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(54) **METHOD FOR ELECTROLYTICALLY DEPOSITING A CHROMIUM OR CHROMIUM ALLOY LAYER ON AT LEAST ONE SUBSTRATE**

VERFAHREN ZUR ELEKTROLYTISCHEN ABSCHIEDUNG EINER CHROM- ODER CHROMLEGIERUNGSSCHICHT AUF MINDESTENS EINEM SUBSTRAT

PROCÉDÉ DE DÉPÔT ÉLECTROLYTIQUE D'UNE COUCHE DE CHROME OU D'ALLIAGE DE CHROME SUR AU MOINS UN SUBSTRAT

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Description**Field of the Invention**

5 [0001] The present invention relates to a method for electrolytically depositing a chromium or chromium alloy layer on at least one substrate. In particular the present invention refers to functional chromium layers, also often referred to as hard chromium layers.

Background of the Invention

10 [0002] Functional chromium layers usually have a much higher average layer thickness (from at least 1 μm up to several hundreds of micro meters) compared to decorative chromium layers (typically below 1 μm) and are characterized by excellent hardness and wear resistance.

15 [0003] During the recent decades, chromium deposition methods relying on hexavalent chromium are more and more replaced by deposition methods relying on trivalent chromium. Such trivalent chromium-based methods are much more health- and environment friendly.

20 [0004] Hexavalent chromium is a serious contaminant in deposition methods relying on trivalent chromium and is typically formed at the anode from trivalent chromium ions in an undesired electrochemical reaction. It is crucial to at least suppress to the best extent possible the formation of such hexavalent chromium or even to prevent it. If hexavalent chromium accumulates in a respective deposition bath the quality of the deposited chromium layer is significantly reduced and eventually the entire deposition method comes to a halt if a critical concentration is exceeded. For example, a total amount of 1 g/L hexavalent chromium in a trivalent chromium deposition bath is in most cases sufficient to completely ruin a deposition bath and is therefore unacceptable.

25 [0005] Historically, there have been several approaches to this problem: In some deposition baths bromide ions have been utilized as suppressors to catalyze anodic oxidation of chemical species such as a variety of organic and inorganic compounds rather than oxidation of trivalent chromium to hexavalent chromium.

[0006] US 4,477,315 A discloses a huge variety of reducing agents in an amount effective to maintain the concentration of hexavalent chromium ions formed in the bath at a level at which satisfactory chromium deposition is still obtained. However, US'315 primarily refers to decorative applications.

30 [0007] Other approaches utilize a membrane or diaphragm in order to separate the anode from the cathode and to prevent that trivalent chromium ions get into contact with the anode.

[0008] WO 2015/110627 A1 refers to an electroplating bath for depositing chromium and to a process for depositing chromium on a substrate using said electroplating bath. It is furthermore disclosed that the electroplating bath is separated from the anode by a membrane, preferably by an anodic or cationic exchange membrane.

35 [0009] However, the utilization of membranes or diaphragms also exhibits significant disadvantages. Very frequently, such membranes are highly susceptible to high currents and often show serious burnings and damages after a certain time interval of bath usage. Furthermore, a plating setup comprising such a membrane or diaphragm is typically more sophisticated to control, demands higher costs, and requires a higher degree of maintenance.

40 [0010] EP 3 106 544 A2 discloses a continuous trivalent chromium plating method and relates to a trivalent chromium solution for decorative purposes. The solution contains boric acid, has a pH in the range between 3.4 and 4.0, and utilizes a specific anode to cathode ratio. The applied current density is in the range from 4 A/dm² to 12 A/dm².

45 [0011] US 2,748,069 relates to an electroplating solution of chromium, which allows obtaining very quickly a chromium coating of very good physical and mechanical properties. The chromium plating solution can be used for special electrolyzing methods, such as those known as spot or plugging or penciling galvanoplasty. In such special methods the substrate is typically not immersed into a respective electroplating solution.

[0012] RU 2139369 C1 refers to a method of electrochemical chrome plating of metals and their alloys.

Objective of the present Invention

50 [0013] It was the objective of the present invention to provide a deposition method for functional chromium layers, which is less susceptible or prone to the presence of tiny amounts of undesired hexavalent chromium, thus, allowing a broad operating range. It is in particular desired that the method is less dependent on the presence of chemical suppressors such as bromide ions as the only suppressing factor. Furthermore, the method should be robust, simple, environmentally more acceptable, and cost efficient.

Summary of the Invention

[0014] This objective is solved by a method for electrolytically depositing a chromium or chromium alloy layer according

to claim 1.

Brief description of the figure

[0015] In Figure 1, a cathode current efficiency (CCE) plot is depicted, wherein on the x-axis the usage of the bath is shown in Ah/L and on the y-axis the cathode current efficiency. In the plot four plating scenarios (A, B, C, and D) are depicted. For more details, see the "Examples" section below in the text.

Detailed Description of the Invention

[0016] Own experiments have shown that a total anodic current density of 6 A/dm² or more and a total cathodic current density of 18 A/dm² or more significantly stabilizes the method as a whole and significantly suppresses the formation of hexavalent chromium on a long term (see examples below in the text). Since the trivalent chromium ions are in contact with the at least one anode, a membrane or a diaphragm in order to separate the trivalent chromium ions from the anode is not needed. In other words, in the method of the present invention no separation means are utilized in order to separate the trivalent chromium ions in the deposition bath from the anode. This reduces costs, maintenance effort and allows a simplified operation of the deposition method.

[0017] In the context of the present invention, the term "at least one" denotes (and is exchangeable with) "one, two, three or more than three". Furthermore, "trivalent chromium" refers to chromium with the oxidation number +3. The term "trivalent chromium ions" refers to Cr³⁺-ions in a free or complexed form. Likewise, "hexavalent chromium" refers to chromium with the oxidation number +6 and thereto related compounds including ions containing hexavalent chromium.

[0018] The term "not comprising" denotes that respective compounds are not intentionally added to the aqueous deposition bath, such as boron containing compounds, in particular boric acid is not contained in the deposition bath. In other words, the aqueous deposition bath is substantially free of such compounds. This does not exclude that such compounds are dragged in as impurities of other chemicals (preferably in a total amount of less than 10 mg/L, based on the total volume of the deposition bath). However, typically the total amount of such compounds is below the detection range and therefore not critical during step (c) of the method of the present invention.

