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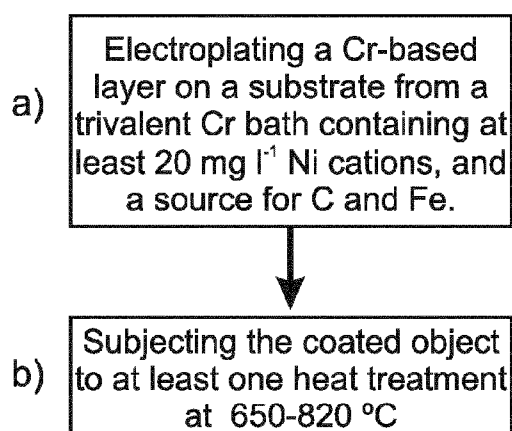
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(54) Title: CHROMIUM-BASED COATING, A METHOD FOR PRODUCING A CHROMIUM-BASED COATING AND A COATED OBJECT

Fig. 1



(57) Abstract: (57) abstract The invention relates to a chromium- based coating comprising chromium (Cr), carbon (C) and iron (Fe), Cr being electroplated from a trivalent Cr bath. The coating is characterized in further comprising nickel (Ni) electroplated from the Cr bath containing at least 20 mg l⁻¹ Ni cations, in that C is at least partially in the form of at least one chromium carbide compound, in that the coating has been heat-treated at a temperature of 650-820 °C or at a temperature of 700-800 °C, and in that the hardness of the coating is at least 1,500 HV on a Vickers microhardness scale as measured according to standard SFS-EN ISO 4516. The invention further relates to a method for producing a coating and to a coated object. (Fig. 1)

CHROMIUM-BASED COATING, A METHOD FOR PRODUCING A CHROMIUM-BASED COATING AND A COATED OBJECT

FIELD OF THE INVENTION

5 The invention relates to a chromium-based coating and a method for producing a chromium-based coating. The invention also relates to an object coated with a chromium-based coating.

BACKGROUND OF THE INVENTION

Chromium coating is widely used as a surface coating for different articles because of its high hardness value, attractive appearance and superior wear and corrosion resistance. Traditionally, Cr deposition is accomplished by electroplating from an electrolytic bath containing hexavalent Cr ions. The process is highly toxic in nature. Lots of efforts have been made to develop alternative coatings and coating processes to replace hexavalent Cr in electroplating. 15 Among those alternative processes, trivalent Cr electroplating seems to be attractive due to its low cost, convenience of fabrication through the use of environmental friendly and non-toxic chemicals, and ability to produce a bright Cr deposit. However, an industrial scale process giving a hard and corrosion resistant Cr deposit through an aqueous trivalent chromium solution is still difficult to achieve.

Many chromium plating processes of prior art are not capable of producing coatings with a Vickers microhardness value of 1500 HV or more as measured according to standard SFS-EN ISO 4516. Further defects of the known chromium-based coatings are their inadequate wear and corrosion resistances. Chromium coating as such is very brittle in character. The number of cracks and micro-cracks in a chromium coating increas- 35

es together with the thickness of the coating, thus impairing the corrosion resistance of the coating.

Deposition of nickel, either by electroless plating or electroplating, has also been proposed as an alternative to hard chrome. Drawbacks of nickel plating include deficiencies in hardness, friction coefficient and wear resistance. Nickel plating and chrome are not interchangeable coatings. The two have unique deposit properties and, therefore, each has its distinct applications.

Partial solutions to the problem have been proposed in the patent documents, WO 2015/107256 A1, WO 2015/107255 A1, WO 2014/111624 A1 and WO 2014/111616 A1, in which chromium-containing coatings are described.

Further, in the document Huang et al 2009 (Hardness variation and corrosion behavior of as-plated and annealed Cr-Ni alloy deposits electroplated in a trivalent chromium-based bath, Surface & Coatings Technology 203: 3686), a method for producing a Cr-Ni alloy -based coating is disclosed. The coating suffers from poor corrosion resistance if heat-treated at a temperature over 350 °C. Therefore, a sequential two-step electrodeposition method is recommended.

In Huang et al. 2014 (Microstructure analysis of a Cr-Ni multilayer pulse-electroplated in a bath containing trivalent chromium and divalent nickel ions, Surface & Coatings Technology 255: 153), on the other hand, a Cr-Ni multilayer comprised of alternating nanosized amorphous Cr-rich and crystalline Ni-rich sublayers was successfully prepared by pulse-current electroplating in a plating bath containing Cr^{3+} and Ni^{2+} ions. In Huang et al. 2009 and Huang et al. 2014, the nickel concentration in the electroplating bath was 0.2 M and 0.4 M, respectively.

