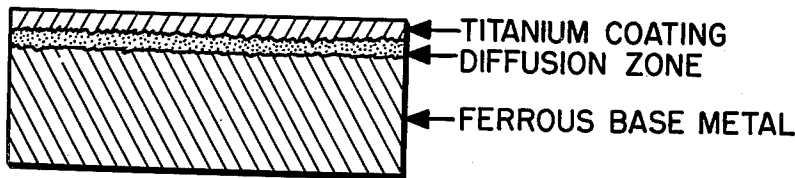
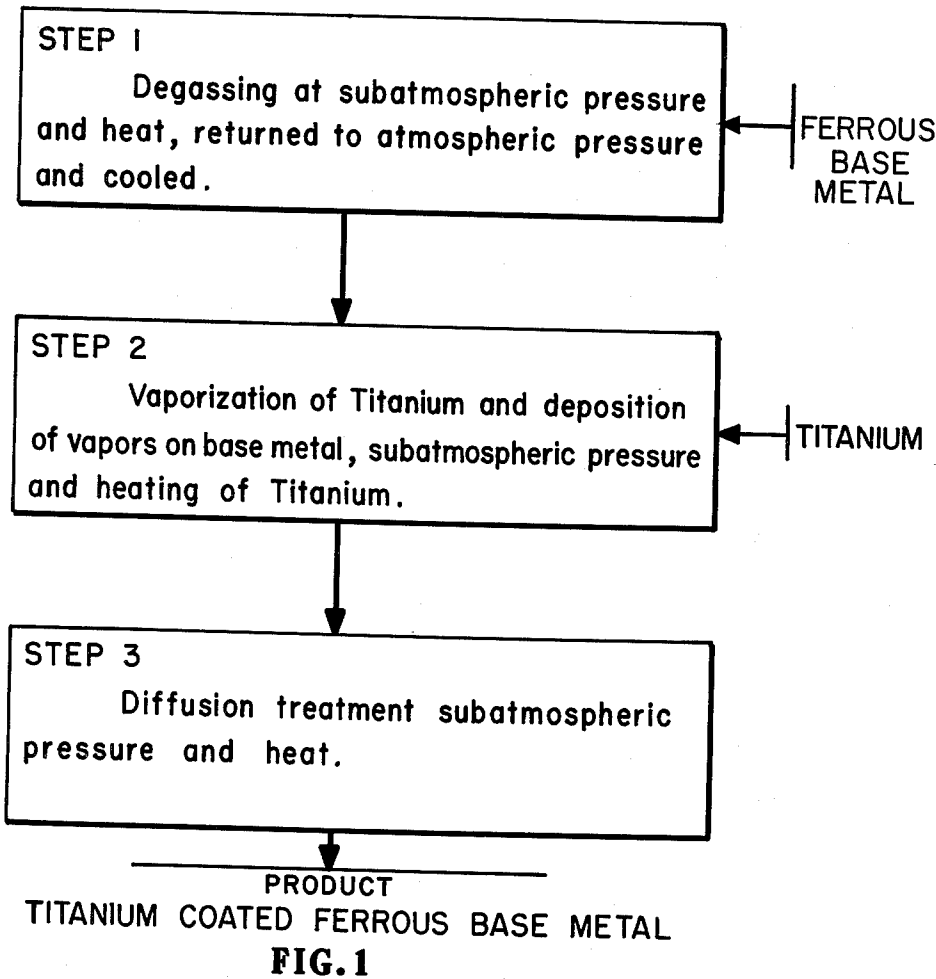


Jan. 1, 1963

C. W. HORN ETAL
TITANIUM COATING PROCESS

3,071,491

Filed Oct. 5, 1960



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3,071,491

TITANIUM COATING PROCESS

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Filed Oct. 5, 1960, Ser. No. 60,760

1 Claim. (Cl. 117—50)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon.

The present invention relates to the method of producing titanium coatings on a base of ferrous metal.

The industrial applications of titanium are increasing rapidly due to the metal's desirable lightness, structural strength and chemical properties.

Titanium's most important chemical property is corrosion resistance. This property is attributed to the rapid formation of surface films which are passive in nature and resistant to attack in most oxidizing media. Aluminum acts similarly in this respect.

When titanium is coupled with some other metals, the corrosion occurring is generally not extreme. However, coupled with the more anodic metals accelerated corrosion will occur. The electromotive series of metals lists titanium below silver, and cathodic to anodic ferrous metals. This, in effect, is a serious situation, since in practical applications, it is necessary to affix titanium to common structural metals. Thus, where large titanium fixtures are attached to small ferrous structures a severe anodic corrosion will result because of the large cathodic area presented by the titanium fixture.