[0019] In the aqueous deposition bath utilized in the method of the present invention boron containing compounds are not desired because they are environmentally problematic. Containing boron containing compounds, waste water treatment is expensive and time consuming. Furthermore, boric acid which is known as well working buffer compound typically shows poor solubility and therefore has the tendency to form precipitates. Although such precipitates can be solubilized upon heating, a respective aqueous deposition bath cannot be utilized during this time. There is a significant risk that such precipitates facilitate an undesired surface roughness. Thus, the aqueous deposition bath utilized in the method of the present invention does not contain boron containing compounds. Surprisingly, the aqueous deposition bath utilized in the method of the present invention performs very well without boron containing compounds. As a result, such compounds are not needed.

[0020] In the method of the present invention no hexavalent chromium is intentionally added to the aqueous deposition bath. Very preferably, the aqueous deposition bath is free of hexavalent chromium, i.e. the total amount of it is zero mg/L. However, as already described above in the text, hexavalent chromium is usually formed at the anode in an undesired electrochemical reaction if trivalent chromium ions are not separated from the anode or otherwise prevented from its oxidation. Furthermore, very tiny amounts of hexavalent chromium are also contaminants of other chemical compounds utilized in the aqueous deposition bath (such contaminants are not intentionally added to the deposition bath). Usually, such tiny amounts of hexavalent chromium are acceptable, for example if the total amount of such hexavalent chromium is below the lower detection limit of typical measuring methods (e.g. photometry with diphenyl-carbazide; lower detection limit is typically 15 to 20 mg per liter deposition bath). If the total amount of hexavalent chromium is more than zero but 15 mg/L or below, it is considered that the respective deposition bath does not contain hexavalent chromium. Furthermore, such a total amount of hexavalent chromium apparently does not at all negatively affect the deposition method in step (c) of the method of the present invention.

[0021] As evident from own examples, a total amount of anodically formed hexavalent chromium exceeding the lower detection limit, e.g. a total amount of 100 mg/L or even 200 mg/L, is in a few cases still tolerable, but very often less preferred. Preferred is an aqueous deposition bath in step (a) comprising 0 mg/L to 150 mg/L hexavalent chromium, based on the total volume of the aqueous deposition bath, more preferred 0 to 100 mg/L, even more preferred 0 mg/L to 45 mg/L, most preferred 0 mg/L to 30 mg/L. The amount refers to a conversion to elementary chromium with a molecular weight of 52 g/mol, which likewise includes hexavalent chromium ions.

[0022] The method of the present invention includes steps (a) and (b), wherein the order is (a) and subsequently (b) or vice versa. In each case, step (c) is carried out after both steps, (a) and (b), have been carried out.

[0023] In the method of the present invention at least one substrate forming the cathode is utilized. Typically, more than one substrate is utilized in the method of the present invention simultaneously, forming an overall cathode surface

with the total cathodic current density of 18 A/dm² or more, and wherein the maximum total cathodic current density is 250 A/dm². This means that the total cathodic current density includes all cathodes (substrates) utilized in step (c) for simultaneous deposition.

[0024] In many cases it is preferred that in the method of the present invention more than one anode is utilized, forming an overall anode surface with the total anodic current density of 6 A/dm² or more, and wherein the maximum total anodic current density is 50 A/dm². This means that the total anodic current density includes all anodes utilized in step (c) for deposition.

[0025] Furthermore, the term "overall [...] surface" (of all utilized cathodes and anodes, respectively) refers to the geometrically derived overall surface actively participating in the deposition process. For example, an anode partly covered by a shielding material exhibits a reduced active surface because the shielded surface area of the anode does not participate in the deposition process. Furthermore, a porous anode usually exhibits a larger surface compared to the geometrically derived surface of the same anode. In the context of the present invention, the term refers to the geometrically derived surface actively participating in the deposition process in order to determine the total anodic and cathodic current density.

[0026] In the method of the present invention the total cathodic current density is higher than the anodic current density, preferably the total cathodic current density is at least twice the total anodic current density. However, in exceptional cases, not according to the invention, it is preferred that the total anodic current density is higher than the total cathodic current density, in particular if the at least one substrate has an extraordinarily large surface.

[0027] The electrical current is a direct current (DC), more preferably a direct current without interruptions during step (c). The direct current is preferably not pulsed (non-pulsed DC). Furthermore, the direct current preferably does not include reverse pulses.

[0028] The present invention is mainly based on the finding that a deposition method for a functional chromium or chromium alloy layer can be effectively stabilized by carefully setting the total anodic current density to 6 A/dm² or more, wherein the maximum total anodic current density is 50 A/dm². A total anodic current density significantly below 6 A/dm², e.g. 5 A/dm² or 5.5 A/dm² is for practical reasons not desired because the positive effect is not noticeable. As a result, no substantial stabilization effect is obtained and undesired amounts of hexavalent chromium are formed.

[0029] According to own experiments, acceptable results were only obtained if the aqueous deposition bath has a pH in the range from 4.1 to 7.0. In particular highly acidic deposition baths (as mostly used for decorative purposes) did not provide satisfying results or could not be used at all if utilized in step (c) of the method of the present invention, even if the defined current densities were applied.

[0030] In the method of the present invention anodically formed hexavalent chromium is efficiently suppressed compared to bromide as the only suppressing factor (see examples below). Thus, the method of the present invention is an improved and more stabilized method. This improved method is more simplified compared to methods known from the art and furthermore results in excellent functional chromium or chromium alloy layers with excellent wear resistance and hardness. According to own experiments, the at least one substrate obtained after step (c) exhibits a Vickers Hardness of at least 700 HV_(0.05) (determined with 50 g "load"). The wear resistance is comparatively good as the wear resistance obtained from hexavalent chromium based deposition methods.

[0031] Preferred is a method of the present invention, wherein the total anodic current density is 8 A/dm² or more, preferably 9 A/dm² or more, more preferably 10 A/dm² or more.