PURPOSE OF THE INVENTION

The purpose of the invention is to provide a new type of a chromium-based coating and a method for producing a chromium-based coating.

5 SUMMARY

The chromium-based coating according to the present disclosure is characterized by what is presented in claim 1.

10 The method for producing a chromium-based coating according to the present disclosure is characterized by what is presented in claim 10.

A coated object according to the present disclosure is characterized by what is presented in claim 22.

15

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the disclosure and constitute a part of this specification, illustrate embodiments of the invention and together with the description help to explain the principles of the invention. In the drawings:

20 Fig. 1 is a flow chart illustration of an embodiment of the method according to the current disclosure.

25 Fig. 2 is a schematic presentation of an embodiment of a coating according to the present disclosure.

30 DETAILED DESCRIPTION OF THE INVENTION

In one aspect, a chromium-based coating comprising chromium (Cr), carbon (C) and iron (Fe), Cr being electroplated from a trivalent Cr bath is disclosed. The coating is characterized in that the coating further comprises nickel (Ni) electroplated from

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the Cr bath containing at least 20 mg l⁻¹ Ni cations, in that C is at least partially in the form of at least one chromium carbide compound, in that the coating has been heat-treated at a temperature of 650-820 °C or at a temperature of 700-800 °C, and in that the hardness of the coating is at least 1,500 HV on a Vickers microhardness scale as measured according to standard SFS-EN ISO 4516. The standard is based on a micro-indentation test of inorganic coatings, including metal coatings.

The coating according to the present disclosure typically comprises 90-95 w-% Cr. The Fe content of the coating is typically 5-8 w-%. The Ni content is typically 0.5-3 w-%. The coating composition can be analyzed by energy dispersive X-ray spectroscopy (EDS). The coating further comprises C, but the amount is not measurable with an EDS measurement. Carbon is present as at least one carbide. Due to the method of manufacture, the coating typically contains further elements in addition to Cr, Ni, Fe and C. For example copper (Cu) and zinc (Zn) may be present. They may exist as pure elements or in various compounds or mixtures with Cr, Ni Fe and C or each other.

In this disclosure, unless otherwise stated, electroplating, electrolytic plating and electrodeposition are to be understood as synonyms. By depositing a layer on the object is herein meant depositing a layer directly on the object to be coated or on the previous layer that has been deposited on the object. In the present disclosure, Cr is deposited through electroplating from a trivalent Cr bath. In this connection, the wording "electroplating from a trivalent chromium bath" is used to define a process step in which a chromium-based layer is deposited from an electrolytic bath in which chromium is present substantially only in the trivalent form.

The Ni source for the current coating is the Cr bath. The bath contains at least 20 mg l⁻¹ Ni cations. The cations can be Ni²⁺ cations or Ni⁴⁺ cations. It is possible that both Ni²⁺ cations and Ni⁴⁺ cations are the source of the Ni in the coating. In one embodiment, the Cr bath contains 20 to 150 mg l⁻¹ Ni cations. In one embodiment, the Cr bath contains 20 to 80 mg l⁻¹ Ni cations. Further, it is possible that the bath contains at least 50 mg l⁻¹ Ni cations. For example, the bath may contain 50 to 100 mg l⁻¹ Ni cations.

The thickness of the Cr-containing layer(s) can vary widely depending on the application. For decorative coating applications, a thinner layer is necessary than for corrosion or wear-resistant coating applications. The thickness of the coating depends on the number and thickness of the layers it comprises. The thickness of the coating can vary between 0.05-200 µm. The thickness of the coating may be, for example 0.5-100 µm. Alternatively, the thickness of the coating may be 0.3-5 µm.

The thickness and the composition of both the coating and its optional constituent layers together determine the properties of the coating. Typically coatings according to the present disclosure are hard. They can be used to replace traditional hard chromium coatings.

In one embodiment, the hardness of the coating is at least 1,500 HV_{0.05}. Embodiments can be envisaged in which the hardness of the coating is at least 2,000 HV.

In one embodiment, the at least one chromium carbide compound comprises Cr₃C₂, Cr₇C₃ or Cr₂₃C₆, or a combination thereof. The term chromium carbide is herein to be understood to include all the chemical compositions of chromium carbide, such as Cr₃C₂, Cr₇C₃ and Cr₂₃C₆. The amount and ration between different

chromium carbide compounds can vary. Chromium carbides advantageously improve the hardness of the coating.

In one embodiment, at least some of the Ni and Cr are dissolved in each other. Ni and Cr are dissolvable in each other in different concentrations. In other words, the metals can be completely dissolved in each other. The metals can alternatively be only partially dissolved in each other. The mutual dissolving may take place during a heat treatment of the coating according to the present disclosure. When the two metals are at least partially dissolved in each other, Ni is not necessarily detectable in an XRD spectrum measurement.

