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(54) COATING OF METALS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of coating the surface of an article of titanium, zirconium or tantalum, or the surface of an article of an alloy of titanium, zirconium or tantalum, with a tinning metal or alloy. The method is a modification of the method described in the specification of our British Patent No. 1,236,997 and the present application is an application for a Patent of Addition to the aforementioned Patent No. 1,236,997.

The surface of an article of titanium, zirconium or tantalum or of an alloy thereof is not readily wetted by a tinning metal or alloy due to the presence of an oxide layer on the surface of the article. Consequently, articles of titanium, zirconium or tantalum or of an alloy thereof are not easily soldered to other metals, e.g. steel. In order to tin satisfactorily the surface of an article of titanium, zirconium or tantalum or of an alloy thereof it is usually necessary to pre-clean the surface to remove the oxide, for example, by pickling in a strong acid, followed by electroplating, e.g. with copper, or electroless plating, e.g. with nickel. The thus tinned article may then be soldered, e.g. to steel, by soldering in known manner.

In the specification of our British Patent No. 1,236,997 we described a method of coating the surface of a sheet of titanium, zirconium or tantalum, or of an alloy thereof, with a tinning metal or alloy which method avoided the necessity of pre-cleaning the sheet. In the aforementioned specification the method described comprised heating the said sheet whilst the surface to be coated was covered with molten tinning metal or alloy and moving an ultrasonically-excited probe over the surface to be coated, the probe being in contact with the surface and with the molten metal or alloy.

We have now found that the method described in the aforementioned specification may be used to coat the surface of an article having a shape other than that of a sheet, and according to the present invention there is provided a method of coating the surface of an article of titanium, zirconium or tantalum, or the surface of an article of an alloy of titanium, zirconium or tantalum, with a tinning metal or alloy, the article having a shape other than that of a sheet and the method comprising contacting the surface of the article at an elevated temperature with a molten tinning metal or alloy and moving an ultrasonically-excited probe over the surface to be coated, the probe being in contact with the surface of the article and with the molten tinning metal or alloy.

It is to be understood that references hereinafter to titanium, zirconium or tantalum metals are to include reference to alloys of at least one of these metals.

The method of the present invention may be applied to an article having a shape other than that of a sheet. By a sheet we mean an article which is generally flat and has a thickness substantially less than its breadth, that is, a broad more or less flat article. The method may be applied to an article other than a sheet which has generally flat surfaces, e.g. a cube or prism, to an article having a curved surface, e.g. a sphere, to a rod, to a sheath, e.g. a tube, or to an irregularly shaped article. The method is particularly suitable for application to a tube of titanium, zirconium or tantalum. The tube may have, for example, a square, rectangular, or triangular cross-section but in general the tube will have a circular cross-section.

The method of the invention may be applied to coat a part only of the surface of the article with the tinning metal or alloy by contacting the surface with the molten tinning metal or alloy and then merely contacting with the probe that part only of the surface which it is desired to coat. In general,

substantially the whole of the surface of the article will be contacted with the molten tinning metal or alloy and the ultrasonic probe will be moved over and contacted with only that part of the surface of the article which it is desired to coat. Clearly, substantially the whole of the surface of the article may be coated by contacting substantially the whole surface with the tinning metal or alloy and then contacting the ultrasonic probe with substantially the whole of the surface of the article.

A tinning metal or alloy is a metal or alloy which will form a coating on the titanium, zirconium or tantalum article and which will enable the thus coated article to be used in a conventional soldering process.

A wide variety of tinning metals or alloys are suitable for use in the method of the ivention. In general metals or alloys may be used which are suitable for use in the tinning of, for example, mild steel.

