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3,182,395 PROCESS FOR CLADDING METALS WITH TITANIUM

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This invention relates to a method of cladding metals, particularly steel, with titanium.

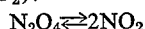
The resistance of titanium to corrosion by sea water, acids and other chemical environments, and its high strength at elevated temperatures is known. Because of these and other desirable properties of titanium, it has been used for cladding other metals, particularly less costly base metals. Bonding of titanium to the base metals by means of high temperature pressure welding, involving subjecting the assembled layers, i.e., the metal pack, to the necessary high temperatures and pressures to effect the bonding, results in poor bonds between the titanium and the base metal layer, which, when steel is used as the base layer, is due to the diffusion of iron, chromium and nickel from the steel into the titanium, with consequent weak and brittle bonds between the titanium and the steel. For the purpose of overcoming these difficulties in the cladding of steel with titanium it has been suggested to interpose an intermediate layer of bonding metal, such as chromium, cobalt, molybdenum, silver (2,908,966, granted October 20, 1959), or nickel (3,015,885, granted January 9, 1962), and subject the resultant assembly to high temperatures and pressures. Patent 3,015,885 describes heating the assembly or pack to a temperature of 1700° F. for thirty minutes or 1600° F. for one hour.

It is a principal object of the present invention to provide a simple process for cladding metals, particularly steel, with titanium resulting in good bonds between the base metal and the titanium.

Other objects and advantages of the present invention will be apparent from the following detailed description thereof.

In accordance with this invention titanium is cladded to the base metal by applying liquid nitrogen tetroxide to the surface of the titanium or base metal to be clad, and while the titanium is in close position with, preferably substantially in contact with, the base metal with the liquid nitrogen tetroxide therebetween, the assembly is subjected to an impact energy of at least about 125 foot pounds per square inch, preferably 200–1000 foot pounds per square inch of base metal surface to be clad with the titanium. Higher impact energies can be used when the metals are supported and are of a strength to withstand such higher energies; as a practical matter, however, there is nothing gained by using higher energy levels of impact and hence such higher energies are not recommended.

Liquid nitrogen tetroxide (N₂O₄) is considered to be an equilibrium mixture containing a small amount of nitrogen dioxide (NO₂).



The expression liquid nitrogen tetroxide or N₂O₄ is used herein to include equilibrium mixtures of NO₂ and N₂O₄ in the liquid phase as well as the liquid nitrogen tetroxide formed when condensing nitrogen dioxide.

This invention is applicable to the cladding of steel, including carbon steel, stainless steels, tin-plated steels and other metals. It will be described hereinafter chiefly in connection with the cladding of steel, but it will be understood the invention is not limited thereto but includes the cladding of metals, generally, with titanium.

In one embodiment of the invention plates of titanium and steel are placed in a rigid container with the titanium plate on top of the steel. Liquid nitrogen tetroxide

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(N₂O₄) is introduced into the container in amount at least sufficient to cover the interface between the titanium and steel, i.e., to cover the crevice between the two plates. The amount of N₂O₄ used is not critical as long as it is enough to cover in the form of a film the surface of the steel or titanium to be adhered to each other. Too large an amount should not be used because it is wasteful of N₂O₄. In general from 25 to 2500 ml. of liquid N₂O₄ per square foot of steel to be clad gives good bonding; the invention however is not to be restricted to this range of amounts of N₂O₄ per square foot of surface.

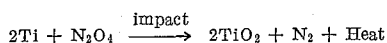
Instead of a titanium plate, granulated titanium or titanium sponge may be placed adjacent a steel surface to be clad with titanium. The titanium is wet with the N₂O₄ either before or after placement on or adjacent the steel surface.

The assembly of steel plate and titanium having the liquid N₂O₄ covering the surface of the steel to be clad, or the titanium, is struck with an impact energy of at least about 125 foot pounds per square inch, preferably from 200 to 1000 foot pounds per square inch, while the assembly is suitably supported. For example, the assembly can be placed on a heat-conducting metal-supporting surface or other supporting surface such as a concrete block having thereon a metal or other heat-conducting member for dissipating the heat generated when the titanium surface is ignited by the impact energy imparted to the assembly. The heat released by the ignition of the titanium surface fuses the titanium to the steel with the formation of a good bond between the titanium and the steel.

