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METHOD OF BRAZING TITANIUM

Willard M. Boam, Fairlawn, N. J., Isidore Friedman, Brooklyn, Henry Paige, New York, and Leo Souzis, Brooklyn, N. Y., and Kurt Strater, Paterson, N. J., assignors to Curtiss-Wright Corporation, a corporation of Delaware

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1 Claim. (Cl. 29—488)

This invention relates to titanium and is particularly directed to a method and means for brazing parts of titanium. As used herein the word "titanium" is used in a broad sense so as to include titanium alloys as well as titanium itself.

In brazing parts of titanium it is necessary that steps be taken to prevent oxidation of the titanium at the surfaces being brazed together. This can be accomplished by brazing in an inert atmosphere. In general however such a procedure is not commercially feasible for large scale production. Titanium parts to be brazed can also be coated with special fluxes to prevent oxidation during the brazing operation. However, fluxes for brazing titanium in air have not been entirely satisfactory.

An object of the present invention comprises the provision of a novel and simple method of preventing oxidation of titanium parts while brazing said parts in air at a temperature of at least 1300° F. A further object of the invention comprises the provision of a novel and simple method of brazing titanium parts by first plating the surfaces of said parts to be brazed together with a thin layer of iron, or cobalt. A still further object of the invention comprises the provision of a novel method of plating titanium parts with a protective adherent metal layer prior to bonding said parts together by brazing so that during the brazing operation said layer prevents oxidation of the surfaces being brazed together.

In accordance with the present invention, prior to brazing titanium parts together, for example with a silver base alloy, said parts are electroplated with a thin layer of iron or cobalt.

In order to obtain an adherent electroplated deposit of iron or cobalt on titanium it is first necessary that the surface to be plated be free of any oxide film. This is accomplished by immersing at least the surface of the titanium part, to be plated and then brazed, in a bath for removing any oxide from said surface. In accordance with the present invention this oxide film removing bath (activating bath) is such as to be compatible with the subsequently-used plating bath in that the constituents of the activating bath if introduced in the plating bath produce no undesirable reactions therein. Accordingly, the part to be plated and then brazed can be transferred directly from the activating bath to the plating bath without first completely rinsing or otherwise cleaning the part after its removal from the activating bath and before its immersion in the plating bath. This procedure minimizes the possibility of the part re-oxidizing after it is removed from the activating bath and before it is immersed in the plating bath.

In preparing the titanium part for iron plating the part is first degreased and then cleaned in a conventional pickling bath, for example by immersing for five minutes in a solution comprising 20% nitric acid (HNO_3), 2% hydrofluoric acid (HF) and 78% water. After removal from the pickle bath the part is rinsed with cold water. Any oxide film remaining on the part is then removed (by conversion to a chloride film) by immersing the part in an activating bath of boiling concentrated hydrochloric acid (HCl) for ten minutes. Then, without first rinsing the part, it is immediately transferred to and, at least the surface to be plated, is immersed in an iron chloride acid plating bath.

The plating bath preferably contains fifty ounces of ferrous chloride ($FeCl_2$) and twenty-five ounces of calcium chloride ($CaCl_2$) per gallon of water. The pH value of the bath is preferably kept within the range of 0.6 to 1.0 by the addition of HCl to the bath. The bath is heated to maintain its temperature within the range of 190°–210° F.

Before immersing at least the surface of the titanium part to be plated and then brazed in the plating bath, said part is connected to one side of an electric circuit so that when immersed it forms the cathode or negative electrode in the bath and the other side of said circuit is connected to a second electrode or anode in the bath, said second electrode preferably being iron. At least said titanium part surface is then immersed in said plating bath and iron is then electroplated on said immersed titanium part surface. A current density of sixty amperes per square foot has been found satisfactory. Because the electric circuit is connected to the titanium part before it is immersed in the bath no non-electrolytic deposit, which generally has poor adherence, can form on the part.

For the purpose of subsequently brazing the titanium part an adherent iron coating is plated on said part, said coating having a thickness range which may extend from 0.0001 to 0.001 inch and preferably is limited to 0.0004 to 0.0006 inch.

After iron plating, the iron plated titanium part is washed, dried and covered with a suitable slushing oil to prevent rusting.

The calcium chloride in the plating bath is inert, its function simply being to provide more chloride ions. If the pH value of the plating bath gets too high the iron plate becomes brittle. There is no lower limit to the usable range of pH values for the plating bath.

With this de-oxidizing and plating procedure the HCl on the titanium part after its removal from the HCl (activating) bath can be carried over directly into the plating bath whereby there is no need for completely cleaning the titanium part, for example by rinsing, to remove all the HCl before the part is immersed in the plating bath. This minimizes any danger of an oxide film reforming on the titanium part as the part is being transferred from the HCl (activating bath) to the plating bath.

