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PROCESS FOR RENDERING A STEEL PIECE SUPERFICIALLY HARD AND CORROSION RESISTIVE, PIECE OBTAINED BY THE CARRYING OUT OF THIS PROCESS AND USE OF THE LATTER

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ABSTRACT OF THE DISCLOSURE

A process for rendering a steel piece superficially hard and corrosion resistant and the product of said process. An intermediate layer of at least one passive metal such as chromium is applied to the steel piece as by reduction of a chromium halide deposited on the piece, said passive metal layer diffusing at least partially into the base metal, and a hardening layer consisting of a refractory metal carbide, nitride or silicide such as titanium carbide for example, is thereafter applied chemically in the gas phase, as by treatment of the coated piece with a gaseous dispersion of titanium chloride in hydrocarbons such as methane, in the presence of hydrogen gas.

The present invention concerns a process for rendering a steel piece superficially hard and corrosion resistant; it also concerns the piece obtained by the carrying out of this process and the use of the latter.

It is known, for the superficial hardening of steel pieces, to chemically apply, in the gas-phase, onto said pieces a hardening layer, e.g. of titanium carbide, up to 10μ thick and having a VNH hardness of 3,000 to 4,000 kp./mm.^{2}.

However, these processes only apply to carbon steel, alloyed or not. These hardened pieces are therefore vulnerable to corrosion attack.

The object of the present invention is to remedy this drawback and to provide a process for simultaneously hardening such steels and make them corrosion resistant.

The process of the invention is characterized by the fact that an intermediate or first layer of at least one passive metal is applied onto the steel piece, said layer diffusing at least partially into the base metal, and that a hardening layer consisting of a metal carbide, nitride, boride, or silicide is thereafter applied chemically in the gas-phase. The term "passive metal" is utilized as defining a metal characterized by resistance to corrosion—so-called passivity to chemical attack—and is to be interpreted as such when reference is made thereto throughout the specification and in the claims.

The piece obtained by the carrying out of this process is characterized by the fact that it is made of a steel base coated with an intermediate or first layer of a passive metal diffusing at least partially into the base metal, this layer being itself coated with a hardening layer consisting of a metal carbide, nitride or silicide.

The use of the present process concerns the manufacture of watch-case elements.

According to a preferred embodiment of the present invention, the above mentioned first layer of at least one passive metal is deposited, as is the hardening layer, in the gas-phase. The metal used can be chromium, tantalum, aluminum, silicon and nickel, the latter being only considered, however, when the second or hardening layer

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does not consist of titanium carbide. In the case of chromium, experiments have shown that the metal deposited forms, together with the carbon of the steel, chromium carbides which fit particularly well, in a carbide containing base, for the subsequent deposition of the titanium carbide hardening layer.

During chromization, the two following reactions occur, one or the other being predominant depending on the reducing agent chosen, hydrogen or metal:

$$CrCl_2+H_2 \rightarrow Cr+2HCl \quad \text{(I)}$$

$$CrCl_2+Fe \rightarrow Cr+FeCl_2 \quad \text{(II)}$$

The starting material is a chromium halide, for instance chromium trichloride known in the trade under the name of $CrCl_3$ Hexahydrate, written $CrCl_2$ in Equations I and II for simplification, but which comprises actually chromium halides corresponding to numbers 2 and 3 of the chromium valences. The reducing agent of reaction I is hydrogen which is progressively added to the chromium halide, whereas in Equation II, the reducing agent, which is generally identical with the base metal, is iron.

According to the conditions chosen, temperature, pressure, gas concentration, nature of the base material, etc., the chromium layer which forms on the surface of the sample diffuses partially or entirely into it.

Deposition temperatures will be preferentially above 800° C. for having a high enough chromium chloride pressure.

Large diffusion zones can be obtained in steels containing less than 0.05% C. Steels which are ferrite rich or which contain elements that take part to the ferrite phase or easily bond with carbon, e.g. Cr, Mo, W, V, Ta, Ti, Zr, Al, Si and Nb favor diffusion. For instance, chromium diffusion layers form easily on stainless steel.

By adding hydrogen in excess to chromium halides, the exchange reaction II is eliminated and the deposition reaction I is favored.

By the use of high carbon steels (C content$\geqslant$ 0.2%), austenite steels or steels containing elements taking part to the formation of the austenite phase, e.g. Ni, Mn, Cu and N, the diffusion is strongly decreased.