[0032] According to the invention the upper limit of the total anodic current density is 50 A/dm². Typically, the total anodic current density is not exceeding 30 A/dm². For the majority of applications a method of the present invention is preferred, wherein the total anodic current density is in the range from 8 A/dm² (preferably 9 A/dm²) to 30 A/dm², preferably in the range from 8 A/dm² (preferably 9 A/dm²) to 28 A/dm², most preferably in the range from 8 A/dm² (preferably 9 A/dm²) to 22 A/dm².

[0033] However, in a few cases a higher total anodic current density is preferred, preferably a maximum total anodic current density of 40 A/dm² or 50 A/dm². Thus, in these cases the total anodic current density is not exceeding 40 A/dm² and 50 A/dm², respectively. Such maximum anodic current densities might be necessary if substrates with sophisticated geometries are subjected to the method of the present invention; in particular if the substrate comprises an inside surface and an outside surface and both surfaces are simultaneously to be deposited in step (c) of the method of the present invention. In such cases the at least one substrate typically has an extraordinarily large surface.

[0034] Preferred is a method of the present invention, wherein the total cathodic current density is 30 A/dm² or more, preferably 35 A/dm² or more. A very much preferred total cathodic current density is 40 A/dm².

[0035] For the majority of applications a method of the present invention is preferred, wherein the total cathodic current density is in the range from 20 A/dm² to 50 A/dm², preferably in the range from 35 A/dm² to 50 A/dm².

[0036] In the method of the present invention, the maximum total cathodic current density is not in particular limited. According to the invention, the maximum total cathodic current density is 250 A/dm², preferably 200 A/dm². Preferred examples include 180 A/dm², 150 A/dm², 100 A/dm², and 80 A/dm². However, in exceptional cases, not being according to the present invention, the maximum total cathodic current density might exceed even 250 A/dm². Such a high maximum

total cathodic current density usually requires high currents, which are possible because no means for separation (such as a membrane or a diaphragm) are used in the method of the present invention. In many cases, such separation means would suffer severe damage if exposed to such high currents. Comparatively high cathodic current densities are desired in order to obtain high deposition rates.

[0037] For the majority of applications, a method of the present invention is preferred, wherein the ratio of the total anodic current density to the total cathodic current density is in the range from 1:2 to 1:8, preferably in the range from 1:2 to 1:6, more preferably in the range from 1:3 to 1:6, even more preferably in the range from 1:3 to 1:5. In particular in the more preferred and even more preferred ranges a very significant suppression of formed hexavalent chromium is obtained.

[0038] In step (a) of the method of the present invention the aqueous deposition bath is provided (providing also includes its manufacturing). Preferred is a method of the present invention, wherein the total amount of the trivalent chromium ions in the deposition bath is in the range from 10 g/L to 30 g/L, based on the total volume of the deposition bath, preferably in the range from 17 g/L to 24 g/L. If the total amount is significantly below 10 g/L in many cases an insufficient deposition is observed and the deposited chromium or chromium alloy layer is usually of low quality. If the total amount is significantly above 30 g/L, the deposition bath is not any longer stable, which includes formation of undesired precipitates.

[0039] A preferred source of the trivalent chromium ions is basic or acidic chromium (III) sulfate or chromium (III) chloride. A well-known basic chromium sulfate is Chrometan. However, other available trivalent chromium salts (organic as well as inorganic) can be used.

[0040] Preferably, the aqueous deposition bath utilized in the method of the present invention contains sulfate ions, preferably in a total amount in the range from 50 g/L to 250 g/L, based on the total volume of the deposition bath.

[0041] The method of the present invention in particular supports chemical suppressors such as bromide ions. Thus, a method of the present invention is preferred, wherein the deposition bath comprises bromide ions, preferably in a total amount of at least 0.06 mol/L, based on the total volume of the deposition bath, preferably at least 0.1 mol/L, more preferably at least 0.15 mol/L. Bromide ions are still an effective means to chemically suppress the formation of anodic hexavalent chromium. However, combined with the total anodic and cathodic current density defined for the method of the present invention, formation of anodic hexavalent chromium is impressively and surprisingly additionally suppressed.

[0042] In the method of the present invention, the aqueous deposition bath preferably contains at least one further compound selected from the group consisting of organic complexing compounds and ammonium ions. Preferred organic complexing compounds are carboxylic organic acids and salts thereof, preferably aliphatic mono carboxylic organic acids and salts thereof. More preferably the aforementioned organic complexing compounds (and its preferred variants) have 1 to 10 carbon atoms, preferably 1 to 5 carbon atoms, even more preferably 1 to 3 carbon atoms. Complexing compounds primarily form complexes with the trivalent chromium ions in the aqueous deposition bath to increase bath stability. Preferably, the molar ratio of the trivalent chromium ions to the organic complexing compounds is in the range from 1:0.5 to 1:10.

[0043] As mentioned above, the pH of the deposition bath is crucial. The above or below mentioned pH-values are referenced to 20°C. Preferred is a method of the present invention, wherein the deposition bath has a pH in the range from 4.5 to 6.5, preferably in the range from 5.0 to 6.0, most preferably in the range from 5.3 to 5.9. If the pH is too acidic or significantly beyond pH 7.0, no satisfying functional chromium or chromium alloy layer is obtained. Furthermore, precipitation easily occurs if the pH is too acidic. As a result, the aqueous deposition bath can be optimally handled if the pH is at least 5.0, preferably at least 5.3. An optimal chromium or chromium alloy layer is obtained if the maximum pH is 6.0 and 5.9, respectively.

[0044] The aqueous deposition bath is sensitive to a number of metal cations which are undesired. Hence, preferred is a method of the present invention, wherein the deposition bath contains copper ions, zinc ions, nickel ions, and iron ions, each independently in a total amount of 0 mg/L to 40 mg/L, based on the total volume of the deposition bath, preferably each independently in a total amount of 0 mg/L to 20 mg/L, most preferably each independently in a total amount of 0 mg/L to 10 mg/L. This preferably also includes compounds comprising said metal cations. Most preferred, none of the above mentioned metal cations are present at all, i.e. they are present each independently in a total amount of zero mg/L. However, own experimental results have shown that a tiny amount of these metal cations can be tolerated. If these tiny amounts are present, these amounts are insufficient to serve as alloying metal in order to form a chromium alloy layer on the at least one substrate. If the above mentioned total amount is significantly exceeded the chromium and chromium alloy layer deposited in step (c) of the method of the present invention exhibits undesired discolorations. Even more preferably, in the aqueous deposition bath utilized in the method of the present invention, chromium is the only side group element.