It is possible that the coating comprises one or more chromium oxide. Without limiting the current disclosure to any specific theory, the chromium oxide(s) may be formed during heat treatment. Examples of chromium oxides that can be present in the coating are CrO_3 , CrO , Cr_2O_3 or their combinations.

It is further possible that the coating comprises chromium nitride (CrN). Without limiting the current disclosure to any specific theory, the chromium nitride may be formed during heat treatment.

Both chromium oxide(s) and chromium nitride may influence the properties of the coating according to the present disclosure.

The abrasion wear of a coating can be measured for example by the Taber abrasion test. The result is expressed as a Taber index, where a smaller value indicates higher abrasion resistance. Typical values of hard chromium coatings range from 2 to 5 when the test is done according to the standard ISO 9352. The test was performed with TABER 5135 Abraser, the type of the wheel was CS 10, rotation speed 72 rpm, load 1,000 g and the total number of cycles 6,000. The wear was determined by measuring the ini-

tial weight of the object, intermediate weights after every 1,000 cycles and the end weight of the object after finishing the test. The coating according to the present disclosure has excellent abrasion resistance indicated by a Taber index of 2 and below under the same test conditions. In one embodiment, the Taber index of the coating measured by the Taber abrasion test according to ISO 9352 is below 2, or below 1.

10 In one embodiment, the coating forms at least two layers with distinctive element compositions. In other words, the coating according to the present disclosure can be used as a combination with other layers of coating. The other layers of coating may comprise
15 different materials, which can be selected from metals and their alloys or from other substances used for coatings. By a layer is herein meant a segment of a coating that is substantially parallel to the surface of a coating and is distinguishable in an electron micrograph (such as transmission electron micrograph, TEM, or scanning electron micrograph, SEM), light micrograph or by energy-dispersive X-ray spectroscopy (EDS). The visibility of the layers can be improved by using methods such as etching or ion etching during
20 cross-sectioning of the coating to be analyzed. The boundaries between layers do not need to be well defined. On the contrary, during a heat treatment, the boundaries of the layers mix to some extent. Without limiting the invention according to the present disclosure to any specific theory, there might be some amount of migration or diffusion of layer components during the heat treatment. The extent to which the components might be migrating or diffusing depends, for example, on the duration and intensity of the heat
25 treatment and the layer components.
30
35

In one embodiment, there is a mixed layer between the substrate and the chromium-based coating, said mixed layer comprising both substrate material and coating components and being produced by heat-treatment of the coated substrate.

By a mixed layer is herein meant a layer that shares some properties with the neighboring layers, but remains distinguishable from them. A mixed layer can be located between the substrate and the chromium-based coating. In cases where the coating comprises more than one layer, the mixed layer can additionally or alternatively be located between two layers of coating. If the coating according to the present disclosure comprises an intermediate layer, the mixed layer can additionally or alternatively be located between an intermediate layer and a coating layer.

If the coating forms at least two layers with distinctive element compositions, a mixed layer may be present between any two layers with distinctive element compositions.

The mixed layer can be a multiphase layer. For example, a mixed layer that is a multiphase layer may comprise Ni-Cr and the Cr-based coating according to the present disclosure. A multiphase layer may comprise Fe-Cr and the Cr-based coating according to the present disclosure. A multiphase layer may comprise X-Cr and the Cr-based coating according to the present disclosure. X denotes any element or compound with which the Cr-based coating according to the present disclosure may be mixed with.

By a phase is herein meant a region in which the physical properties of the substance are constant. One layer can comprise a single phase or it can comprise more than one phase, each of which can be formed of one or more element, substance or compound. A layer can comprise more than one element, substance or compound, in which case each of them can independently

comprise one or more phases. In every case in which there are two or more phases in a layer - representing one or more element, substance or compound - the layer is called a multiphase layer.

5 When the coating according to the present disclosure comprises more than one layer, there can be an intermediate layer between the two layers of coating. For example, the intermediate layer may contain copper or an alloy of copper. For example, the intermediate
10 layer may contain molybdenum or an alloy of molybdenum. The intermediate layer may contain inorganic nonmetallic solid selected from the group comprising metal oxides, metal carbides, metal borides, metal nitrides, metal silicides, and mixtures thereof.

15 Further, the adhesion between two neighboring layers can be enhanced. For example, a strike layer can be positioned between the layers. A strike layer is one possible alternative of an intermediate layer. The strike layer may comprise sulphamate nickel,
20 bright nickel, titanium, or any other suitable material. The surface structure of the layer that is first coated on the substrate can be amended through etching, for example. The surface of the first layer can be treated with strong acid, preferably with 30 %
25 (w/w) hydrochloric acid, before depositing the strike layer.