Steels having standard numbers (Werkstoffnummer) 1,2000 to 1,3500 build, when chromium is deposited, chromium carbide layers having good adhesion and no pores, and being hard and wear resistant.

Gaseous HCl can also be reacted with Cr metal to form $CrCl_2$ which will be reduced thereafter to a layer of Cr metal. A 100:1 to 20:1 mixture of argon and HCl is reacted, at a temperature above 800° C. (preferentially at 850° C.) on granulated or pulverized chromium evenly dispersed in a container entirely made of alumina. The equilibrium reaction I applies there, but in the opposite direction.

In place of HCl, elementary chlorine can be used for making $CrCl_2$ according to the following equation:

$$Cr + Cl_2 \xrightarrow{\Delta} CrCl_2$$

For the deposition of chromium, the mixture obtained above, $Cr/Ar/H_2$/remainder of HCl, is allowed to react with the substrate, either directly or diluted with H_2. Large volumes of gas under atmospheric or reduced pressure (preferentially 50 to 100 torr) are used for eliminating, as quickly as possible, the gaseous products which are normally HCl and $FeCl_2$.

It is also possible to produce the first layer with several metals, e.g. by the deposition of a first layer of Si and a second with Cr.

Care should be exercised so that the first layer is not softer than the base-material.

The final hardening coating, that is the second layer, which is known as well as the methods for obtaining it, will be also obtained chemically in the gas-phase. It will consist of a carbide, nitride or silicide, of a metal from Groups III to VI of the Periodical Table, e.g. tantalum or titanium carbide.

In the case of, for instance, titanium carbide, a titanium compound such as $TiCl_4$ is progressively evaporated from an evaporator for liquids and continuously added to a gaseous flow of hydrocarbons. Such are methane, acetylene or ethylene, which are added in their normal gaseous state, and dicyclopentadiene which must be vaporized beforehand.

A 1:1:100 to 5:5:100 gaseous mixture of CH_4, $TiCl_4$ and H_2 can be used on the base-material in an Inconel reactor, avoiding carefully all iron parts.

From the equation

$$CH_4 + TiCl_4 \xrightarrow{\Delta, H_2} TiC + 4HCl \qquad \text{(III)}$$

there is an increase in the volume of the products that is the reason for which working under a reduced pressure of 10–100 torr (temperature 800–900° C.) is preferable.

The said second layer can also be made of an alumina layer or, further, of a composite layer, e.g. of chromium carbide and titanium carbide or of titanium carbide and nitride for having color hues varying from golden to silvered.

The present process permits obtaining any hard and corrosion resistant pieces, particularly watch-case elements such as middle parts, bezels, protective caps for middle parts, bezels, etc.

What we claim is:

1. A watch element comprising a shaped steel substrate having (an at least partially diffused) a gas-phase chemically deposited chromium sulface layer (of at least one corrosion resistant material having metallic characteristics selected from the group consisting of chromium, tantalum, aluminum, silicon, and nickel) at least partially diffused into said steel substrate, and a gas-phase chemically deposited second layer (formed on said first layer) on said chromium layer, said second layer (selected from the group consisting of titanium carbide, titanium nitride, a mixture of titanium carbide and titanium nitride, chromium carbide, tantalum carbide, nickel boride and aluminum oxide) comprising titanium carbide.

2. The watch element as claimed in claim **1** wherein said first layer is the reduction product obtained by reacting chromium trichloride with a reducing agent.

3. The watch element as claimed in claim **1** in which said first layer is at least as hard as the substrate material.

4. The watch element as claimed in claim **1** in which said first layer is the reduction product of the reaction product of one of gaseous HCl and chlorine gas on chromium metal applied directly to said substrate.

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RALPH S. KENDALL, Primary Examiner

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117—106 A, 106 C, 107.2 R; 29—195; 58—88 R

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CERTIFICATE OF CORRECTION

PATENT NO. : 3,796,588

DATED : March 27, 1974

INVENTOR(S) : HANS E. HINTERMANN and WERNER HANNI

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3,line 33, change "sulface" to --surface--; Column 3, lines 31 to 39 and Column 4, lines 1 to 4, all material within parentheses and the parentheses should be deleted, Claim 1 should read as follows:

-- 1. A watch element comprising a shaped steel substrate having a gas-phase chemically deposited chromium surface layer at least partially diffused into said steel substrate, and a gas-phase chemically deposited second layer on said chromium layer, said second layer comprising titanium carbide. --

Signed and sealed this 1st day of July 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

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