[0045] Furthermore, a method of the present invention is preferred, wherein the deposition bath does not comprise glycine, aluminium ions, and tin ions. This ensures a functional chromium and chromium alloy layer, respectively, with the desired attributes as outlined throughout the text. Own experiments have shown that in a number of cases aluminium and tin ions, in particular aluminium ions, significantly disturb and even inhibit the deposition in step (c).

[0046] Preferred is a method of the present invention, wherein the aqueous deposition bath does not contain sulfur containing compounds with a sulfur atom having an oxidation number below +6. It is assumed that the absence of said sulfur containing compounds results in an amorphous chromium layer and chromium alloy layer, respectively. Thus, a method of the present invention is preferred, wherein the layer deposited in step (c) is amorphous, determined by x-ray diffraction. This applies to the chromium or chromium alloy layer obtained during step (c) of the method of the present invention and prior to any further post-deposition surface treatment that might affect the atomic structure of the deposited layer, changing it from amorphous to crystalline or partly crystalline. It is furthermore assumed that such sulfur containing compounds negatively affect the hardness of the functional chromium or functional chromium alloy layer deposited in step (c).

[0047] The method of the present invention is preferably designed for industrial application and large scale use. This means that typically a plurality of substrates is immersed in the deposition bath in one single deposition scenario. Furthermore, the bath is usually in active use over several weeks and months, which includes a reuse of the deposition bath after step (c) for a subsequent deposition scenario. In order to ensure a long bath life time, improved method stability, as obtained with the method of the present invention, is much beneficial. A method of the present invention is preferred, wherein the method is repeated with the aqueous deposition bath obtained after step (c) and another substrate. Thus, the method of the present invention is preferably a continuous method.

[0048] Preferred is a method of the present invention, wherein the aqueous deposition bath provided in step (a) is repeatedly utilized in the method of the present invention, preferably for a usage of at least 70 Ah per liter aqueous deposition bath, preferably at least 100 Ah per liter, more preferably at least 200 Ah per liter, most preferably at least 300 Ah per liter.

[0049] In step (b) of the present invention the at least one substrate and the at least one anode is provided.

[0050] Preferred is a method of the present invention, wherein the at least one substrate is a metal or metal alloy substrate, preferably a metal or metal alloy substrate independently comprising one or more than one metal selected from the group consisting of copper, iron, nickel, and aluminium, more preferably a metal or metal alloy substrate comprising iron. Most preferably, the at least one substrate is a steel substrate, which is a metal alloy substrate comprising iron. In many technical applications a steel substrate with a wear resistant functional chromium or chromium alloy layer is needed. This can in particular be achieved by the method of the present invention.

[0051] In some cases the substrate is preferably a coated substrate, more preferably a coated metal substrate (for preferred metal substrates see the text above). The coating is preferably a metal or metal alloy layer, preferably a nickel or nickel alloy layer, most preferably a semibright nickel layer. In particular preferred is a steel substrate coated with a nickel or nickel alloy layer. However, preferably other coatings are alternatively or additionally present. In many cases such a coating significantly increases corrosion resistance compared to a metal substrate without such a coating. However, in some cases the substrates are not susceptible to corrosion due to a corrosion inert environment (e.g. in an oil bath). In such a case a coating, preferably a nickel or nickel alloy layer, is not necessarily needed.

[0052] Preferred is a method of the present invention, wherein the at least one anode is independently selected from the group consisting of graphite anodes and mixed metal oxide anodes (MMO), preferably independently selected from the group consisting of graphite anodes and anodes of mixed metal oxide on titanium. Such anodes have shown to be sufficiently resistant in the deposition bath of the present invention.

[0053] Preferably, the at least one anode does not contain any lead or chromium.

[0054] In step (c) of the method of the present invention the deposition of the chromium or chromium alloy layer takes place. In most cases, a method of the present invention is preferred, wherein the layer deposited in step (c) is a chromium alloy layer. Preferred alloying elements are carbon and oxygen. Carbon is typically present because of organic compounds usually present in the aqueous deposition bath. Preferably, the chromium alloy layer does not comprise one, more than one or all elements selected from the group consisting of sulfur, nickel, copper, aluminium, tin and iron. More preferably, the only alloying elements are carbon and/or oxygen, most preferably carbon and oxygen. Preferably, the chromium alloy layer contains 90 weight percent chromium or more, based on the total weight of the alloy layer, more preferably 95 weight percent or more.

[0055] Preferred is a method of the present invention, wherein the deposition bath in step (c) has a temperature in the range from 20°C to 90°C, preferably in the range from 30°C to 70°C, more preferably in the range from 40°C to 60°C, most preferably in the range from 45°C to 60°C. If the temperature significantly exceeds 90°C, an undesired vaporization occurs, which negatively affects the concentration of the bath components (even up to the danger of precipitation). Furthermore, the formation of hexavalent chromium is significantly less suppressed. If the temperature is significantly below 20°C the deposition is insufficient. Temperatures significantly below 40°C are generally acceptable but in a few cases the deposition quality and the extent of deposition are not sufficient, in particular between 20°C und 35°C. In a number of cases the chromium and chromium alloy layer gets undesirably dull, adhesion of said layer and deposition rate is low, and reproducibility is in some cases difficult. However, optimal and improved results are obtained at a temperature of at least 40°C, preferably a temperature in the range from 40°C to 90°C, more preferably in the range from 40°C to 70°C, even more preferably in the range from 40°C to 60°C. Most preferred is a temperature of at least

45°C, preferably a temperature in the range from 45°C to 90°C, more preferably in the range from 45°C to 70°C, even more preferably in the range from 45°C to 60°C.

[0056] During step (c), the aqueous deposition bath is preferably continually agitated, preferably by stirring.