 In one embodiment, the coating is coated directly on a substrate. By a substrate is herein meant
30 any surface on which the coating according to the present disclosure is coated on. Generally, the coating according to the present disclosure can be used on variable substrates. Therefore, in many applications, there is no need to provide an underlayer or a strike
35 layer on the substrate before coating. The substrate can be made of a metal or of metal alloy. For example, the substrate may be steel, copper or nickel. The sub-

strate can be made of ceramic material. The substrate does not need to be homogenous material. In other words, the substrate may be heterogeneous material. The substrate can be layered. For example, the substrate can be a steel object coated by a layer of nickel phosphorus alloy (Ni-P). It is possible for the substrate to comprise a Ni strike layer under the coating according to the present disclosure.

10 In one embodiment, the coating further comprises a top layer. Thin film deposition, such as physical vapor deposition (PVD), chemical vapor deposition (CVD) or atomic layer deposition (ALD) can be used for producing the top layer. By a top layer is
15 herein meant a layer positioned on the outer surface of the coated object. Providing a top layer on the coated object may be used for adjusting the colour of the coated object or for altering the friction and/or wear-resistance properties of the coated object. The
20 top layer may comprise metal, metal alloy, ceramic, or diamond like carbon.

In one aspect, a method for producing a chromium-based coating according to the current disclosure on an object by electroplating from a trivalent Cr bath is disclosed. The method is characterized in that it comprises the steps of

a) depositing a layer of Cr from a trivalent Cr bath on an object, the bath comprising at least one source for trivalent Cr, at least 20 mg l⁻¹ Ni cations, at least one source for C and at least one source for Fe, so that Ni, C and Fe are incorporated into the Cr layer; and

b) subjecting the coated object to at least one heat treatment at a temperature of 650-820 °C, or at a temperature of 700-800 °C, to amend the mechanical and physical properties of the coating.

At step a) of the method, a Cr layer is deposited on a coatable object. During the Cr deposition, Ni and Fe are codeposited from the bath. C is also included
5 in the deposited layer. The Cr electroplating step can be carried out using any commercially available Cr(III) bath. One example of an electrolyte solution that has been used in the trivalent chromium coating step is the one sold by Atotech Deutschland GmbH under
10 trade name Trichrome Plus®. In one embodiment, the at least one source for Ni is NiCl_2 or metallic Ni. The concentration of Ni cations in the Cr bath may be, for example 20 to 150 mg l $^{-1}$. The concentration of Ni cations in the Cr bath may be, for example 20 to 80 mg
15 l $^{-1}$. Further, it is possible that the concentration of Ni cations in the Cr bath may be at least 50 mg l $^{-1}$. For example, the bath may contain 50 to 100 mg l $^{-1}$ Ni cations.

The determination of Ni concentration in the
20 bath is performed with methods known in the art. For example, atomic absorption spectroscopy (AAS) may be used. The methods require extensive dilution of the bath solution for carrying out the analysis. Typically, a dilution factor of 25 is used. Therefore, the
25 measurement values are prone to have inaccuracies in the range of some mg l $^{-1}$.

The current density during the electroplating can influence the exact coating composition, as the
30 relative coating efficiencies of different ions vary according to the current density. In one embodiment, the current density during the coating is 10-50 A dm $^{-2}$, or 15 A dm $^{-2}$. It is thus possible to use a current density of 15 A dm $^{-2}$. Also current densities, such as 20
35 or 40 A dm $^{-2}$ are suitable.

At step b) of the method, the coated object is subjected to a heat treatment to amend the mechanical and physical properties of the coating.

Additionally, depending on the material of the coated object (i.e. substrate material), also the object properties can be amended. For example, if the coated object is steel and the heat treatment is carried out at a suitable temperature, the steel can be hardened at step b). Such a heat treatment can be performed at a temperature of, for example, 700 °C or 800 °C.

Hardening is a metallurgical process used to increase the hardness of a metal. As an example, steel can be hardened by cooling from above the critical temperature range at a rate that prevents the formation of ferrite and pearlite and results in the formation of martensite (quenching). Hardening may involve cooling in water, oil or air, according to the composition and size of the article and the hardenability of the steel. In case the hardening of a metal object is carried out in connection with a heat treatment of the coated object, it is possible to subsequently subject the object to annealing or tempering in a second heat treatment, which is carried out after quenching. It is also possible to subject an already hardened metal object to a further hardening during the heat treatment of the coated object even though the metal object had originally been hardened before the coating.

The method can comprise further heat treatments especially targeted for amending the mechanical and physical properties of the coated object.

