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[54] **COATING OF A STEEL OR IRON WITH A CHROMIUM CONTAINING SURFACE LAYER**

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[57] **ABSTRACT**

A ductile chromium coating is produced on a carbon-containing steel or iron substrate by first coating the substrate with at least one metal from the group consisting of Cu, Ag, Au, Pd, Pt, Rh, Ir, Ru, Os and CuNi alloy and then depositing a metal layer consisting essentially of chromium by electrolysis from a salt bath at a temperature in excess of 700°C.

2 Claims, No Drawings

COATING OF A STEEL OR IRON WITH A CHROMIUM CONTAINING SURFACE LAYER

The present invention relates to a process for the preparation of a ductile surface coating of chromium on steel or iron.

To coat steel and iron objects with a chromium layer is an old, well-known technique widely used. Normally the coating with chromium is carried out by means of electrolysis in an aqueous solution containing chromic acid. The temperature of the electrolyte is usually 50°-60°C.

A chromium layer prepared by means of water electrolysis serves substantially only a decorative purpose, as the layer normally has bad corrosion properties. This is due to the fact that such a chromium layer is criss-crossed by a great number of microcracks, through which corrosive media may penetrate to the steel underlayer and corrode this. For this reason chromium coated objects exposed to atmospheric corrosion, e.g., car details, are coated with a corrosion protective layer of nickel or nickel and copper between the steel underlayer and the chromium layer. The chromium layer is not ductile, and therefore objects to be chromium coated must have the form intended for final use before the chromium coating, which is a great disadvantage for such details as piston rings and springs. The brittleness of chromium layers prepared by means of water electrolysis depends on a relatively high oxygen content.

It is also known to coat steel objects or substrates, preferably such having a low content of carbon, at high temperature with a coherent chromium layer according to the so-called pack-diffusion method (chromizing). The chromium layers obtained are tight and have very good corrosion properties. There are several different pack-diffusion methods, and they are characterized in that the surface coating is obtained at a high temperature, often more than 1000°C, and that the chromium atoms are conveyed to the surface of the steel in the form of gaseous chromium halide, e.g. CrCl_2 . This reacts with the iron atoms of the underlayer forming chromium and gaseous iron halide. It is also known that the chromium layer to some extent reacts with the carbon in the steel underlayer, a very brittle layer of chromium carbide being obtained between the steel underlayer and the chromium layer. The greatest disadvantages of the known methods are thus that they do not provide ductile and tight chromium layers on medium and high carbon steels or iron.

According to the present invention steel or iron substrates are coated with a metal layer, substantially consisting of chromium. This chromium layer is in the ductile state. In this way the excellent corrosion properties of the chromium are utilized at the same time as the coated material is ductile.

A steel or iron coated according to the present invention can thus be used as constructional material, especially in corroding atmosphere, e.g. for piston rings, springs, mine hoisting ropes, bracing wires and fence wire.

The present process is characterized in that the steel or iron surface is coated with a layer substantially consisting of one or several of the metals Cu, Ag, Au, Pd, Pt, Rh, Ir, Ru or Os or of a CuNi-alloy and that a layer substantially consisting of chromium is then precipitated by electrolysis in a salt melt containing a chro-

mium halide or by reduction of a gaseous chromium halide.

Thus, according to the invention a layer of a metal is first precipitated on the steel or iron surface, acting as a barrier for a carbon diffusion from the iron, and then a layer is precipitated substantially consisting of chromium. According to the invention the precipitation of chromium either takes place electrolytically in a salt bath containing a chromium halide or by reduction of a chromium halide in gaseous phase. In both cases the precipitation must take place at a high temperature.

The first layer, the so-called barrier layer, can thus according to the invention consist of one or several of the metals copper, silver, gold, palladium, platinum, rhodium, iridium, ruthenium or osmium or an alloy of one or several of these metals as main constituent. Copper has been found to be most suitable, and especially good results of the end product have been obtained, when this barrier layer of copper also contains some amount of nickel. The barrier layer can be coated according to some known method, preferably electrolytically. It is an advantage if this layer is heat treated before the chromium layer is coated. In this way a stronger adhesion to the underlayer is obtained by diffusion in the boundary surface. If no special heat treatment is carried out before the chromium coating, the diffusion takes place during the chromium coating, as this must be carried out at a high temperature according to the invention.

The barrier layer will prevent diffusion of carbon from the iron to the chromium layer deposited on the barrier layer. This prevents the development of chromium carbides making the chromium layer brittle. The thickness of the barrier layer must be adapted to the carbon content in the steel or iron to be coated. Thus a high carbon steel requires a thicker barrier layer than a low carbon steel. The thickness of the barrier layer is also dependent on the temperature selected during the chromium coating. At temperatures within a higher temperature range, e.g. more than 1000°C, a thicker barrier layer is required than if the chromium coating takes place at for instance 800°C.