[0057] Preferred is a method of the present invention, wherein in step (c) the chromium or chromium alloy layer is deposited with a deposition rate in the range from 0.3 $\mu\text{m}/\text{min}$ to 1.2 $\mu\text{m}/\text{min}$, based on a total cathodic current density of 40 A/dm². This means that the deposition rate is to be evaluated and referenced, respectively, at a total cathodic reference current density of 40 A/dm². It does not mean that the method of the present invention needs to be carried out at only 40 A/dm² in order to obtain a deposition rate in the above mentioned range. Thus, other deposition rates need to be referenced to 40 A/dm². Above mentioned deposition rates typically result in economically acceptable deposition times in combination with the demanded quality of the chromium or chromium alloy layer.

[0058] Furthermore, preferred is a method of the present invention, wherein the average layer thickness of the chromium or chromium alloy layer deposited in step (c) is 1.0 μm or more, preferably 2 μm or more, more preferably 4 μm or more, even more preferably 5 μm or more, most preferably the average layer thickness is in the range from 5 μm to 200 μm , preferably 5 μm to 150 μm . These are typical layer thicknesses for functional chromium or chromium alloy layers. Such thicknesses are needed to provide the needed wear resistance, which is typically demanded. In some cases the lower limit preferably and specifically includes 6 μm , 8 μm , 10 μm , 15 μm or 20 μm .

[0059] Very preferred is a method of the present invention, wherein

in step (c) the chromium or chromium alloy layer is directly deposited onto the substrate, or

the substrate defined in step (b) additionally comprises a nickel or nickel alloy layer and in step (c) the chromium or chromium alloy layer is deposited on said nickel or nickel alloy layer, preferably on a semibright nickel layer.

[0060] Most preferably, the chromium or chromium alloy layer is directly deposited onto a steel substrate.

[0061] The present invention is described in more detail by the following non limiting examples.

Examples

[0062] In a first step four identical deposition bath samples (approximately 1 L each) have been prepared, each sample containing a typical amount of 10 g/L to 30 g/L trivalent chromium ions, 50 g/L to 250 g/L sulfate ions, at least one organic complexing compound, ammonium ions, and bromide ions. No boron containing compounds have been used.

[0063] In a second step each of the above mentioned samples was utilized in a respective test plating scenario (A, B, C, and D) with the parameters as shown in Table 1. Scenarios B, C, and D are according to the invention, wherein scenario A is a comparative example because the total anodic current density is below 6 A/dm².

Table 1

	A	B	C	D
ACD* [A/dm ²]	3	6	10	20
CCD** [A/dm ²]	40			
total usage time [Ah/L]	89.1	99.6	99.6	89.1
bath temperature [°C]	50			
pH	5.3 to 5.9			
anode	plurality of graphite anodes			
* total Anodic Current Density				
** total Cathodic Current Density				

[0064] In each scenario, a functional chromium layer was successively deposited on several test plating specimens (10 cm steel rods coated with a nickel layer), and only trivalent chromium ions, the at least one organic complexing compound, and a hydroxide have been replenished in intervals according to their consumption and/or drag out during the respective scenario (no further compounds have been replenished). The average chromium layer thickness was at least 10 μm .

[0065] Throughout each scenario, the cathodic current efficiency (CCE) was determined according to Faraday's law and used as a marker to evaluate the quality of each deposition bath sample in terms of hexavalent chromium contamination.

[0066] Furthermore, during each scenario in each deposition bath sample the total amount of hexavalent chromium has been determined by means of classic photometry with diphenylcarbazide. In samples of scenarios B, C, and D no hexavalent chromium was detectable (i.e. hexavalent chromium was far below 20 mg/L). The respective deposition bath sample of scenario A showed after 75 Ah/L a total amount of hexavalent chromium of more than 1 g per liter deposition bath and after 86 Ah/L of more than 2.3 g per liter deposition bath. As confirmed by test plating scenario A, a total amount of hexavalent chromium of 1 g/L or more results in a cathodic current efficiency of zero and, thus, no chromium layer is anymore deposited in step (c).

[0067] In Fig. 1 the experimental results are visualized. Fig. 1 confirms that the cathodic current efficiency in scenarios B, C, and D remains comparatively constant, wherein in scenario A the cathodic current efficiency dramatically dropped to an extent that this deposition bath sample was not any more usable. Thus, total anodic and cathodic current densities as defined in the method of the present invention effectively suppress anodically formed hexavalent chromium.

Claims

1. A method for electrolytically depositing a chromium or chromium alloy layer on at least one substrate, the method comprising the steps

(a) providing an aqueous deposition bath with a pH in the range from 4.1 to 7.0,

- comprising trivalent chromium ions,
- comprising 0 mg/L to 200 mg/L hexavalent chromium, based on the total volume of the deposition bath, and
- not comprising boron containing compounds,

(b) providing the at least one substrate and at least one anode, and

(c) immersing the at least one substrate in the aqueous deposition bath and applying an electrical direct current such that the chromium or chromium alloy layer is deposited on the at least one substrate, wherein

the at least one substrate forms the cathode having a total cathodic current density and the at least one anode having a total anodic current density, with the proviso that

- the total anodic current density is 6 A/dm² or more, wherein the maximum total anodic current density is 50 A/dm²,
- the total cathodic current density is 18 A/dm² or more, wherein the maximum total cathodic current density is 250 A/dm²,
- the total cathodic current density is higher than the total anodic current density, and
- the at least one substrate and the at least one anode are present in the deposition bath such that the trivalent chromium ions are in contact with the at least one anode.

2. The method of claim 1, wherein the total anodic current density is 8 A/dm² or more, preferably 9 A/dm² or more, more preferably 10 A/dm² or more.

3. The method of claim 1 or 2, wherein the total cathodic current density is 30 A/dm² or more, preferably 35 A/dm² or more.

4. The method of any of the preceding claims, wherein the ratio of the total anodic current density to the total cathodic current density is in the range from 1:2 to 1:8, preferably in the range from 1:2 to 1:6, more preferably in the range from 1:3 to 1:6, even more preferably in the range from 1:3 to 1:5.

5. The method of any of the preceding claims, wherein the total amount of the trivalent chromium ions in the deposition bath is in the range from 10 g/L to 30 g/L, based on the total volume of the deposition bath, preferably in the range from 17 g/L to 24 g/L.