The impact energy can be applied to the assembly of titanium and steel having the liquid N₂O₄ wetting the titanium, or steel, or both in any desired manner. For example, a weight can be applied under the action of gravity, dropped the necessary height to impart the impact energy to the assembly, or a manually or power actuated hammer or other impact member can be used.

The following explanation is given to facilitate a better understanding of the invention without, however, limiting the invention to this explanation.

Titanium reacts with N₂O₄ under the impact energy herein disclosed as follows:



The titanium dioxide (TiO₂) is dissolved in the molten titanium produced by the heat of reaction melting the titanium in the vicinity of the reaction; the N₂ for the most part escapes. Where granular or sponge titanium is used, the granules or sponge is melted to form molten titanium containing some dissolved titanium dioxide, which molten titanium quickly cools to produce a tightly bonded titanium coating on the steel surface. Employing a titanium plate on a steel plate with the liquid N₂O₄ filling the crevice between the two, depending on the thickness of the titanium plate either the surface in contact with the steel plate or the entire titanium plate is rendered molten. Heat dissipation into the metals and the inability of fresh oxidizer to enter into the closing joint or crevice between the plates, due in part to the amount of N₂O₄ present, limits the propagation of the reaction. The titanium is thus fused to the steel and tightly bonded thereto.

The reaction is practically instantaneous, as is also the melting and subsequent solidification of the titanium. Hence diffusion of metals present in the steel into the titanium is minimized. This may explain the formation of the tight bond between the titanium and the steel.

When bonding titanium plates to steel, the placement of finely divided particles of alumina, e.g., No. 240 Al₂O₃, having a particle size range of from 30 to 70 microns, between the metal surfaces concentrates the impact in the

areas of these particles and thus reduces the total force required for ignition of the titanium. Only a few grains or particles of Al_2O_3 are required per square inch of surface, on which these grains are placed; from about 0.01 to 1.0 gram of alumina is used per square foot of titanium bonded to the base metal. Upon ignition of the titanium surface, as hereinabove described, the alumina is trapped in the molten titanium. Since the amount of Al_2O_3 is small, the Al_2O_3 does not deleteriously affect the titanium coating or its bond with the steel.

Preferably but not necessarily the titanium is soaked in the liquid N_2O_4 , prior to impact, for a period of time, for example, from a few hours to a day or longer. To prevent evaporation of N_2O_4 during the soaking, desirably the soaking is carried out while maintaining the titanium in contact with the liquid N_2O_4 at a temperature below $21^\circ C.$, for example, about $0^\circ C.$ This can readily be effected by placing the titanium while in contact with liquid N_2O_4 in a refrigerator. This soaking step need not be used as good results are obtained without it; it does, however, increase the impact sensitivity of the titanium.

The following examples are given to exemplify and illustrate the invention; it will be understood that the invention is not limited to these examples:

Example I

A few grains of No. 240 Al_2O_3 were placed in the bottom of a tin-plated steel cup ($2\frac{3}{16}$ inches diameter and $1\frac{1}{8}$ inches deep) and a titanium plate 2 inches long, 0.5 inch wide and 0.67 inch thick placed on the grains of Al_2O_3 . 25 milliliters of liquid N_2O_4 was introduced covering the titanium plate. The cup was placed on a steel plate bolted to a concrete block. The titanium plate was then impacted with a 0.5 inch diameter flat-end striker weighing ten pounds dropped 11.3 feet. Ignition of the titanium took place resulting in the fusion of the titanium plate to the bottom of the cup with the substantially instantaneous formation of a tightly bonded titanium cladding on the inside of the bottom of the cup.