Suitable tinning metals include tin and zinc. Suitable tinning alloys include binary alloys of tin with zinc, cadmium and bismuth, for example, alloys of tin with 1% to 30% by weight of zinc, bismuth or cadmium, binary alloys of bismuth with cadmium, lead, tin and zinc, for example, alloys of bismuth with 1% to 30% by weight of cadmium, lead or zinc, binary alloys of cadmium with bismuth, lead and zinc, for example, alloys of cadmium with 30% by weight of bismuth, cadmium with 1% by weight of Pb, and cadmium with 30% by weight of zinc, a binary alloy of lead with 30% by weight of zinc, and binary alloys of zinc with bismuth, cadmium, lead and tin, for example alloys of zinc with 1% to 30% by weight of bismuth, cadmium, lead or tin. Other suitable tinning metals and alloys for use in the method of the invention may be found by means of simple experiment. The preferred tinning alloy is an alloy of tin with from 1% to 30% by weight of zinc.

The method of the present invention may be used to coat the surface of an article of titanium, zirconium or tantalum with a tinning metal or alloy. Where the article is of an alloy the alloy may be of titanium or zirconium or tantalum with one or more metals other than titanium, zirconium or tantalum. Alternatively, the alloy may be an alloy of two or more metals selected from titanium, zirconium and tantalum optionally with one or more other metals.

Examples of alloys to which the method may be applied include titanium-zirconium alloys containing up to 14% by weight of zirconium, alloys of titanium containing up to 5 weight % of a platinum mettal, e.g. platinum, rhodium or iridium, and alloys of titanium containing up to 10 weight % of niobium or tantalum.

The temperature at which the coating method may be operated may vary over a broad range. If necessary, the tinning metal or alloy may be heated in order to maintain it at the desired temperature. The article to be treated may suitably be preheated to the desired temperature. The minimum temperature will depend inter alia on the temperature at which the particular tinning metal or alloy which is used becomes molten and the minimum temperature will clearly be above this latter temperature. It is generally preferred to use a temperature in the range from 300°C to 450°C. Below 300°C the tinning effect produced may not be as satisfactory as may be desired. A more preferred temperature range is 350°C to 430°C. Suitable temperatures may be chosen by means of simple experiment. The precise temperature to be used will depend on the particular tinning metal or alloy which is used.

The ultrasonic probe may be excited by conventional means, for example, by means of a piezoelectric or a magnetostriction generator and the probe may suitably resonate at a frequency of about 20,000 Hz. Low frequencies should be avoided due to excessive noise and very high frequencies should be avoided as the tinning effect obtained may not be as great as that obtained at the preferred frequency.

The head of the probe may with advantage be shaped so as to conform with the shape of the surface of the article to be coated with tinning metal or alloy. For example, where the article is flat the head of the probe may suitably be flat and where the article is in the form of a rod or tube having a circular cross-section the head of the probe may suitably be concave in shape and have a radius of curvature substantially the same as that of the outer surface of the rod or tube.

The surface of the article may be contacted with the ultrasonic probe and with the molten tinning metal by, for example, immersing the article in a bath containing the molten tinning metal or alloy and immersing the probe in the molten tinning metal or alloy and contacting the probe with the surface of the article. Where the article is in the form of a rod or tube of circular cross-section and the head of the probe is concave in shape so as to conform with the outer surface of the rod or tube then it may be necessary to provide means for rotating the rod or tube in the bath so as to be able progressively to present substantially the whole of the outer surface of the rod or tube to the head of the probe. Alternatively, where the article is a rod or tube the head of the probe may have an annular shape such as just to allow passage of the rod or tube through the head. In this case the probe may be positioned below the surface

of the molten tinning metal or alloy and the rod or tube may be passed beneath the surface and into contact with and through the annular head on the probe. Where a tube is used the ends of the tube may suitably be plugged.

The use of such an annular head may also serve to control the thickness of the tinning metal or alloy on the surface of the rod or tube. Alternatively, or in addition, the coating on the rod or tube may be reduced to the desired thickness after the rod or tube has been removed from the bath of tinning metal or alloy, for example, by scraping the coating until the desired thickness is achieved, or by passing the rod or tube through a heated die of appropriate shape.