6. The method of any of the preceding claims, wherein the deposition bath comprises bromide ions, preferably in a total amount of at least 0.06 mol/L, based on the total volume of the deposition bath, preferably at least 0.1 mol/L, more preferably at least 0.15 mol/L.

7. The method of any of the preceding claims, wherein the deposition bath has a pH in the range from 4.5 to 6.5, preferably in the range from 5.0 to 6.0, most preferably in the range from 5.3 to 5.9.
8. The method of any of the preceding claims, wherein the deposition bath contains copper ions, zinc ions, nickel ions, and iron ions, each independently in a total amount of 0 mg/L to 40 mg/L, based on the total volume of the deposition bath, preferably each independently in a total amount of 0 mg/L to 20 mg/L, most preferably each independently in a total amount of 0 mg/L to 10 mg/L.
9. The method of any of the preceding claims, wherein the deposition bath does not comprise or in a total amount of less than 10 mg/L, based on the total volume of the deposition bath, glycine, aluminium ions, and tin ions.
10. The method of any of the preceding claims, wherein the method is repeated with the aqueous deposition bath obtained after step (c) and another substrate.
11. The method of any of the preceding claims, wherein the at least one substrate is a metal or metal alloy substrate, preferably a metal or metal alloy substrate independently comprising one or more than one metal selected from the group consisting of copper, iron, nickel, and aluminium.
12. The method of any of the preceding claims, wherein the at least one anode is independently selected from the group consisting of graphite anodes and mixed metal oxide anodes, preferably independently selected from the group consisting of graphite anodes and anodes of mixed metal oxide on titanium.
13. The method of any of the preceding claims, wherein the deposition bath in step (c) has a temperature in the range from 20°C to 90°C, preferably in the range from 30°C to 70°C, more preferably in the range from 40°C to 60°C, most preferably in the range from 45°C to 60°C.
14. The method of any of the preceding claims, wherein in step (c) the chromium or chromium alloy layer is deposited with a deposition rate in the range from 0.3 µm/min to 1.2 µm/min based on a total cathodic current density of 40 A/dm².
15. The method of any of the preceding claims, wherein the average layer thickness of the chromium or chromium alloy layer deposited in step (c) is 1.0 µm or more, preferably 2 µm or more, more preferably 4 µm or more, even more preferably 5 µm or more, most preferably the average layer thickness is in the range from 5 µm to 200 µm, preferably 5 µm to 150 µm.

Patentansprüche

1. Verfahren zur elektrolytischen Abscheidung einer Chrom- oder Chromlegierungsschicht auf mindestens einem Substrat, wobei das Verfahren die Schritte umfasst:
 - (a) Bereitstellen eines wässrigen Abscheidungsbad mit einem pH-Wert im Bereich von 4,1 bis 7,0,
 - umfassend dreiwertige Chromionen,
 - umfassend 0 mg/L bis 200 mg/L sechswertiges Chrom, bezogen auf das Gesamtvolumen des Abscheidungsbad, und
 - nicht umfassend borhaltige Verbindungen,
 - (b) Bereitstellen des mindestens einen Substrats und mindestens einer Anode, und
 - (c) Tauchen des mindestens einen Substrats in das wässrige Abscheidungsbad und Anlegen eines elektrischen Gleichstroms, so dass die Chrom- oder Chromlegierungsschicht auf dem mindestens einen Substrat abgeschieden wird, wobei
 - das mindestens eine Substrat die Kathode bildet, die eine gesamte kathodische Stromdichte aufweist, und
 - wobei die mindestens eine Anode eine gesamte anodische Stromdichte aufweist,
 - mit der Maßgabe, dass
 - die gesamte anodische Stromdichte 6 A/dm² oder mehr beträgt, wobei die maximale gesamte anodische Stromdichte 50 A/dm² beträgt,
 - die gesamte kathodische Stromdichte 18 A/dm² oder mehr beträgt, wobei die maximale gesamte katho-

dische Stromdichte 250 A/dm² beträgt,

- die gesamte kathodische Stromdichte höher als die gesamte anodische Stromdichte ist, und
- das mindestens eine Substrat und die mindestens eine Anode in dem Abscheidungsbad derart vorhanden sind, dass die dreiwertigen Chromionen in Kontakt mit der mindestens einen Anode sind.

