PROCESS FOR SURFACE-TREATING IRON AND STEEL MATERIALS TO BESTOW HIGH ACID AND WEAR RESISTIVITY

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My invention relates to a process for surface-treating iron and steel to obtain an alloy layer in layer form by utilizing the strong diffusing action of electrolytically active titanium to form a layer of iron-titanium alloy on its surface layer and at the same time, forming a nitride layer rapidly on said alloy by utilizing the property of the iron-titanium alloy which is formed in order to bestow high acid resistivity and at the same time, to provide wear resistivity by forming super hard nitride layer.

In my U.S. Patent 3,074,860 there is disclosed a titanium plating process which is the first step in the present process.

Briefly stated, this step involves dissolving a water-soluble titanium compound, wherein the titanium has a valency of two or three, in an aqueous solution. In the case where a titanium compound in which titanium has a valency of three is employed, the compound is converted into a titanium compound in which titanium has a valency of two by reduction by means of a reducing metal or agent, or by electrolytic reduction, or by the combination of said two reduction methods, and the titanium compound in which titanium has a valency of two thus converted is employed to form a titanium compound in which titanium has a valency of two or a titanium compound in which titanium has a valency of two is made alkaline such that a sufficient reducing condition will exist in the electrolyte solution during the electrolysis operation, and it is then electrolyzed.

As noted supra, a water-soluble titanium compound in which titanium has a valency of two or three is used as a starting material. When a titanium compound in which the valency of titanium is three is employed, it is preferable to use a titanium compound which can easily be converted into a titanium compound in which the valency of titanium is two, for example, halides, complex salts, etc.

When a titanium compound in which titanium has a valency of three is employed, the compound is converted into a titanium compound in which titanium has a valency of two by means of a reducing metal or agent or by electrolytic reduction or by the combination of said two reduction methods.

Titanium compounds in which titanium has a valency of three have the advantage that they are more stable and more easily obtainable. However, when a titanium compound in which titanium has a valency of three is employed, the compound must be converted into a titanium compound having a valency of two before electrolysis by employing a reducing metal or agent or by electrolytic reduction or by the combination of said two reduction methods. For example, the reduction can be accomplished by the use of sponge titanium, or formaldehyde, or hydrazine hydrate, or pyrogallic acid, or by combinations of two of these reducing agents. It may be also accomplished by electrolytic reduction either by itself or in combination with the use of one of the aforementioned reducing agents.

An aqueous solution of a water-soluble titanium compound in which titanium has a valency of two, which may be a titanium compound in which titanium has a valency of two, or a titanium compound in which titanium has a valency of two which has been converted from a titanium compound in which titanium has a valency of three, must be adjusted so as to be alkaline. The aqueous alkaline solution is then subjected to electrolysis. When the electrolysis is carried out with the solution alkaline such that a sufficient reducing condition exists in the electrolyte solution, the metallic titanum having a high purity is deposited on the cathode.

The reason why electrolytic production of metallic titanium which had been very difficult has been made possible by my process may be explained by the fact that, according to my process, titanium compound in which titanium has a valency of two is employed and a sufficient reducing condition exists in the electrolyte solution during the electrolysis so that the oxidation of the titanium compound in which titanium has a valency of two in the electrolyte to a titanium compound in which titanium has a valency of three is prevented and, also, the oxidation of metallic titanium deposited on the cathode is prevented. The fact that the hydrogen ion concentration of the electrolyte solution is in the alkaline range produces the favorable result of bringing the potential at which hydrogen is evolved and the potential at which metallic titanium is deposited close to each other. By the combined effects of above, pure metallic titanium is deposited on the cathode while hydrogen is being evolved on it. Thus, metallic titanium is deposited on the cathode under similar conditions which prevail in the electrolytic production of manganese.

