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(54) **Process for electrodepositing a metallic coating of a nickel-cobalt alloy on an object**

Verfahren zum elektrolytischen Absetzen einer Metallschicht aus einer Nickel-Cobalt-Legierung auf einen Gegenstand

Procédé de dépôt électrolytique d'une couche métallique en alliage nickel-cobalt sur un objet

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**FR-A- 1 580 290**

- **SURFACE AND COATING TECHNOLOGY, vol. 27, 1986, pages 103-115, Elsevier Sequoia, NL; A.M. ABD EL-HALIM et al.: "Some characteristics of Ni-Co alloy powders electrodeposited from dilute sulphate baths"**

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## Description

The present invention relates to a process for electrodepositing a metallic coating, mainly composed of a nickel-cobalt alloy, on a surface of an object, in particular a strip-iron, by means of an electrolysis bath wherein at least one anode is arranged in a substantially chloride-free electrolyte solution which comprises at least nickel sulphate, cobalt sulphate and boric acid, according to which process at least said surface is immersed in the electrolyte solution and an electric voltage is applied between said anode and the object acting as cathode.

Such a process is known from the french patent n° 1580290. According to the known process an electrolysis bath is used for depositing simultaneously nickel and cobalt. The electrolysis is carried out at low current densities, of 12,9 A/dm<sup>2</sup> at the most, and for depositing nickel and cobalt, use is made of a soluble anode. In the known process the bath comprises a solution containing nickel sulfate, cobalt sulfate and boric acid. The bath comprises 10 to 40 g/l nickel sulphate, 10 to 40 g/l cobalt sulphate, 0 to 60 g/l boric acid and also additional ion sulphates and ion formate generally under the form of salts. The electrolysis is realized at a temperature comprised between 32 and 60°C and with a current density varying between 1,08 and 12,9 A/dm<sup>2</sup>.

A problem which arises when using such a bath is that nickel is deposited easier than cobalt resulting in a low cobalt content of the nickel-cobalt alloy deposited on the surface. Therefore, in order to solve this problem, an electrolyte solution is required comprising a relatively high cobalt concentration so as to be sure that an appropriate cobalt content is obtained in the deposited coating. However, this solution is not economical and has a small efficiency.

An object of the invention is to provide a process by which the cobalt is deposited in a satisfactory manner without hampering the nickel deposition and without requiring high cobalt concentration in the electrolyte solution.

To this end, in the process according to the invention the electrolysis is realized in the electrolyte solution to which sulphuric acid has been added, and is characterized in that the voltage which is applied between the cathode and the anode, which is a substantially insoluble anode, is of such a value that at said cathode, a current density of at least 30 A/dm<sup>2</sup> is realized. It has been found that by using a high current density in the bath described in the preamble, a simultaneous nickel-cobalt deposit of a good quality is obtained. By using a current density of at least 30 A/dm<sup>2</sup>, the deposition process goes on in a quicker and more efficient way. A surprising effect of applying a higher current density is that the cobalt is deposited easier so that even a small cobalt content in the electrolyte solution ensures already the presence of cobalt over the whole deposited coating. The higher current density requires the use of an insoluble anode. Sulphuric acid is added to the electrolyte to in-

crease the conductivity of the bath.

In a preferred embodiment of the process according to the invention, the applied electric voltage is of such a value that said current density is comprised between 50 and 300 A/dm<sup>2</sup> and in particular between 240 and 250 A/dm<sup>2</sup>. It was found that the best quality of the deposit was obtained with a current density between 240 and 250 A/dm<sup>2</sup>. Indeed, at these current densities a homogeneous coating was obtained.

Preferably, a solution having a sodium sulfate concentration of upto the solubility limit is used as electrolyte solution. This maximum value is imposed by the solubility of the sodium sulfate in the bath. Above this value, a negative effect on the appearance of the deposit is obtained.