2. Verfahren nach Anspruch 1, wobei die gesamte anodische Stromdichte 8 A/dm² oder mehr, vorzugsweise 9 A/dm² oder mehr, bevorzugter 10 A/dm² oder mehr beträgt.
3. Verfahren nach Anspruch 1 oder 2, wobei die gesamte kathodische Stromdichte 30 A/dm² oder mehr, vorzugsweise 35 A/dm² oder mehr beträgt.
4. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Verhältnis der gesamten anodischen Stromdichte zu der gesamten kathodischen Stromdichte im Bereich von 1:2 bis 1:8 liegt, vorzugsweise im Bereich von 1:2 bis 1:6, bevorzugter im Bereich von 1:3 bis 1:6, noch bevorzugter im Bereich von 1:3 bis 1:5.
5. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Gesamtmenge der dreiwertigen Chromionen in dem Abscheidungsbad im Bereich von 10 g/L bis 30 g/L liegt, bezogen auf das Gesamtvolumen des Abscheidungs-bades, vorzugsweise im Bereich von 17 g/L bis 24 g/L.
6. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Abscheidungsbad Bromidionen umfasst, vorzugsweise in einer Gesamtmenge von mindestens 0,06 mol/L, bezogen auf das Gesamtvolumen des Abschei-dungs-bades, vorzugsweise mindestens 0,1 mol/L, bevorzugter mindestens 0,15 mol/L.
7. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Abscheidungsbad einen pH-Wert im Bereich von 4,5 bis 6,5, vorzugsweise im Bereich von 5,0 bis 6,0, am meisten bevorzugt im Bereich von 5,3 bis 5,9 hat.
8. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Abscheidungsbad Kupferionen, Zinkionen, Ni-ckelionen und Eisenionen enthält, jeweils unabhängig in einer Gesamtmenge von 0 mg/L bis 40 mg/L, bezogen auf das Gesamtvolumen des Abscheidungs-bades, vorzugsweise jeweils unabhängig in einer Gesamtmenge von 0 mg/L bis 20 mg/L, am meisten bevorzugt jeweils unabhängig in einer Gesamtmenge von 0 mg/L bis 10 mg/L.
9. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Abscheidungsbad nicht Glycin, Aluminiumionen und Zinnionen umfasst, oder diese in einer Gesamtmenge von weniger als 10 mg/L umfasst, bezogen auf das Gesamtvolumen des Abscheidungs-bades.
10. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Verfahren mit dem wässrigen Abscheidungsbad, das nach Schritt (c) erhalten wird, und einem anderen Substrat wiederholt wird.
11. Verfahren nach einem der vorhergehenden Ansprüche, wobei das mindestens eine Substrat ein Metall- oder Me-talllegierungssubstrat ist, vorzugsweise ein Metall- oder Metalllegierungssubstrat, das unabhängig ein oder mehr als ein Metall ausgewählt aus der Gruppe bestehend aus Kupfer, Eisen, Nickel und Aluminium umfasst.
12. Verfahren nach einem der vorhergehenden Ansprüche, wobei die mindestens eine Anode unabhängig ausgewählt ist aus der Gruppe bestehend aus Graphitanoden und Mischmetalloxidanoden, vorzugsweise unabhängig ausge-wählt ist aus der Gruppe bestehend aus Graphitanoden und Anoden aus Mischmetalloxid auf Titan.
13. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Abscheidungsbad in Schritt (c) eine Temperatur im Bereich von 20 °C bis 90 °C, vorzugsweise im Bereich von 30 °C bis 70 °C, bevorzugter im Bereich von 40 °C bis 60 °C, am meisten bevorzugt im Bereich von 45 °C bis 60 °C aufweist.
14. Verfahren nach einem der vorhergehenden Ansprüche, wobei in Schritt (c) die Chrom- oder Chromlegierungsschicht mit einer Abscheidungsrate im Bereich von 0,3 pm/min bis 1,2 pm/min abgeschieden wird, bezogen auf eine gesamte kathodische Stromdichte von 40 A/dm².
15. Verfahren nach einem der vorhergehenden Ansprüche, wobei die durchschnittliche Schichtdicke der in Schritt (c) abgeschiedenen Chrom- oder Chromlegierungsschicht 1,0 µm oder mehr, vorzugsweise 2 µm oder mehr, bevor-zugter 4 µm oder mehr, noch bevorzugter 5 µm oder mehr beträgt, wobei am meisten bevorzugt die durchschnittliche Schichtdicke im Bereich von 5 µm bis 200 µm, vorzugsweise 5 µm bis 150 µm liegt.

Revendications

1. Procédé de dépôt électrolytique d'une couche de chrome ou d'alliage de chrome sur au moins un substrat, le procédé comprenant les étapes suivantes :

(a) obtention d'un bain de dépôt aqueux avec un pH dans la gamme de 4,1 à 7,0,

- comprenant des ions chrome trivalents,
- comprenant 0 mg/L à 200 mg/L de chrome hexavalent, rapporté au volume total du bain de dépôt, et
- ne comprenant pas de composés contenant du bore,

(b) obtention de l'au moins un substrat et d'au moins une anode, et

(c) immersion de l'au moins un substrat dans le bain de dépôt aqueux et application d'un courant électrique continu de telle sorte que la couche de chrome ou d'alliage de chrome soit déposée sur l'au moins un substrat, dans lequel

l'au moins un substrat forme la cathode ayant une densité de courant cathodique totale et l'au moins une anode ayant une densité de courant anodique totale, à condition que

- la densité de courant anodique totale soit de 6 A/dm² ou plus, la densité de courant anodique totale maximale étant de 50 A/dm²,
- la densité de courant cathodique totale soit de 18 A/dm² ou plus, la densité de courant cathodique totale maximale étant de 250 A/dm²,
- la densité de courant cathodique totale soit supérieure à la densité de courant anodique totale, et
- l'au moins un substrat et l'au moins une anode soient présents dans le bain de dépôt de telle sorte que les ions chrome trivalents soient en contact avec l'au moins une anode.

2. Procédé de la revendication 1, dans lequel la densité de courant anodique totale est de 8 A/dm² ou plus, de préférence 9 A/dm² ou plus, mieux encore 10 A/dm² ou plus.

3. Procédé de la revendication 1 ou 2, dans lequel la densité de courant cathodique totale est de 30 A/dm² ou plus, de préférence 35 A/dm² ou plus.

4. Procédé de l'une quelconque des revendications précédentes, dans lequel le rapport entre la densité de courant anodique totale et la densité de courant cathodique totale se situe dans la gamme de 1:2 à 1:8, de préférence dans la gamme de 1:2 à 1:6, mieux dans la gamme de 1:3 à 1:6, mieux encore dans la gamme de 1:3 à 1:5.

5. Procédé de l'une quelconque des revendications précédentes, dans lequel la quantité totale des ions chrome trivalents dans le bain de dépôt se situe dans la gamme de 10 g/L à 30 g/L, rapporté au volume total du bain de dépôt, de préférence dans la gamme de 17 g/L à 24 g/L.

6. Procédé de l'une quelconque des revendications précédentes, dans lequel le bain de dépôt comprend des ions bromure, de préférence dans une quantité totale d'au moins 0,06 mol/L, rapporté au volume total du bain de dépôt, de préférence au moins 0,1 mol/L, mieux encore au moins 0,15 mol/L.

7. Procédé de l'une quelconque des revendications précédentes, dans lequel le bain de dépôt a un pH dans la gamme de 4,5 à 6,5, de préférence dans la gamme de 5,0 à 6,0, idéalement dans la gamme de 5,3 à 5,9.