Example II

In this example a one-quarter inch diameter stainless steel shear pin, and its guide, were coated with titanium. A clean section of titanium 0.525" x 0.525" and 0.67" thick was clamped by two stainless steel clamps over a 0.381" diameter hole in a small anvil and the anvil having this section of titanium thereon placed in the bottom of a cup similar to that used in Example I. 25 milliliters of liquid N_2O_4 was placed in the cup covering the titanium. The shear pin was positioned with one end thereof in contact with the liquid N_2O_4 on the titanium section directly above the hole in the anvil. The assembly thus produced was placed in a refrigerator at $0^\circ C.$ for 24 hours to enable the titanium to soak in the liquid N_2O_4 . Thereafter the assembly was placed onto a steel plate bolted to a concrete block. A ten pound weight was dropped from a height of 11.3 feet onto the shear pin. A $\frac{1}{4}$ " circle was sheared from the titanium which ignited and the molten titanium splattered the pin and pin guide, substantially instantaneously cladding these stainless steel parts with tightly bonded titanium.

It will be noted that the present invention provides a simple process for cladding metals, particularly steel with titanium, resulting in good bonds between the base metal and the cladding titanium due, in part at least, to the fact that the cladding is effected practically instantaneously with consequent minimization of the diffusion of iron, chromium, nickel and other constituents of the base metal, e.g., steel, into the titanium. Furthermore, this invention results in such cladding without the necessity of interposing a layer or layers of a metal such as nickel, chromium, cobalt, molybdenum or silver between the titanium and the base metal and without subjecting the assembly of base metal and titanium to high temperatures for relatively prolonged time periods or to pressing as involved in conventional pack techniques.

This invention is not to be limited to the description thereof herein contained because various modifications and alterations, as would occur to one skilled in the art, can be made. The invention includes not only the cladding of uncoated base metals such as steel but also the cladding of coated base metals, for example, where the steel has a coating of nickel or other metal thereon and where the cladding with the titanium is effected by subjecting the assembly having either the base metal or titanium wet with liquid N_2O_4 to impact energy to ignite the titanium and effect the cladding.

What is claimed is:

1. The process of cladding titanium onto a base metal, which comprises forming an assembly of base metal and titanium with at least one of the adjacent surfaces of the metals wet with liquid nitrogen tetroxide and subjecting the assembly to impact energy of at least 125 foot pounds per square inch of base metal surface to be clad to ignite at least a portion of the titanium and clad the base metal with the titanium.
2. The cladding process as defined in claim 1, in which the titanium and base metal are in the form of plates in contact with each other, the liquid nitrogen tetroxide covers the contacting surfaces between the plates and the resultant assembly is subjected to impact energy of from 125 to 1000 foot pounds per square inch of surface of the base metal to be clad.
3. The cladding process of claim 2, in which particles of aluminum oxide are interposed between the titanium and base metal.
4. The cladding process of claim 1, in which the titanium is in particulate form.
5. The cladding process of claim 1, in which the titanium is sponge titanium.
6. The cladding process of claim 1, in which the titanium is soaked in the liquid nitrogen tetroxide before the assembly is subject to said impact energy.
7. The process of cladding steel with titanium which comprises placing titanium close to the surface of the steel to be clad, wetting at least one of the (a) surface of said titanium adjacent the surface of the steel to be clad and (b) the surface of the steel to be clad with liquid nitrogen tetroxide; and subjecting the resultant assembly to impact energy of at least 125 foot pounds per square inch of surface of the steel to be clad.
8. The process of cladding steel with titanium which comprises placing a titanium plate on a steel plate, covering the contacting surfaces with liquid nitrogen tetroxide and applying to the resultant assembly impact energy of 125 to 1000 foot pounds per square inch of steel surface to be clad.
9. The process of cladding steel with titanium defined in claim 8, in which finely divided particles of aluminum oxide are interposed between the titanium and steel.
10. The process of cladding steel with titanium which comprises wetting titanium with liquid nitrogen tetroxide, placing the steel to be clad at least in closely spaced relation to the wetted surface of the titanium and applying impact energy of from 125 to 1000 foot pounds per square inch of surface of the steel to be clad to the steel to bring it forcibly in contact with the titanium, ignite and melt the titanium whereby the molten titanium is deposited on the steel and forms a titanium cladding thereon.

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