At step b), for example crystalline forms of the coating constituents may be formed. Depending on the length and temperature of the heat treatment, it is also possible that diffusion takes place between the coating and substrate. This may lead to the formation of mixed

layers. However, it is possible that the diffusion is so limited that no mixed layer is formed. After the heat treatment(s), the boundary between two layers or between the coating and the substrate is typically not clear-cut, but some amount of diffusion may have taken place.

The method according to the present disclosure may comprise more than one heat treatment. The method can comprise, for example, two heat treatments. The method can comprise, for example, three heat treatments. The method can comprise more than three heat treatments. The heat treatments do not need to be identical. The length of a heat treatment may be 15-60 minutes. The coated object can be cooled after at least one heat treatment. Water or air can be used for cooling.

Heat treatment can be carried out, for instance, in a conventional gas furnace in ambient gas atmosphere or in a protective gas atmosphere. In one embodiment, step b) is performed in an ambient atmosphere. The length of such a heat treatment may be, for example 30 minutes.

Heat treatment can be carried out by induction, flame heating, laser heating or salt bath heat treatment. In one embodiment, the at least one heat treatment in step b) is induction heating or furnace heating. Induction heating is a no-contact process that quickly produces intense, localized and controllable heat. With induction, it is possible to heat only selected parts of the coated metal substrate. Flame heating refers to processes where heat is transferred to the object by means of a gas flame without the object melting or material being removed. Laser heating produces local changes at the surface of the material while leaving the properties of the bulk of a given component unaffected. Heat treating with laser involves solid-state transformation, so that the surface of the metal is not melted. Both mechanical and chemical properties of a coated article can often be great-

ly enhanced through the metallurgical reactions produced during heating and cooling cycles.

In one embodiment, the object to be coated is of metal and the hardening of the metal of the object is carried out at the same time as the coated object is heat treated. For simultaneous heat treatment and hardening of the object, especially induction heating is suitable, since it is uniform and the hardening of the metal object can be achieved only in the vicinity of the surface, in the range of few millimeters below the surface.

In one embodiment, the at least one heat treatment in step b) is induction heating and the object is cooled by cooling liquid for 0.1-60 seconds, or for 0.5-10 seconds, or for 0.8-1.5 seconds, after the end of the heating. The object can thus be cooled for 0.1-60 seconds. The object can be cooled for 0.5-10 seconds. The object can be cooled for 0.8-1.5 seconds. One way of performing the induction heating and the subsequent cooling is to pass the object to be treated through a stationary induction coil that is situated at a predetermined distance from a stationary jet of cooling liquid. After the object exits the induction coil, it will move to the jet of cooling liquid. Alternatively the object to be treated can be stationary and the induction coil and cooling stream moving. Thus, the lag time between the end of the heating and the beginning of the liquid cooling can be controlled by the relative speeds of the object to be treated and the heating and cooling means. For example, the heat treatment of step c) may be induction heating, the distance between the heating coil and the cooling jet is 25 mm and the speed of the induction coil and the cooling liquid jet relative to the object to be heated is 500-3,000 mm min⁻¹, preferably 1,500 mm min⁻¹. The cooling liquid can be, for example, water or suitable emulsion.

The method according to the present disclosure may comprise a step of depositing an intermediate layer. The intermediate layer may comprise a metal or metal alloy or ceramic. The method according to the present disclosure may comprise a step of electroplating an intermediate nickel layer between the two layers of the chromium-based coating according to the present disclosure. If the coating comprises more than one layer with distinctive element composition, the intermediate layer can be located between any of these layers.

In one embodiment, the method comprises an additional step c) of depositing a top layer after step b) by thin film deposition, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD) or electroplating or electroless plating. The methods for producing a top layer are well established and selecting a suitable one and adjusting its parameters is within the knowledge of the skilled person. The top layer can be made of any suitable material that is able to give the coated surface the desired properties. Suitable materials comprise, for instance, metals, metal alloys, ceramics, nitrides (TiN, CrN), and diamond like carbon (DLC). Ni-P can be deposited as the top layer. Nickel-phosphate compounds lend themselves for coloring or other modifications. As an example, acid post dip processes can be used for producing a darker-colored surface, which can be black in extreme cases. Processes for producing black NiP coatings are known in the art.

In most applications, the coated object is first heat treated and then a top layer is deposited.

In one embodiment, the method comprises an additional step c) of depositing a top layer before step b) by thin film deposition, such as physical vapor deposition (PVD), chemical vapor deposition (CVD),

atomic layer deposition (ALD) or electroplating or electroless plating. In other words, it is possible to produce a thin film deposited top layer on the coated object before a heat treatment. It is also possible that step c) comprises a heat treatment on its own. In this case, the heat treatment is optimized for completion of the top layer and therefore its parameters can be different from those of the heat treatment in step b) of the current method. Selecting heat treatment parameters for finalizing the top layer is within the knowledge of the skilled person.