Preferably, a solution having a boric acid concentration of about 30 to 60 g/l and preferably of about 50 g/l and a sulfuric acid concentration of about 5 to 15 g/l and more particularly of about 10 g/l is used as electrolyte solution. A sulfuric acid content of 10 g/l influences very advantageously the conductivity without having, however, a negative effect on the Faraday efficiency.

A preferred embodiment of a process according to the invention is characterized in that the electrolysis is realized at a temperature comprised between 50 and 80°C and preferably at a temperature of about 70°C. In this temperature range, the object is not subjected to high thermal constraints.

Preferably, said object surface and said anode are disposed substantially in parallel relationship to one another and the electrolyte solution is injected between said surface and the anode. This allows to obtain good agitation conditions of the electrolyte in the cell.

Other particularities and advantages of the invention will become apparent from the following description of a process for electrodepositing nickel-cobalt alloys according to the invention. This description is only given by way of example and does not limit the scope of the invention. The invention is illustrated by means of the annexed drawings.

The sole figure shows a schematical sectional view of an electrolysis cell for applying a process according to the invention.

The invention relates to a process for electrodepositing a metallic coating, mainly composed of a nickel-cobalt alloy, on a surface of an object, in particular on a strip-iron or a sheet-iron. This electrolysis is carried out for example by means of an electrolysis cell 1 which comprises, as schematically illustrated in the figure, two anodes 2 and 3, preferably plate-shaped anodes disposed horizontally and substantially in parallel relationship to one another, between which an electrolyte solution 5 is injected according to arrows 4, at a speed in the range of 3 m/s by means of an injection device 12. The cell 1 also comprises chutes 6 and 7 for collecting the electrolyte solution 5 which can then be injected again between the two anodes 2 and 3 after being enriched. For enriching the solution, at least nickel sulfate and co-

balt sulfate are added in order to maintain the bath composition substantially constant.

The strip-iron 8 is guided between the two anodes 2 and 3, in a direction indicated by arrow 9, by means of rollers 10 and 11 which form an electric conductor. The strip-iron, which is in galvanic contact with rollers 10 and 11, for ms thus a cathode. An electric voltage is applied between the cathode, comprised of the strip-iron 8, and the anodes 2 and 3 by means of a direct current voltage source, which has not been represented in the figure, in such a manner that a predetermined current density is realized at both sides of the strip-iron 8. If necessary, this voltage and consequently the current density may be different at each side of the strip-iron 8 resulting in a different amount of nickel-cobalt alloy being deposited on both sides of the strip-iron 8. The cell may also comprise only one anode which allows to deposit the nickel-cobalt alloy on only one side of the strip-iron.

The employed anodes 2 and 3 are substantially insoluble anodes which are for example comprised of a lead-silver anode or a titanium anode coated by a noble metal such as ruthenium or iridium. As such anodes do not provide any nickel or cobalt, the electrolyte solution must contain all the nickel and cobalt which has to be deposited. Moreover, this electrolyte solution may practically not contain chlorides, a.o. for preventing corrosion of the anodes.

The use of the process according to the invention allows to deposit a metallic coating of a superior quality on the strip-iron 8. To this end, use is made according to the invention of a chloride-free solution containing at least nickel sulfate, cobalt sulfate, boric acid and sulfuric acid and this in combination with a cathode current density of at least 30 A/dm<sup>2</sup>. Comparative tests showed that due to this combination it is possible to realize after tempering high quality metallic deposits, by which are meant here a.o. uniform deposits having a fine grain structure.

It has been found, in contrast to the theories developed in the state of the art, that by applying a high cathode current density the cobalt is deposited easier so that the cobalt content in the nickel-cobalt alloy is increased with respect of the coatings deposited by the known processes of co-depositing nickel and cobalt wherein a low cathode current density, comprised between 0 and 13 A/dm<sup>2</sup>, is applied. According to the state of the art, it is known that in this range of low current densities, an increase of the current density reduces the cobalt content in the deposited nickel-cobalt alloy. However, it was found that by using substantially insoluble anodes and by applying a current density situated according to the invention between 30 and 300 A/dm<sup>2</sup>, a higher cobalt content in the deposited alloy is obtained, with the cobalt content being higher the more the cathode current density increases.