Severe corrosion of items to be affixed to titanium objects or items standing alone will be greatly curtailed by an application of a titanium protective coating. We have considered a number of ways of applying such a coating.

Cladding was found to be prohibitively expensive since clad or rolled on layers of titanium are relatively thick ($\frac{1}{32}$ inch). Making the item wholly of titanium would also entail great expense.

Attempts at electroplating with titanium have all ended in failure. It is our belief that this method of coating is impossible due to titanium's extreme chemical activity.

It is known to coat items by the phenomenon of vacuum evaporation of low melting point metals from heated sources, a process known as "metallization," wherein the metal is boiled or driven off in the form of vapor, and collected or deposited on surrounding objects within a vacuum chamber. The objects to be coated are at temperatures sufficiently low to cause condensation of the vaporized metal.

To provide a satisfactory metallized coating with low melting point metals, such as cadmium, it is necessary to first rough the surface of the base metal before coating it. This furnishes the essential bond between the base and the coating.

This method was attempted using titanium, but the coating was found to be porous and therefore defective, the porosity being traced to two sources: the surface roughening of the base metal and absorbed gases in the base metal. Our invention relates to the elimination of these sources of difficulty.

It is the object of this invention to provide a method of forming a metallized titanium protective coating upon a ferrous base metal by other than electrochemical deposition.

It is the further object of this invention to provide a method of forming a metallized titanium protective coating upon a ferrous base metal in order to obviate electrolytic action between ferrous metal items attached to titanium items.

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It is the further object of this invention to provide a method of forming a metallized titanium coating upon a ferrous base metal in order to create a highly corrosive resistant coating.

It is the further object of this invention to provide a method of forming a satisfactory metallized titanium coating upon a ferrous base metal without roughening the surface of the base metal.

It is the further object of this invention to provide a method of forming a satisfactory metallized titanium coating upon a ferrous base metal in which there is vacuum evaporation of the titanium from a heated source and condensation of the vapor formed upon the base metal.

More specifically, it is the object of this invention to provide a method of forming a satisfactory metallized titanium coating which circumvents the problems which would be created by use of the low melting point process of coating.

Our earlier investigations on metallizing techniques indicated the necessity of producing a mechanical bond between the coating and base metal. Surface conditioning of the base metal by one of a number of treatments (fine quartz pressure blast, coarse emery scrub and HCl etch) produced good bonding of metallized coatings of low melting point metals (cadmium, zinc, and tin) without detrimental effects on the coating. Unfortunately, when using a high melting point metal (titanium) to coat, the treatments of the base metal did not produce, in addition to good bonding, a non-porous coating. This porosity, evidenced by numerous pinholes, resulted in accelerated corrosion of the base metal.

We attempted to remedy this by diffusion bonding of the titanium coating to a smooth base metal under high temperature and vacuum. A good bond resulted between the coating and the base metal. This result was possible since both iron and titanium melt within a relatively small temperature range. This type of bonding would be impossible with iron and cadmium, since cadmium melts at a lower temperature than iron and would boil away before the iron was heated enough to diffuse with the contiguous metal.

The diffusion step, although producing good bonding, did not result in a non-porous titanium coating. It was discovered that additional porosity developed because entrapped gases had been driven off the base metal during the high temperature deposition of the coating. This problem does not arise in the deposition of low melting point metals because the evaporation temperature of the coating metal does not reach the point where gases will be driven off the base metal.

This failing was corrected by removal of gases from the base metal under high temperature and vacuum. The process is called "degassing."

The type of base metal used has a definite effect upon the length of time of degassing. During the refining, melting and casting of metals, large volumes of gas may be absorbed during solidification. The amount of gas entrapped during solidification determines the type of steel. If no gas is present, the steel is termed "killed"; increasing gas entrapment results in steel which is semi-killed, capped or rimmed.

Porosity is obviously greatest in undegassed base metals, and is not completely eliminated even when using a degassed killed type steel. Even in properly degassed panels, some porosity is evident. The occurrence of pinholes in properly degassed killed type steel is, however, much less than undegassed rim type steel.

From the foregoing, it can be concluded that undesirable porosity is caused by a combination of gas evolution during metallization and surface roughness of the base metal. Since surface roughness cannot be utilized in

creating a bond between the titanium coating and base, we have devised a new method of diffusion bonding using a smooth base metal. The problem of gas evolution during metallization was cured by degassing the base metal before metallization. Thus, it is clear that the degassing and diffusion steps of our process solve problems not presented in processes involving metallization by low melting point metals and are believed to be novel and resulting in a process that is advantageous and not suggested by the prior art.