In one embodiment, the steps a) and b) are repeated at least once before step c). In other words, the electroplating step a) and the heat treatment b) can be repeated once or more before depositing a top layer. In one embodiment, the steps a), b) and c) are repeated at least once.

In one embodiment, the object to be coated is of metal and the method comprises an additional step i) of carburizing the object before step a). The carbon content of a steel substrate is increased through carburizing.

The method according to the present disclosure can comprise further process steps. These can be for example pretreatment steps. An example of such is chemical and/or electrolytic degreasing to remove oil and dirt from the surface to be coated. Another example is pickling to activate the surface before the actual coating and plating steps. Also additional protective layers can be used. As an example a coating comprising copper or zinc can be used as a temporary protective layer. Such a coating can be removed by, for example dissolving with a suitable solution (e.g. acid) or grinding, to expose the coating according to the present disclosure. These pre- and post-treatment

steps belong to the knowledge of the skilled person and can be selected according to the intended application.

5 In one aspect, a coated object is disclosed. The coated object is characterized in that it comprises a coating according to the present disclosure or a coating produced by a method according to the present disclosure. For example, the coated object may be a
10 gas turbine, shock absorber, hydraulic cylinder, linked pin, a ball valve or an engine valve. The object that is coated can be of any material, such as ceramic, metallic or metal alloy material that is used for functions requiring high hardness and corrosion
15 resistance. There are many applications in which a coated object according to the present disclosure can be used.

 The embodiments of the invention described
20 hereinbefore may be used in any combination with each other. Several of the embodiments may be combined together to form a further embodiment of the invention. A method, a coating or an object, to which the invention is related, may comprise at least one of the em-
25 bodiments of the invention described hereinbefore.

 The method and the coating according to the present disclosure offer at least one of the following advantages over prior art:

30 - An advantage of the coating according to the present disclosure is that it can be coated on many different kinds of substrates. The coating can be electroplated directly over a substrate.

 - An advantage of the coating according to
35 the present disclosure is that it has high hardness and good wearing resistance. The corrosion resistance of the coating may be improved over prior-art solu-

tions. The resistance of the coating to sulfuric acid can be improved over prior-art solutions.

- A further advantage of the coating according to the present disclosure is that the Ni-containing Cr-based coating can be hardened at a temperature which is high enough for hardening of the substrate.

EXAMPLES

The description below discloses some embodiments of the invention in such a detail that a person skilled in the art is able to utilize the invention based on the disclosure. Not all steps of the embodiments are discussed in detail, as many of the steps will be obvious for the person skilled in the art based on this specification.

FIGURE 1

Fig. 1 is a flow-chart presentation of an embodiment of the current method. In step a) of the method, a Cr-based layer is deposited on a substrate. The Cr is deposited from a bath of trivalent Cr containing at least 20 mg l⁻¹ Ni cations. The presence of Ni and Fe in the bath leads to their codeposition into the Cr-based layer. C is also included in the coating. At step b) of the method, the coated object is subjected to at least one heat treatment at a temperature of 650-820 °C. As a result of the heat treatment, the mechanical and physical properties of the coating are amended, leading to the formation of a hard coating with a Vickers microhardness of at least 1,500 HV as measured according to standard SFS-EN ISO 4516. Depending on the specifics of the heat treatment, it is possible that also the mechanical and physical properties of the substrate are affected to a predetermined depth. If the substrate is steel, the substrate is typically hardened.

FIGURE 2

Fig. 2 is a schematic presentation of a structure of a coating according to the present disclosure. The coating layer C is depicted with light gray. The surface of the coating layer C in the figure is at the top of fig. 2. The substrate S is depicted with black color at the bottom of the figure. Between the coating layer C and the substrate, a mixed layer M is visible. The coating layer C means the coating according to the present disclosure. The mixed layer M is depicted to be approximately of equal thickness as the coating layer C. In most applications, the mixed layer M is, however, thinner than the coating layer C. For example, the coating layer C may be 7 μm thick and the mixed layer M may be 1 μm thick.

EXAMPLE 1

A trivalent chromium-containing bath was prepared as is known in the art. For example, an electrolyte solution comprising 20-23 g l^{-1} trivalent chromium ions and 60-65 g l^{-1} boric acid (as sold by Atotech Deutschland GmbH under the trade name Trichrome Plus®) can be used. NiCl_2 was added to the electrolyte solution to achieve Ni^{2+} concentration of 50 mg l^{-1} (approximately 0.85 mM). The bath was subjected to a normal initial plating, after which it was ready for use.

A chromium coating was coated on a substrate at a current density of 15 A dm^{-2} for 30 min, at a pH of 2.6 (step a) of the method) with anode/cathode surface ratio of 2:1. Two anodes were used, each having its own power supply. This was to ascertain the uniform distribution of the current density over the object to be coated.