Briefly stated the present invention relates to first mechanically polishing or chemically cleaning the steel, titanium is then plated electrolytically in the same manner as in the plating of the usual heavy metals and then zinc is electrolytically plated on this to cover the titanium completely. After the above plating has been completed, the treated steel is dipped in sodium cyanide solution and heated to 600-800° C. As the melting temperature of zinc is 420° C., the zinc melts during the process, first at the surface and, when the temperature becomes higher, the zinc begins to vaporize. In this case, electrolytic titanium of the middle layer begins to vaporize at about 550° C. but it does not form an alloy with zinc, as zinc and electrolytic titanium have such properties that it is difficult to form an alloy but, rather, the titanium diffuses to the mild steel side to form an alloy layer with it. After melting, the zinc gradually diffuses as the temperature rises and escapes from the surface of the steel to shut off air and oxides from the fresh iron-titanium alloy surface and thus contacts actively with the cyanide solution to form a nitride layer quickly and effectively on the surface of the steel.

An alternative process is after electro-plating electrolytic titanium, the so treated steel is heated to 150° C.-400° C. in a reducing or non-oxidizing atmosphere to diffuse the electrolytic titanium to the steel to prevent vaporization and then the nitride layer is formed rapidly by heating to the aforementioned temperature in the aforementioned cyanide bath.

Alloy steel, cast steel, cast iron and cast iron alloy can also be surface-treated in approximately the same manner. Furthermore, this process of heating to form a nitride layer may be carried out in a gas atmosphere in which the nitrogen compound has been decomposed and released or in a nitrogen atmosphere to prevent oxidation. For example, heating may be carried out in an atmosphere of ammonia and hydrogen mixture.

The nitride layer formed in the above manner has a very high acid resistance which is characteristic of metallic nitrides, is very resistant to corrosion from the common
mineral acids, organic acids and other chemicals and also its resistance against sea water corrosion is very high.

It also has super hardness, which is a characteristic of the nitride layer and its wear resistance is high. Furthermore, there is almost no difference in the dimension before and after hardening, also decrease in hardness by heating to the usual tempering temperature is small, resistance against oxidation is very high and formation of oxide scale is very small.

The nitride layer formed in this manner has a very high resistance against peeling as compared with the usual nitride layers and furthermore, its impact resistance is very high. The remarkable feature of the base texture of this structure is that the iron-iron solid solution and the alloy layer which is formed by diffusion of titanium have a strong fixing power.

Wide industrial utilization for this process can be anticipated since the operation can be carried out easily, cheaply and in a short time. That is, the process can be utilized for precision parts in the watch-making industry, parts for internal combustion engines, chemical machinery and equipment, ship and rolling stock parts and household utensils and kitchen wares.

The following example is an illustrative presently-preferred embodiment of the present invention. Titanium is electroplated to a thickness of 3,000 mm. by the process of U.S. Patent No. 3,074,860 on mild steel sheet having a carbon content of 0.15%, zinc is electro-plated on this further to a thickness of 1,000 mm., the sheet is then dipped for one hour in a sodium cyanide solution which is heated to 230° C., then removed from the solution and its surface cleaned. The thus-treated sheet has a Vickers hardness of over 800 and has high corrosion resistance as it is not affected even by 35% concentrated hydrochloric acid at room temperature. The difference in dimension before and after the treatment according to this invention was tested on gears made from mild steel of the same composition as gear pump and was found to be so small that it could not be measured with a micrometer and it was ascertained that it has a life 3 times that of high-quality stainless steel products as the result of application of the present process.

I claim:

1. A process for surface treating a member selected from the group consisting of iron and steel which comprises electro-plating electrolytically-active titanium in an aqueous alkaline solution over the entire surface of said member and immediately thereafter electro-plating zinc thereon to completely cover the resultant titanium plating, and then immersing the so-treated member in a cyanide salt bath at a temperature of about 600°–800° C. until the zinc has melted and vaporized, thereby forming a titanium-iron alloy and a nitride layer on the surface of said member.

2. A process for surface treating a member selected from the group consisting of iron and steel which comprises electro-plating electrolytically-active titanium in an aqueous alkaline solution over the entire surface of said member, heating the titanium-treated member to a temperature of about 150°–400° C. in a non-oxidizing atmosphere, thereby diffusing the titanium in said member, and then immersing the so-treated member in a cyanide salt bath at a temperature of about 600°–800° C. until a nitride layer is formed on the surface of said member.

3. A process for surface treating a member selected from the group consisting of iron and steel which comprises electro-plating electrolytically-active titanium in an aqueous alkaline solution over the entire surface of said member and heating the titanium-treated member to a temperature of about 600°–800° C. in a nitrogen gas atmosphere until a nitride layer is formed.

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