In a preferred embodiment of the process according to the invention, a current density of between 50 and 300 A/dm<sup>2</sup> and preferably between 150 to 300 A/dm<sup>2</sup> is applied. A current density of at least 150 A/dm<sup>2</sup> offers

the advantage that the cobalt is deposited so easy that obtaining a homogenous nickel-cobalt alloy does not involve any problems even with low cobalt contents in the electrolyte solution. By applying, for example, a cathode current density comprised between 240 and 250 A/dm<sup>2</sup> and an electrolyte solution containing 0.2 % cobalt sulfate, a deposited nickel-cobalt alloy coating can be obtained having a cobalt content of about 2 %. In order to allow such high current densities, the used electrolyte solution has to meet certain conditions such as, for example, with respect to the conductivity. A specific composition of the electrolysis bath is also necessary in combination with these high current densities, for realizing high quality deposits.

In this way, in a preferred embodiment of the invention, an electrolyte solution containing between about 30 and 60 g/l and preferably 50 g/l boric acid and about 5 to 15 g/l and preferably 10 g/l sulfuric acid is used. By using the combination of boric and sulfuric acid, it is possible to combine a good conductivity with a good Faraday efficiency. Indeed, the used sulfuric acid has an advantageous influence on the conductivity but a negative effect on the Faraday efficiency, whereas the boric acid has an advantageous influence on the Faraday efficiency but reduces slightly the conductivity.

The Faraday efficiency is, moreover, also influenced by the temperature of the electrolyte solution, which is comprised between 50 and 80°C, and is preferably substantially equal to 70°C during the electrolysis. An increase of this temperature has an advantageous effect on the efficiency but is limited as a consequence of the technical constraints of the materials. Agitating the electrolyte solution by injecting it between the two anodes increases also the Faraday efficiency. Moreover, sodium sulfate may be added to the electrolyte solution, more precisely an amount of upto the solubility limit of sodium sulfate. By adding sodium sulfate, the conductivity of the electrolyte solution increases also. However, the added amount of sodium sulfate may not be too large since this has a negative effect on the appearance of the deposit.

The electrolyte solution used in a preferred embodiment contains about 200 to 270g/l nickel sulfate, preferably 222 to 242 g/l and an amount of about 232 g/l nickel sulfate is particularly preferred. This solution contains, moreover, cobalt sulfate starting from the lowest contents of about 0.1 % of the electrolyte solution. It was found that due to such a specific electrolyte solution, with a relatively low nickel sulfate content, in combination with the described high current densities, high quality deposits can be obtained. An additional advantage of higher current densities is that the deposition proceeds at higher speeds.

As to the quality of the metallic deposits obtained by applying the process according to the invention, it was found experimentally that due to the high current density, very fine-grained uniform metal deposits are obtained. Due to the fine grain structure, the deposits are

brilliant and very resistant to corrosion considering the high density of the coating. As a consequence of the uniform growth of the coating during the electrolysis, a homogenous layer having a substantially uniform thickness is deposited. Consequently, the smallest thicknesses, i.e. possibly even smaller than 0.5 micrometres, are already sufficient to provide the deposited metallic coating with good anti-corrosion properties. In this way, a considerable amount of metal to be deposited may be saved by using the process according to the invention. This process causes further an increase of the electrical performance of the metallic deposit. The presence of cobalt in the deposited coating has a positive influence on the corrosion resistance and on the hardness of this deposit without reducing the stamping possibilities. Moreover, the cobalt increases the melt temperature of the nickel-cobalt alloy which reduces considerably the problem of sticking together when hardening rolls of strip-iron.