The substrate was then rinsed and heat-treated at 700 $^{\circ}\text{C}$ for 30 min (step b) of the method). The coating thickness was approximately 15-20 μm and

hardness 1,500-1,700 HV_{0.05}. The coating comprised approximately 1 % (w/w) Ni measured through an EDS measurement. Attention was paid to the evenness of air and liquid movement, as well as to their efficiency to ascertain evenness of coating.

EXAMPLE 2

A steel object is carburized prior to electroplating a coating according to the present disclosure. The object is carburized to the same depth as the hardening of the object will be performed at step b) of the method. The carbon content is at least approximately 0.5 % (w/w) in the carburized part of the object.

After carburization, the object is coated and the coating is heat-treated at a temperature of 500-700 °C for 30 minutes. The metal object is then hardened by induction hardening. The carburization may be advantageous as it allows the hardening of the steel at temperatures below 800 °C.

It is obvious to a person skilled in the art that with the advancement of technology, the basic idea of the invention may be implemented in various ways. The invention and its embodiments are thus not limited to the examples described above; instead they may vary within the scope of the claims.

CLAIMS

1. A chromium-based coating comprising chromium (Cr), carbon (C) and iron (Fe), Cr being electroplated from a trivalent Cr bath, characterized in that the coating further comprises nickel (Ni) electroplated from the Cr bath containing at least 20 mg l⁻¹ Ni cations, in that C is at least partially in the form of at least one chromium carbide compound, in that the coating has been heat-treated at a temperature of 650-820 °C or at a temperature of 700-800 °C, and in that the hardness of the coating is at least 1,500 HV on a Vickers microhardness scale as measured according to standard SFS-EN ISO 4516.

2. The chromium-based coating according to claim 1, wherein the Cr bath contains 20 to 150 mg l⁻¹ Ni cations or wherein the Cr bath contains 20 to 80 mg l⁻¹ Ni cations.

3. The chromium-based coating according to claim 1 or 2, wherein the at least one chromium carbide compound comprises Cr₃C₂, Cr₇C₃ or Cr₂₃C₆, or a combination thereof.

4. The chromium-based coating according to any of the preceding claims, wherein at least some of the Ni and Cr are dissolved in each other.

5. The chromium-based coating according to any of the preceding claims, wherein the Taber index of the coating measured by the Taber abrasion test according to ISO 9352 is below 2, or below 1.

6. The chromium-based coating according to any of the preceding claims, wherein the coating forms at least two layers with distinctive element compositions.

7. The chromium-based coating according to any of the preceding claims, wherein the coating is coated directly on a substrate.

8. The chromium-based coating according to any of the preceding claims, wherein the coating further comprises a top layer.

9. The chromium-based coating according to
5 any of the preceding claims, wherein there is a mixed layer between the substrate and the chromium-based coating, said mixed layer comprising both substrate material and coating components and being produced by heat-treatment of the coated substrate.

10 10. A method for producing a chromium-based coating according to any of the preceding claims on an object by electroplating from a trivalent Cr bath, characterized in that the method comprises the steps of

15 a) depositing a layer of Cr from a trivalent Cr bath on an object, the bath comprising at least one source for trivalent Cr, at least 20 mg l^{-1} Ni cations, at least one source for C and at least one source for Fe, so that Ni, C and Fe are incorporated into the Cr
20 layer; and

b) subjecting the coated object to at least one heat treatment at a temperature of $650\text{-}820^\circ\text{C}$, or at a temperature of $700\text{-}800^\circ\text{C}$, to amend the mechanical and physical properties of the coating.

25 11. The method according to claim 10, wherein the at least one source for Ni is NiCl_2 or metallic Ni.

12. The method according to any of claims 10-11, wherein step b) is performed in an ambient atmosphere.
30

13. The method according to any of claims 10-12, wherein the current density during the coating is $10\text{-}50 \text{ A dm}^{-2}$, or 15 A dm^{-2} .

14. The method according to any of claims 10-13, wherein the at least one heat treatment in step b) is induction heating or furnace heating.
35

15. The method according to any of claims 10-14, wherein the at least one heat treatment in step b) is induction heating and the object is cooled by cooling liquid for 0.1-60 seconds, or for 0.5-10 seconds, or for 0.8-1.5 seconds, after the end of the heating.

16. The method according to any of claims 10-15, wherein the method comprises an additional step c) of depositing a top layer after step b) by thin film deposition, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD) or electroplating or electroless plating.

17. The method according to any of claims 10-16, wherein the method comprises an additional step c) of depositing a top layer before step b) by thin film deposition, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD) or electroplating or electroless plating.