The chromium coating in salt melt is carried out at a temperature high enough for a metal diffusion occurring through the interfaces. To obtain a diffusion within the time of electrolysis the temperature should therefore exceed 700°C. The upper limit of the temperature depends on the composition of the salt melt, but for practical reasons 1100°C should not be exceeded.

Usually the salt melt substantially consists of sodium chloride or potassium chloride or preferably a mixture thereof. In addition it must contain a chromium halide, preferably chromium (II)chloride. It is also suitable that the melt is protected with a neutral atmosphere, e.g. argon gas, to avoid oxidation.

The chromium coating in gaseous phase is carried out through reduction of a chromium halide, preferably chromium(II)chloride, in gaseous phase with hydrogen gas. This reduction must be carried out at a temperature higher than 1000°C.

At the chromium coating in salt melt as well as in gaseous phase the chromium halide used can to a small extent be replaced with another metal halide, e.g., nickel halide, the coating being formed by an alloy substantially consisting of chromium.

By the present invention, the presents of high amounts of oxygen is avoided in the chromium layer.

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High amounts of oxygen cause embrittlement of the chromium layer. The barrier layer prevents the formation of carbide in the chromium layer. The relatively high temperatures at which the chromium coating is carried out result in good contact between the coating layers and the underlayer due to metal diffusion. All this leads to a product that after the coating with chromium can still be shaped or worked to some extent without the chromium layer breaking.

The invention will be more closely described in the following examples.

EXAMPLE 1.

A steel wire, which at an analysis showed 0.12 percent C, 0.22 percent Si and 0.5 percent Mn was coated with a copper layer of 0.003 mm thickness by means of electrolysis at room temperature for 1.5 min. The electrolyte consisted of an aqueous solution containing 25 g/l copper cyanide, 34 g/l sodium cyanide and 15 g/l sodium carbonate. The current density was 10 A/dm². A chromium layer of 0.007 mm thickness was applied to this copper layer by means of electrolysis in salt melt for 10 min. at 750°C, the current density being 3.6 A/dm². 2. The electrolysis was carried out in argon atmosphere. The composition of the salt melt was 49.5 percent by weight of NaCl, 49.5 percent by weight of KCl and 1 percent by weight of CrCl₂. The chromium layer obtained was coherent, fine-granular and ductile. The coated wire was wound around its own diameter without the chromium layer breaking or delaminating from the underlayer.

EXAMPLE 2.

A high carbon flat wire, which at analysis showed 0.81 percent C, 0.23 percent Si and 0.54 percent Mn, was coated with a nickel layer of 0.002 mm thickness by means of electrolysis at room temperature. The current density was 5 A/dm² and the time of electrolysis was 2 min. The composition of the electrolyte was 300 g/l nickel sulphate, 30 g/l nickel chloride and 30 g/l boric acid.

Then a copper layer of 0.003 mm thickness was applied to this nickel layer by means of electrolysis. The same electrolyte and in other respects the same conditions as in example 1 were used.

Finally a chromium layer of 0.005 mm thickness was applied by means of electrolysis in argon atmosphere at

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a temperature of 900°C in a salt melt consisting of 49 percent by weight of NaCl, 49 percent by weight of KCl and 2 percent by weight of CrCl₂.

The chromium layer obtained was ductile and the flat wire could be bent 180° without the coating layer breaking or flaking.

EXAMPLE 3.

A copper layer of 0.003 mm thickness was applied by means of electrolysis to a high carbon band steel. The band steel showed at analysis 0.80 percent C, 0.23 percent Si and 0.54 percent Mn. The electrolysis was carried out in the same electrolyte and in other respects under the same conditions as in example 1. Then the band steel was coated electrolytically with another layer of nickel. The thickness of the nickel layer was 0.005 mm. The nickel electrolyte consisted of an aqueous solution containing 300 g/l nickel sulphate, 45 g/l nickel chloride, 35 g/l boric acid and a wetting agent, viz. sodium dioctylsulphosuccinate, which was added as a solution of 7 percent in an amount of 5 ml per liter of electrolyte. The electrolysis was carried out at 50°C with a current density of 15 A/dm² for 2 min.

Finally the band steel was coated with a chromium layer of 0.012 mm thickness by means of electrolysis in a salt melt of 47.5 percent by weight of NaCl, 47.5 percent by weight of KCl and 5.0 percent by weight of CrCl₂. The electrolysis was carried out at 900°C in argon atmosphere. The current density was 7.1 A/dm² and the time of electrolysis was 10 min. The band was bent 180° without the chromium layer breaking or delaminating.

What is claimed is:

1. A process for producing a ductile metal coating consisting essentially of chromium on carbon-containing steel or iron substrate which comprises, applying a barrier layer of at least one metal selected from the group consisting of Cu, Ag, Au, Pd, Pt, Rh, Ir, Ru, Os and CuNi alloy to said substrate and then depositing on said barrier layer a layer consisting essentially of said chromium by electrolysis from a molten salt bath containing chromium halide at a temperature in excess of 700°C.

2. The process of claim 1, wherein the temperature of said salt bath is at least about 1000°C.

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