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# METHOD FOR THE PRODUCTION OF STRONGLY ADHESIVE METAL FILMS ON TITANIUM AND TITANIUM ALLOYS WITH A METALLIZATION PROCESS

H.-J. Hahn

Translation of "Verfahren zur Herstellung fest haftender metallischer Überzüge auf Titan und Titanlegierungen im Metallspritzverfahren", West German patent specification No. 24 42 742, July 3, 1975, pp. 1-4

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16. Abstract

A process for the spray-application of a strongly adhesive, thick antifriction layer on titanium and titanium alloys is proposed. The titanium/titanium alloy component to be coated is first subjected to cleaning in a pickling bath with reducing additives and sand-blasting, then coated with an intermediate layer of nickel, after which the final layer is applied. The formation of TiNi at the interface ensures strong bonding of the antifriction layer.

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**Method for the Production of Strongly Adhesive Metal Films on Titanium and Titanium Alloys with a Metal Spraying Process**

Hans-Jürgen Hahn

## Patent Claims

1. Process for the application of strongly adhesive metallic films for antifriction layers on titanium or titanium alloy components in a metal spray process, following a treatment of the components by grit blasting or chemical pickling, characterized by the fact that a protective film of a strong reduction agent such as solutions of hydrazine or hydroxylamine derivatives are applied to the components, and that a thin intermediate layer of nickel is applied to insure better adhesion of the wear-resistant layer which is to be applied afterward.

2. Process according to Claim 1, characterized by the fact that complexing hydrazine or hydroxylamine derivatives in the form of their salts are added already during blasting and cleaning in acid pickling baths.

3. Process according to Claims 1 or 2, characterized by the fact that the adhesion of the wear-resistant layer is improved by hardening at temperatures around 300° C and the formation of the intermetallic compound TiNi at the interface.

4. Process according to Claims 1 through 3, characterized by the fact that highly porous sintered layers are sprayed onto the components and that these are impregnated in a vacuum with oil or other antifriction liquids.

5. Process according to Claims 1 through 3, characterized by the fact that solid slip additives in the form of molybdenum sulfide or graphite are sintered in during the spray application of the antifriction layer.

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The invention concerns a process to apply adhesive metal films to titanium and titanium alloys with a metal spraying process.

Titanium and titanium alloys have a number of excellent properties as a result of which their technological application, especially in aeronautics and space travel, has considerably gained in significance. However, titanium and its alloys also have a number of disadvantages which are not acceptable especially in the above-mentioned fields, e.g. its poor antifriction properties, its extreme abrasion, and its tendency to wear due to dry friction. Further, titanium parts are also subject to fretting corrosion which is caused by high surface pressure at screw, bolted, or other types of connections.

A number of processes has been suggested to eliminate or at least alleviate these disadvantageous properties. For instance, in order to improve the wear characteristics of titanium components, it has been suggested to subject them to heat treatment in a salt bath, or to treat them with currentless or electrodeposition.

Many of these processes can only be advantageously utilized if the stress to which the components are subjected is relatively small. If greater stresses occur, the application of additional materials becomes a necessity, such as, for instance, the application of a steel film. However, this results in a considerable --and frequently inacceptable-- loss of the weight advantages which are attained by the use of titanium. This holds particularly true in view of the fact that considerable problems arise with the application of strongly adhesive metal films as titanium has a strong tendency to bond to oxygen and nitrogen. Even at room temperatures, new oxide and nitride layers form very quickly on recently cleaned titanium surfaces. These very thin layers are electroconductive; and, as a result, while electrodeposition is possible, the coating does not adhere well and is often not reproducible.

The affinity of titanium and titanium alloys to oxygen and nitrogen and the resultant formation of non-metallic layers hamper application of adhesive metal films to these materials.

The German Auslegeschrift [patent specification] No. 1,072,860 presents a process to clean the surfaces of metals and alloys which have a great affinity to oxygen and nitrogen. In this process, the surface to be cleaned is subjected to the reaction of an organic liquid, e.g. ester and alcohol. This is to prevent the reaction of the halogens with the liquid which results in compounds that are detrimental to metallization. However, experience has shown that with this process, too, it is very difficult to apply thicker antifriction layers in order to attain adhesive surfaces.

A fusion welding process has become known by which a metal sprayed layer is bonded to a relatively smooth metal surface. In this process, a nickel electrode deposits small nickel particles on the surface of the base metal, which are then fused to it. While the nickel is being fused to the base metal, the subsequently sprayed layers are only mechanically connected to the base metal and the protruding nickel particles. The bond of these layers is entirely unsatisfactory, especially for aeronautics and space applications.

The other process known to date for the application of additional layers is the so-called spray welding process. In this process, a molybdenum layer is sprayed onto the base metal. This does result in a good bond between the base metal and the sprayed-on metal, however, the bond between the molybdenum and the base metal requires considerable additional measures if it is to be sufficient for those applications which are most frequently required. Such additional measures include, for instance, the application of an undercut network of grooves to the surface of the base metal, so that the adhesive bond is supplemented by the additional force of the mechanical interlock between the base layer and the sprayed-on molybdenum. Another disadvantage of the above-mentioned composite processes is the fact that they require high temperatures and thus cause deformations in the base metal.