18. The method according to claim 10-17, wherein the steps a) and b) are repeated at least once before step c)

19. The method according to claim 10-18, wherein the steps a), b) and c) are repeated at least once.

20. The method according to any of claims 10-19, wherein the object to be coated is of metal and the method comprises an additional step i) of carburizing the object before step a).

21. The method according to any of claims 10-20, wherein the object to be coated is of metal and the hardening of the metal of the object is carried out at the same time as the coated object is heat treated.

22. A coated object, characterized in that it comprises a coating according to any of claims 1-9 or a coating produced by a method according to any of claims 10-21.

Fig. 1

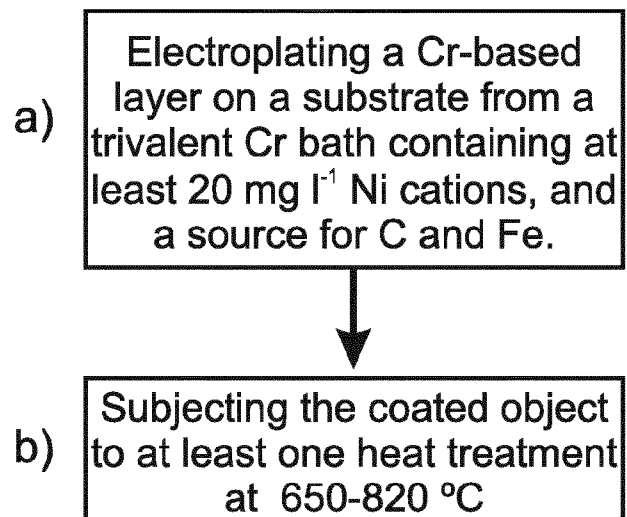
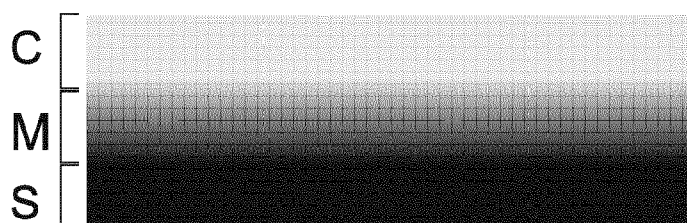


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2015/050587

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C25D, C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base, and, where practicable, search terms used)

EPO-Internal, WPIAP, COMPDX, INSPEC, PUBCOMP, PUBSUBS, TDB, NPL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1482747 A (BNF METALS TECH CENTRE) 10 August 1977 (10.08.1977) page 6, lines 25-46; page 12, lines 6 – 49 page 7, line 70-72; table 3 on page 12	1-22
A	Qijun Zhong et al. 'The electrodeposition of Ni-Fe-Cr alloy coatings on mild steel surfaces and evaluation of corrosion resistance', Advanced Materials Research, Trans Tech Publications, Switzerland, 2013, Vols. 785-786, p. 948-952 the whole document, especially abstract and page 949	1-22
A	M. El-Sharif et al. 'Effect of heat treatment on microstructure of Cr-Ni-Fe coatings prepared by electrodeposition'. Materials Science Forum, Trans Tech Publications, Switzerland, 1994, Vols. 163-165, p. 633-638 the whole document	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

11 December 2015 (11.12.2015)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2015/050587

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Ziangzhu He et al. 'Effect of Ni ²⁺ on Chromium electrodeposition in Cr(III) Plating Bath', Advanced Materials Research, Trans Tech Publications, Switzerland, 2011, Vols. 150-151, p. 1555-1559 abstract	1-22
A	WO 2015107255 A1 (SAVROC LTD [FI]) 23 July 2015 (23.07.2015) page 12, line 23- page 13, line 7	1-22

INTERNATIONAL SEARCH REPORT
Information on Patent Family Members

International application No.
PCT/FI2015/050587

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
GB 1482747 A	10/08/1977	AU 7383874 A	08/04/1976
		BE 820802 A2	03/02/1975
		CA 1030094 A	25/04/1978
		DE 2447897 A1	17/04/1975
		FR 2247550 A1	09/05/1975
		FR 2247550 B1	27/04/1979
		IT 1020962 B	30/12/1977
		JP S5066442 A	04/06/1975
		JP S5742713 B2	10/09/1982
		NL 7413211 A	14/04/1975
		SE 7412152 A	11/04/1975
		US 3917517 A	04/11/1975
.....			
WO 2015107255 A1	23/07/2015	None	
.....			

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2015/050587

CLASSIFICATION OF SUBJECT MATTER

IPC
C25D 3/06 (2006.01)
C25D 3/10 (2006.01)
C25D 3/12 (2006.01)
C25D 3/20 (2006.01)
C25D 5/50 (2006.01)