complete oxidation on subsequent exposure to high temperatures.

Specific examples of the practice of the invention are as follows:

Commercial titanium was rolled at a temperature of about 850° C. to a thickness of .030". Specimens cut from this sheet were cleaned by sand blasting and mechanical grinding, finally polishing on 600-grit paper, and degreasing in carbon tetrachloride. The specimens thus prepared were dipped in molten aluminum at a temperature of about 725° C., for times of 1, 2, 4 and 8 minutes. All specimens received an adherent coating of aluminum, the coating being about .002" thick except on the 8 minute dip specimens, on which it was thicker. The coated specimens along with control samples of uncoated sheet were then heated in air for 24 hours at 1050° C. The uncoated control samples were completely converted to titanium-dioxide, showing a weight gain of about 81 mg./sq. cm. The specimen which had been immersed for 1 minute showed a weight gain of about 18 mg./sq. cm., and for 1 minute showed a weight gain of about 18 mg./sq. cm., and was coated with a removable tan scale. The specimen which had been immersed for 2 minutes showed a weight gain somewhat over 20 mg./sq. cm., and was coated with a very adherent tan scale. The specimens immersed for 4 and 8 minutes showed weight gains of only about 9 mg./sq. sm., and were coated with very adherent gray scales. The surfaces of all specimens were substantially hardened but toward the center hardness decreased rapidly.

Other specimens, prepared and coated as above, were heated in air for 24 hours at 850° C., with even more satisfactory results. The uncoated control samples showed a weight gain of about 9 mg./sq. cm., while the aluminized specimens gained from .09 to 2.5 mg./sq. cm. The thickness of the aluminum oxide coating increased from about 2 mils to about 5 mils with increase in the immersion time. The oxide coating is relatively hard and is bonded to the titanium by a layer of about .5 mil thickness of an intermetallic compound having a hardness of about 250 Vickers—probably titanium-aluminum. This intermetallic layer shows plainly on micro-photographs of 100 magnification. The original hardness (210 Vickers) of the titanium within the intermetallic bonding layer remains substantially unchanged. Ductility is not materially altered, and aluminum clad titanium can be cold rolled to 50% reduction without spalling or flaking.

Aluminum coatings can also be applied with beneficial results to titanium alloys which are embrittled by gas absorption at elevated temperatures. For example, an alloy of 10% maganese, 5% molybdenum, 5% chromium, balance titanium, as rolled and vacuum annealed, showed a bend ductility of zero. After air exposure at 300° C. for 60 hours, the aluminum-coated alloy still had a bend ductility of zero-T, while the bend ductility of the uncoated sample was 4 T. After air exposure at 900° C. for 5 minutes, the bend ductility of the uncoated specimen was 11 T, while that of the coated specimen remained at zero T.

The invention thus enables the use of titanium and its alloys at service temperature substantially higher than has heretofore been deemed possible.

What is claimed is:

1. The method of bonding a coating of aluminum onto a titanium base comprising the steps of thoroughly clean-

ing the surface of the titanium, and immersing the cleaned titanium in a bath of molten aluminum at a temperature between 725° C. and 900° C. for a time between 15 seconds and 8 minutes.

2. The method of bonding a coating of aluminum onto a titanium base comprising the steps of thoroughly cleaning the surface of the titanium, and immersing the cleaned titanium in a bath of molten aluminum at a temperature of about 725° C. for a time between 1 minute and 8 minutes.

3. The method of bonding a coating of aluminum onto a titanium base comprising the steps of thoroughly cleaning the surface of the titanium, and immersing the cleaned titanium in a bath of molten aluminum at a temperature of about 900° C. for a time between 15 seconds and 90 seconds.

4. A method of drawing wire made of titanium and titanium-base alloys which comprises immersing said wire in a lead bath maintained at about 870° to 925° C. for an interval sufficient to form an adherent lead coating on said wire, cooling the so coated wire below about 650° C., and drawing the same through a die of smaller sectional dimensions than the so coated wire.

5. A method of drawing wire made of titanium and titanium-base alloys which comprises immersing said wire in a lead bath maintained at about 870° to 925° C. for an interval sufficient to form an adherent lead coating on said wire, cooling the so coated wire to about 350° to 650° C., and drawing the same through a die of smaller sectional dimensions than the so coated wire.

6. The method of bonding a layer of metal selected from the group consisting of aluminum, tin, copper and lead onto a titanium base comprising the step of immersing the titanium base in a molten bath of said metals aluminum, tin and lead, respectively, and a fused bath of cuprous chloride for applying said coatings, respectively, and at a temperature at least 65° C. in excess of the melting point of said metal and between 650° C. and 925° C. for a time between 5 seconds and 8 minutes.



7. The method of bonding a coating of copper onto a titanium base comprising the step of immersing the titanium base in a molten bath containing cuprous chloride at a temperature between 650° C. and 700° C. for a time between 5 seconds and 35 seconds.

8. The method of bonding a coating of lead onto a titanium base comprising the steps of immersing the titanium base in a molten bath of lead at a temperature between 870° C. and 925° C. for a predetermined time, subsequently cooling the bath to a temperature between 350° C. and 650° C. and then removing the coated titanium from the bath.

9. The method of bonding a coating of tin onto a titanium base comprising the step of immersing the titanium base in a molten bath of tin at a temperature between 780° C. and 790° C. for a time between 1 minute and 2 minutes.

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