German patent specification No. 1,293,515 discusses a process in improve adhesion of metal layers by roughening the surface of the base metal prior to the application of the layers. The surface is roughened by sparks from a metallic electrode which does not consume itself, and which causes small recesses and holes to form. After the surface has been roughened, a thin intermediate metal layer is sprayed on which is also roughened by sparks from a metallic electrode which does not consume itself, and at the same time fused to the base metal. In this process, the intermediate layer consists of a metal whose melting point is lower than that of the final metal layer. After the electric spark treatment, the surface is subjected to a slight blasting process with an abrasive to remove the carbon-containing deposits left by the sparks. However, this process does not solve the problems of the application of adhesive layers on titanium and titanium alloys, as even molybdenum layers applied according to the plasma technique do not adhere satisfactorily to titanium.

To date, it has been attempted to counteract the oxidation between the cleaning and the metallization phases by constant moistening with water. However, as water usually contains air and other gases in their dissolved states, this process cannot quite eliminate the undesired surface reactions, either, and it can only be used when followed by an electrodeposition. In order to apply metal sprayed layers, the titanium component would have to be dried immediately prior to the process; it would then be exposed to air, and oxidation would begin immediately.

In order to improve the antifriction properties of the component, layers with self-lubricating deposits from sintered bronze with oil reserves are applied to the pores and to titanium alloys as counter-acting materials. However, experience has shown that after grit blasting of the surface, such sprayed-on bronze adheres so poorly to titanium and titanium alloys that the applied sintered layers separate easily even under relatively light loads and are thus useless as antifriction layers.

The invention is based on the task of creating a process which eliminates the aforementioned problems in the spray metal application of strongly adhesive metal layers on titanium and its alloys.

This task is solved by applying a protective film of a strong reduction agent to the components, such as solutions of hydrazine or hydroxylamine derivatives, and by spray-applying a thin intermediate layer of nickel so as to ensure better adhesion of the wear-resistant layer which is to be applied. These measures now make it possible to expose the cleaned titanium surfaces to air for a limited period of time without resulting in the oxidation effects which reduce adhesion. This is even true for the higher temperature required for metal spraying.

The process according to the invention further calls for the addition of strong reducing salts in the form of fluorides of hydrazine or hydroxylamine derivatives even during blasting and cleaning in acid pickling baths. This causes the oxides and nitrides of titanium to dissolve while complexing into as hydrozonium-hexafluortitanate $(N_2H_5)_2[TiF_6]$ or hydroxylammonium hexaflurotitanate $(NH_3OH)_2[TiF_6]$. At the same time, the dissolved oxygen from the air is also removed in the pickling baths, thus preventing renewed oxidation.

For various titanium alloys, the invention calls for improving the adhesion of the wear-resistant layer by hardening at temperatures around 300° C and formation of the intermetallic compound TiNi at the interface. The antifriction layers obtained in this manner adhere so well that they can withstand metal cutting work without chipping off.

The process according to the invention furthermore calls for the spray application of highly porous sintered layers which are vacuum-impregnated with oil or other antifriction liquids.

In order to improve the antifriction properties, solid slip additives in the form of molybdenum sulfide or graphite are to be sintered in when the antifriction layer is sprayed onto the component.

The following description contains data which have actually been obtained, however, these data should only be considered examples within the scope of the process according to the invention. The extent of the invention is not limited to the examples described herein.

Bolts and bearing shells of a Ti6A14V alloy are to receive a self-lubricating antifriction layer. For this purpose, the titanium alloy components are first subjected to a generally known surface treatment of degreasing and grit blasting. Immediately after this treatment, a solution of asymmetrical dimethylhydrazine --with a ratio of approximately 1:80-- is sprayed onto the components. This immediately forms a thin protective film which, for a period of at least three minutes, prevents any surface oxidation of the metallic blank surface due to exposure to air. Within these three minutes, the intermediate layer of nickel is sprayed onto the components, and the prepared, still hot components are now sprayed immediately with, for instance, sintered bronze SnBz6 according to DIN 17,662, with a thickness of 1 mm. This layer adheres so strongly to the titanium component that the surface can undergo metal cutting work without any problems. The resultant porous bronze layer is now impregnated with an oil with high pressure additives (hypoid oil) in a vacuum at 50° C. This bronze antifriction layer works perfectly and is able to withstand stress.

The thin nickel layer between the titanium surface and the antifriction metal, which must be applied in a thick layer, is a suitable adhesive agent. In order to attain good bonding between the titanium or the titanium alloy and the nickel layer, the intermetallic compound TiNi must form through the diffusion of nickel into the component. This occurs immediately when the nickel layer is sprayed on, as this diffusion takes place at the working temperature.

The antifriction properties of the deposited material can be improved even further when metallic powders with additions of solid slip additives, e.g. molybdenum sulfide or graphite, are used for the metal spray application.

If a wet pickling process is used to remove the oxide layer, experience has proven that a solution of 40% hydrofluoric acid and asymmetrical dimethylhydrazoniumfluoride, dissolved in an appropriate quantity of water, is especially effective in forming the anti-oxidation film. The prevailing opinion in the field holds that pickling solutions containing hydrofluoric acid generally will not allow a strongly adhesive metal layer to be applied to the pickled surfaces of a titanium component. However, the process according to the invention has clearly proven that the opposite is true.

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