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(54) **Preheating substrates prior to coating to remove hydrogen**

(57) In a method for coating articles having a metallic surface by applying a hard surface coating e.g. by chemical vapor deposition or physical vapor deposition, at temperatures below 400°C., onto an electrochemically and/or chemically produced metal layer (electroless plating), the article is heated to 100°C. - 400°C. for 2 to 24 hours prior to coating to remove hydrogen from the surface.

The coated article has a pleasing appearance and a high scratch, abrasion and corrosion resistance. The coating is particularly suited for decorative articles, watch movements, watch bands, watch crowns, surgical and optical instruments, cigarette lighters, ball-point pens and tools.

GB 2 045 810 A

SPECIFICATION

An improved method for coating articles having a metallic surface and a coated article obtained thereby

This invention relates to an improved method for coating articles having a metallic surface with a hard coating layer, and a coated article obtained thereby.

It is known to apply coatings of nitride- carbide- and boride-containing or similar hard materials on various articles. The most important methods which have been used for this purpose are the CVD method (chemical vapor deposition) and the PVD method (physical vapor deposition).

With these methods, it is possible to achieve a sufficient and lasting adhesion of the surface coating layer on the base or substrate only if coating temperatures of higher than 300°C., advantageously of hither than 400°C. are used. It is a disadvantage of these methods that locally high temperatures occur on the surface of the base, which may detrimentally affect the material of which the article is made. The current methods thus can only be utilized on articles made of materials which can tolerate temperatures of at least 300°C. to 400°C., without any danger to the properties of the end product due to irreversible unwanted effects, like warping, recrystallization and the like.

A PVD method has been developed in which the locally occurring high surface temperatures on the substrates are reduced so much during the application of the nitride-, carbide- and boride-containing hard materials, like TiN, ZrN, TiC, CrB and similar ones, or combinations thereof, and by this method the choice of substrate materials is enlarged. Thus it has become possible to coat, by commercially acceptable procedures, commercially manufactured articles which initially consist of materials, for example, chromium, nickel, stainless steel, brass, zinc, aluminium or alloys of said materials, particularly articles having an electroplated and/or chemical vapor deposited surface layer of those metals, with a thin coating layer of hard materials, like TiN, ZrN, TiC, CrB and similar ones, or combinations thereof.

However, it has been proved that the durability of the solidity of this hard coating layer is insufficient because the hard, thin, coating layer becomes loose, sooner or later, after it has been applied.

An object of the invention is to provide a durable coating of articles with hard materials, wherein the articles are not exposed to a temperature higher than 400°C.

The invention provides an improved method for coating articles having a metallic surface with a hard coating layer, characterised in that before coating the hard coating layer on the article, the article or its surface to be coated is heated for a time of from 2 to 24 hours at a temperature of from 100°C. to 400°C. to remove hydrogen from the surface of the article.

The said hard coating layer may be a nitride-, carbide- and/or boride-containing layer. The metallic surface may be of chromium, nickel, molybdenum, tungsten, cobalt, stainless steel, brass, zinc, aluminium, or alloys and/or combinations thereof.

The extraction of hydrogen particularly from an electroplated and/or chemically manufactured surface layer of the articles, which may not be exposed to a locally occurring surface temperature of higher than 400°C. is achieved, according to the invention, by heating the article or the surface layer of the article, prior to the coating treatment, for a time period of 2 to 24 hours, at 100°C. to 400°C. The hard coating layer can then be applied, advantageously according to the CVD or the PVD method. According to those methods, a thin, dense, continuous, hard, coating layer is deposited on and is metallurgically bonded to the underlying metal surface layer of the article.

The surfaces which are obtained with the invention treatment are distinguished not only by their hardness, but also by their beautiful pleasing appearance. They are therefore commercially utilizable in a variety of different ways and they are practically indestructible. The coating can be applied to decorative articles, watch movements, watch bands, watch crowns, surgical and optical instruments, articles of use like cigarette lighters, ball-point pens, etc. and tools.

The product has a commercially satisfactory, permanent, non-separable, surface coating layer of a hard material, for example a surface coating made of titanium nitride, zirconium nitride, chromium boride or similar hard material or combination thereof, applied on an electroplated and/or chemically produced (electroless plating) metal base, preferably made of chromium, nickel, molybdenum, tungsten, cobalt or combination thereof.

Tests have shown that electroplated and/or chemically produced layers, especially those made of chromium, nickel, molybdenum and tungsten or combination thereof, contain stored hydrogen. The hydrogen has the characteristic that it slowly effuses to the surface. Hard, thin, coating layers, like TiN, ZrN and similar ones, are very dense and therefore they are practically impermeable to hydrogen. When the hydrogen effuses to the surface of substrate, the hard material, coating layer is therefore lifted off from the inside of the article and thus the usability of the article is jeopardized. This does not occur when the hard coating layer is applied at a high temperature, namely above 400°C., because at such high temperatures an appreciable amount of the hydrogen is not contained in the substrate. If the hard layer is applied at a lower temperature, however, it has been found that a significant amount of hydrogen is present in the surface layer of the substrate. According to the invention, this hydrogen is removed in advance by a special preliminary heat treatment at a relatively low temperature applied over a long time period. The subsequently applied hard coating layer will not come loose if the substrate has been treated in this way to remove hydrogen before the hard coating layer is applied.

As the hard material, it particularly is suitable to apply a titanium nitride (TiN) or zirconium nitride (ZrN) coating layer, which is applied to an electroplated and/or chemically applied chromium or nickel layer. This surface has a gold-colored appearance and is scratch-, abrasion- and corrosion-resistant.

Although a particular preferred embodiment of the invention has been disclosed in detail for illustrative purposes, it will be recognized that variations or modifications of the disclosed apparatus, including the rearrangement of parts, lie within the scope of the present invention.

CLAIMS

1. An improved method for coating articles having a metallic surface with a hard coating layer, characterised in that before coating the hard coating layer on the article, the article or its surface to be coated is heated for a time of from 2 to 24 hous at a temperature of from 100°C. to 400°C. to remove hydrogen from the surface of the article.

2. A method according to Claim 1, wherein the said hard coating layer is a nitride-containing, carbide-containing and/or boride-containing layer.

3. A method according to Claim 1 or Claim 2, wherein the said hard coating layer is applied by the chemical vapor deposition method or the physical vapor deposition method.

4. A method according to any of Claims 1 to 3, wherein the said article has a metallic surface of chromium, nickel, molybdenum, tungsten, cobalt, stainless steel, brass, zinc, aluminium, or alloys and/or combinations thereof.

5. A method according to any of Claims 1 to 4, wherein said metallic surface is a metal surface coating.

6. A method according to any of Claims 1 to 5, wherein the said metal surface is an electroplated metal surface.

7. A method according to any of Claims 1 to 5, wherein the said article has a chemically applied metal surface.

8. A method according to Claim 5 and/or Claim 6, wherein the said electroplated and/or chemically applied metal surface is a chromium or nickel or an alloy of chromium and nickel.

9. A method according to Claim 8, wherein the hard coating layer applied to said metal surface is titanium nitride and/or zirconium nitride.

10. A coated article obtained by a method according to any of Claims 1 to 9.

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