After at least the surfaces of the titanium parts to be bonded together have been plated with iron, as described, said parts are brazed together in air, for example with a silver base alloy at a temperature of about 1300° F. Because the parts have been plated with iron the silver brazing procedure can be and is quite conventional.

The iron plate on the titanium part must be thick enough to prevent contamination or oxidation of the titanium by the air during the brazing operation but not so thick that the strength of the resulting brazed joint depends on the strength of the iron plate. A thickness of iron plate or coating of 0.0004 to 0.0006 inch has been found highly satisfactory for this purpose.

A coating of iron is suitable for this purpose because it does not melt at the brazing temperature, because its solubility in silver and copper base brazing alloys is negligible, because it can readily be cleaned by ordinary fluxes and because the iron plate is readily wet by silver and copper base brazing alloys. In addition the iron coating prevents the formation in the brazed joint of an undesirable intermetallic compound interface which heretofore has been characteristic of all titnaium brazed joints.

Instead of plating the titanium parts to be brazed with iron they may be plated with cobalt. For this purpose the titanium part to be plated is first degreased and cleaned. The part is then immersed in an activating bath to remove any oxide surface film. A suitable bath for this purpose preferably contains 0.4% by volume of a hydrofluoric acid solution of which 48% by weight is hydrofluoric acid with the balance water, 9–10% by volume of a sulfuric acid solution containing 96% by weight sulfuric acid with the balance water, and 90–91 percent water. The part is immersed in this bath at room temperature for a period of 15 minutes.

The titanium part is removed from the activating or deoxidizing bath and immersed in the cobalt plating bath without any intervening washing or rinsing of the part. The cobalt plating bath preferably contains 504 grams per liter of cobalt sulfate ($CoSO_4$), 45 grams per liter of boric acid (H_3BO_3) and 14 grams per liter of sodium fluoride (NaF). In addition hydrofluoric acid is added to adjust the pH of the bath to a range of 1.0–3.0.

Before immersion in the plating bath, the titanium part is connected to one side of an electric circuit so that when immersed it forms the cathode or negative electrode in the bath and the other side of the electric circuit is connected to a second electrode or anode in the bath, said second electrode preferably being made of cobalt. At least the surface of the titanium part to be plated is then immersed in the plating bath and cobalt is then electroplated on said immersed titanium surface. During the plating operation the bath is agitated and kept at a temperature of 140–160° F. A relatively high current density of about 80 amperes per square foot is used initially for a short period of time and then a lower current density for the remainder of the plating period. After the plating operation the part is rinsed and dried.

A high initial density of the plating current is used so that a complete coating of cobalt is quickly plated over the titanium part. The lower final current density is used so that the cobalt plate is of more uniform thickness. For the purpose of subsequently brazing the titanium part, said cobalt plate may have a thickness range of 0.0001 to 0.001 inch. Preferably, however, the thickness range of the cobalt plate is limited to 0.0002 to 0.0005 inch, a coating within this range being highly satisfactory to prevent contamination or oxidation of the titanium part during the subsequent brazing operation.

As in the case of the iron plating, the part to be plated need not be washed or rinsed after its removal from the

activating bath and prior to its immersion in the plating bath since all the constituents of the activating bath are also present in the palting bath.

After the titanium parts to be bonded together are thus plated with cobalt, said parts are brazed together in air, for example with a silver base alloy at a temperature of about 1300° F. in accordance with conventional brazing techniques.

The cobalt plate and plating procedure has certain advantages over iron in that the activating bath attacks the titanium to a lesser extent, the activating and plating baths function at lower temperatures and the cobalt plate has superior corrosion resistance. On the other hand the iron plate can more readily be cleaned by ordinary fluxes.

While we have described our invention in detal in its present preferred embodiment, it will be obvious to those skilled in the art, after understanding our invention, that various changes and modifications may be made therein without departing from the spirit or scope thereof. We aim in the appended claim to cover all such modifications.

We claim as our invention:

The method of bonding together two parts in which at least one of said parts is of titanium; said method comprising the steps of immersing at least the surface of said one part to be bonded to the other part in a bath of boiling hydrochloric acid for at least ten minutes; while still wet with said hydrochloric acid, connecting said part to the negative side of an electric circuit; after making said electric circuit connection and while still wet with said hydrochloric acid, immersing at least said surface of the part in a ferrous chloride bath; while immersed in said latter bath, electroplating a layer of iron having a thickness of 0.0004 to 0.0006 inch on at least said surface; and then brazing said parts together at a temperature of at least 1300° F.

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