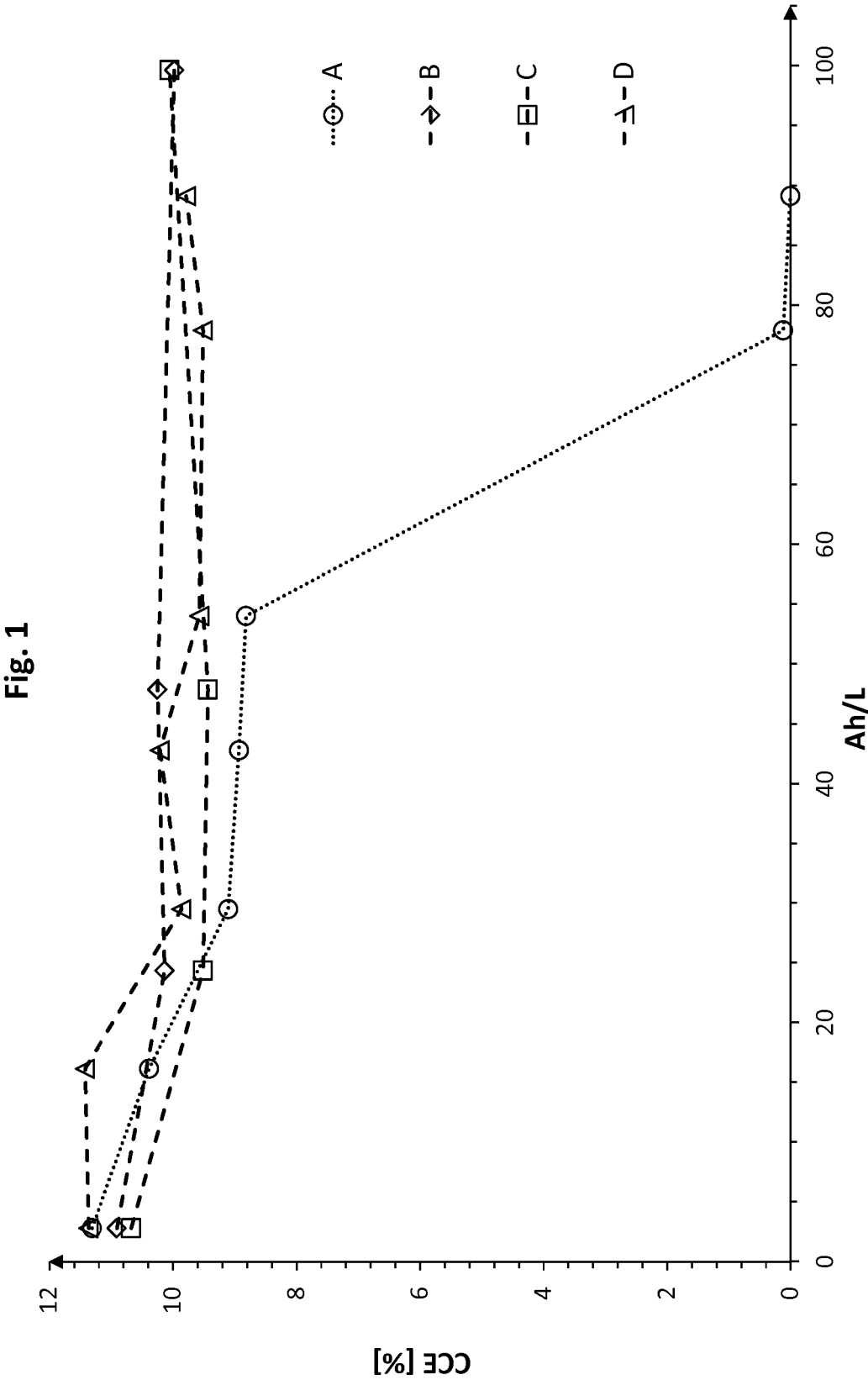
8. Procédé de l'une quelconque des revendications précédentes, dans lequel le bain de dépôt contient des ions cuivre, des ions zinc, des ions nickel et des ions fer, chacun indépendamment dans une quantité totale de 0 mg/L à 40 mg/L, rapporté au volume total du bain de dépôt, de préférence chacun indépendamment dans une quantité totale de 0 mg/L à 20 mg/L, idéalement chacun indépendamment dans une quantité totale de 0 mg/L à 10 mg/L.

9. Procédé de l'une quelconque des revendications précédentes, dans lequel le bain de dépôt ne comprend pas, ou comprend dans une quantité totale de moins de 10 mg/L, rapporté au volume total du bain de dépôt, de la glycine, des ions aluminium, et des ions étain.

10. Procédé de l'une quelconque des revendications précédentes, le procédé étant répété avec le bain de dépôt aqueux

obtenu après l'étape (c) et un autre substrat.

11. Procédé de l'une quelconque des revendications précédentes, dans lequel l'au moins un substrat est un substrat de métal ou d'alliage métallique, de préférence un substrat de métal ou d'alliage métallique comprenant indépendamment un ou plus d'un métal choisi dans le groupe constitué par le cuivre, le fer, le nickel, et l'aluminium.
12. Procédé de l'une quelconque des revendications précédentes, dans lequel l'au moins une anode est indépendamment choisie dans le groupe constitué par les anodes de graphite et les anodes d'oxyde métallique mixte, de préférence indépendamment choisie dans le groupe constitué par les anodes de graphite et les anodes d'oxyde métallique mixte sur titane.
13. Procédé de l'une quelconque des revendications précédentes, dans lequel le bain de dépôt à l'étape (c) a une température dans la gamme de 20 °C à 90 °C, de préférence dans la gamme de 30 °C à 70 °C, mieux encore dans la gamme de 40 °C à 60 °C, idéalement dans la gamme de 45 °C à 60 °C.
14. Procédé de l'une quelconque des revendications précédentes dans lequel, à l'étape (c), la couche de chrome ou d'alliage de chrome est déposée avec une vitesse de dépôt dans la gamme de 0,3 pm/min à 1,2 pm/min, sur la base d'une densité de courant cathodique totale de 40 A/dm².
15. Procédé de l'une quelconque des revendications précédentes, dans lequel l'épaisseur de couche moyenne de la couche de chrome ou d'alliage de chrome déposée à l'étape (c) est de 1,0 μm ou plus, de préférence 2 μm ou plus, mieux 4 μm ou plus, mieux encore 5 μm ou plus, idéalement l'épaisseur de couche moyenne se situe dans la gamme de 5 μm à 200 μm, de préférence 5 μm à 150 μm.



REFERENCES CITED IN THE DESCRIPTION

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