Further objects and advantages of the present invention will be apparent from the following description, reference being had to the accompanying drawing, wherein preferred embodiments of the present invention are clearly shown.

In the drawing:

FIGURE 1 of the drawing shows a flow diagram representing the steps in the general process of forming a titanium coating on a ferrous metal base.

FIGURE 2 of the drawing shows a fragmentary cross-sectional view of the article produced by the process of this invention.

The following example, which is for illustrative purposes only and not necessarily limited thereto, more specifically illustrates the process represented in general by the flow diagram of FIGURE 1 as to the time of each step, and to the pressures and temperatures related to each of the three process steps.

The base to be coated is a killed steel with a smooth surface.

Step one of the process relates to the degassing or the driving off of absorbed gases in the ferrous metal base and is accomplished by heating it in a vacuum of 10^{-3} mm. of mercury at a temperature in the range of 1750–1825° F. for a period of three to five minutes. The base metal is then cooled and returned to room pressure.

Step two of the process relates to the deposition of the coating within the vacuum chamber. The vacuum chamber is reevacuated to a vacuum of 5×10^{-4} mm. of mercury. Metallization is accomplished by electrically heating a tungsten crucible, in which the titanium charge is held, to the temperature at which the titanium will be vaporized. Vaporization is continued until the thickness of the deposited titanium is in the range of 0.4–1.2 mils. This will require approximately eight minutes. A thicker coating will, of course, require more time. The chamber is now returned to room pressure.

Step three of the process relates to the forming of a diffusion zone between the titanium coating and ferrous base. FIGURE 2 shows this intermediate zone and the definite intergrading or alloying of titanium and the ferrous base which is believed to be entirely novel and not existent in the case of titanium clad metal, nor in electroplated titanium which is believed impossible and not produced. Diffusion treatment is applied to both coating and base metal after the vacuum chamber has been reevacuated to a vacuum of 5×10^{-4} mm. of mercury, at a temperature in the range of 1600–1675° F. and for a period of three minutes. This step provides excellent bonding without the need for pressure or grit blasted base metal surfaces.

At the completion of the diffusion treatment, the vacuum is broken and the process is complete. The use of a vacuum in this last step is necessary in order to eliminate the tendency of the titanium coating to oxidize.

An alternative to running the process in the discontinuous fashion discussed above is to degas, metallize and

diffuse in one process, without returning the sample to room pressure between steps.

The coating produced by this novel process has a diversity of industrial uses. Some of the more important uses appear in the following list.

Titanium coatings can be used on all components presently plated with cadmium or zinc. Typical examples of such item are: torsion bar anchors, torsion bar anchor retainers, shock absorber bearing assemblies, hose clamps, fuel tank cap assemblies, etc.

Titanium coatings are particularly suited to applications where massive corrosion products would interfere with the proper functioning of electrical components. Titanium is superior in this respect to the cadmium plating that is presently employed on electrical items such as: contact points, binding screws and nuts, receptacle housings, instrument housings (fuel gages, ammeters, voltmeters, etc.).

Titanium can be substituted for lead as a coating for battery hold-down bolts.

Future production of missiles and airborne vehicles will use increasing amounts of wrought and cast titanium alloys. Steel and other dissimilar alloys, when joined to titanium components (as discussed previously), provide conditions which lead to harmful galvanic corrosion. Vacuum deposited titanium coatings applied to the dissimilar metals in accordance with this method will eliminate galvanic corrosion.

Vacuum deposited titanium is a potential substitute for titanium in the manufacture of condensers.

It is understood that various modifications may be apparent to those skilled in the art without departing from the spirit and scope of the invention, and the invention is not to be limited to the illustrated embodiments, except as included in the appending claim.

We claim:

A process for a titanium coating on a base of ferrous metal having a smooth surface comprising the following steps in sequence: degassing the base by heating said base for a period of three to five minutes at a temperature within the range of 1750° F. to 1875° F. and at a subatmospheric pressure of 10^{-3} mm. of mercury; returning said base to room pressure and cooling in air to room temperature; metallizing said base with a titanium coating within the range of 0.4–1.2 mils in thickness by subjecting titanium to subatmospheric pressures of 5×10^{-4} mm. of mercury and vaporization temperature for a period of the order of eight minutes and condensing the resulting titanium vapor on said base; returning said base to room pressure; subjecting the thus metallized product to a diffusing treatment by heating the product for a period of the order of three minutes at a temperature within the range of 1600° F. to 1675° F. and at a subatmospheric pressure of 5×10^{-4} mm. of mercury; and returning said base to room pressure and cooling in air to room temperature.

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