The coated article of titanium, zirconium or tantalum may be bonded to an article of another metal, for example, a steel article, e.g. a pre-tinned steel or article, by a conventional soldering process and according to a further embodiment of the present invention there is provided a method of making a composite structure which method comprises bonding an article of titanium, zirconium or tantalum, or an article of an alloy of titanium, zirconium or tantalum, to another metal or alloy, said article having been coated with a tinning metal or alloy by a method as herein before described.

Steel may be pre-tinned in conventional manner by contacting the surface of the steel with a molten tinning metal or alloy, for example, with a lead-bismuth alloy or with a lead-tin alloy, e.g. an alloy containing 30% by weight of lead and 70% by weight of tin.

A wide range of soldering alloys may be used for soldering coated articles of titanium, zirconium or tantalum, to a pretinned article of another metal. For example, the soldering alloy may be a lead-tin alloy or a lead-bismuth alloy.

The invention is now illustrated by the following Example.

EXAMPLE

A 3-ft long tube of commercial purity titanium having an outside diameter of 1-inch was placed in a bath of a molten tin/zinc alloy (70% by weight tin and 30% by weight zinc) and held by means of clamps below the surface of the molten alloy. The alloy was heated to maintain it at a temperature of 400°C and the ends of the tube were sealed by means of metallic plugs to prevent ingress of alloy into the bore of the tube.

An ultrasonically-excited probe consisting of a half wavelength resonant steel probe (having a natural frequency of 20,000 Hz) coupled to a magnetostriction transducer and having a concave head of $\frac{1}{2}$-inch radius of curvature was moved over the surface of the tube and in contact with the surface of the tube. The tube was then rotated about its axis approximately one-third of a turn and the probe was again moved over the surface of the tube and in contact with the surface. The tube was again rotated and the above procedure repeated until substantially the whole of the outer surface of the tube had been contacted with the probe.

The tube was then removed from the bath and excess alloy was allowed to drain from the tube.

The surface of the tube was found to be coated with a strongly-bonded layer of tin/zinc alloy. The thus tinned tube could be soldered to mild steel using a conventional dip-tinning technique to form a strong bond between the titanium and the mild steel.

WHAT WE CLAIM IS:—

1. A method of coating the surface of an article of titanium, zirconium or tantalum, or the surface of an article of an alloy of titanium, zirconium or tantalum, with a tinning metal or alloy, the article having a shape other than that of a sheet and the method comprising contacting the surface of the article at an elevated temperature with a molten tinning metal or alloy and moving an ultrasonically-excited probe over the surface to be coated, the probe being in contact with the surface of the article and with the tinning metal or alloy.

2. A method as claimed in claim 1 in which the article is in the form of a tube.

3. A method as claimed in claim 1 or claim 2 in which the tinning metal alloy is tin or zinc or a binary alloy of tin with zinc, cadmium or bismuth.

4. A method as claimed in any one of claims 1 to 3 in which the temperature of the tinning metal or alloy is in the range 300°C to 450°C.

5. A method as claimed in any one of claims 1 to 4 in which the head of the probe is shaped to conform with the surface of the article.

6. A method as claimed in claim 1 substantially as hereinbefore described with reference to the Example.

7. A coated article of titanium, zirconium or tantalum, or a coated article of an alloy of titanium, zirconium or tantalum, prepared by a method as claimed in any one of claims 1 to 6.

8. A method of making a composite structure which method comprises bonding an article of titanium, zirconium or tantalum, or an article of an alloy of titanium, zirconium or tantalum, to another metal or alloy, said article having been coated with a tinning metal or alloy by a method as claimed in any one of claims 1 to 6.

9. A method as claimed in claim 8 in which the other metatl or alloy is a pretinned steel article.

10. A method as claimed in claim 8 substantially as hereinbefore described with reference to the Example.

11. A composite structure prepared by a method as claimed in any one of claims 8 to 10.

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