According to an alternative embodiment, the metallic coating may not only be deposited on a strip-steel but also on other objects, possibly of another material, such as, for example, materials previously coated with copper. It is also possible to add other materials to the electrolyte solution, which have also an effect on the deposited metallic coating. An example of these materials are the brighteners.

#### Claims

1. A process for electrodepositing a metallic coating, mainly composed of a nickel-cobalt alloy, on a surface of an object (8), in particular a strip-iron, by means of an electrolysis bath wherein at least one anode (2;3) is arranged in a substantially chloride-free electrolyte solution (5) which comprises at least nickel sulphate, cobalt sulphate and boric acid, according to which process at least said surface is immersed in the electrolyte solution and an electric voltage applied between said anode and the object acting as cathode, the electrolysis being realized in the electrolyte solution to which sulphuric acid has been added, and characterized in that the voltage which is applied between the cathode and the anode, which is a substantially insoluble anode, is of such a value that at said cathode, a current density of at least 30 A/dm<sup>2</sup> is realized.
2. A process according to claim 1, characterized in that the applied electric tension is of such a value that said current density is comprised between 50 and 300 A/dm<sup>2</sup>, preferably between 150 and 300 A/dm<sup>2</sup> and in particular between 240 and 250 A/dm<sup>2</sup>.
3. A process according to claim 1 or 2, characterized in that a solution having a sodium sulfate concentration of up to the solubility limit is used as electro-

lyte solution.

4. A process according to anyone of the claims 1 to 3, characterized in that a solution having a nickel sulfate concentration comprised between 200 and 270 g/l, preferably between 222 and 242 g/l and in particular of about 232 g/l is used as electrolyte solution.
5. A process according to anyone of the claims 1 to 4, characterized in that a solution having a boric acid concentration of about 30 to 60 g/l and preferably of about 50 g/l and a sulfuric acid concentration of about 5 to 15 g/l and more particularly of about 10 g/l is used as electrolyte solution.
6. A process according to anyone of the claims 1 to 5, characterized in that the electrolysis is realized at a temperature comprised between 50 and 80°C and preferably at a temperature of about 70°C.
7. A process according to anyone of the claims 1 to 6, characterized in that a lead-silver anode is used as insoluble anode.
8. A process according to anyone of the claims 1 to 6, characterized in that a titanium anode coated with a noble metal is used as insoluble anode.
9. A process according to anyone of the claims 1 to 8, characterized in that said object surface and said anode are disposed substantially in parallel relationship to one another and the electrolyte solution is injected between said surface and the anode.

#### Patentansprüche

1. Verfahren zur Elektroabscheidung einer metallischen Beschichtung, die hauptsächlich aus einer Nickel-Cobalt-Legierung bestehen, auf einer Oberfläche eines Objektes (8) und insbesondere eines Eisenblechstreifens, mit Hilfe eines Elektrolysebades, worin wenigstens eine Anode (2, 3) in einer im wesentlichen chloridfreien Elektrolytlösung (5) angeordnet ist, die wenigstens Nickelsulfat, Cobaltsulfat und Borsäure umfaßt, wobei gemäß diesem Verfahren wenigstens die Oberfläche in die Elektrolytlösung eingetaucht wird und eine elektrische Spannung zwischen der Anode und dem Objekt, das als Kathode wirkt, angelegt wird, wobei die Elektrolyse in der Elektrolytlösung verwirklicht wird, zu der Schwefelsäure zugegeben wurde, dadurch gekennzeichnet, daß die Spannung, die zwischen der Kathode und der Anode angelegt wird, die eine im wesentlichen unlösliche Anode darstellt, einen solchen Wert besitzt, das an der Kathode eine Stromdichte von wenigstens 30 A/dm<sup>2</sup> verwirklicht

wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die angelegte elektrische Spannung einen solchen Wert besitzt, daß die Stromdichte zwischen 50 und 300 A/dm<sup>2</sup>, bevorzugt zwischen 150 und 300 A/dm<sup>2</sup> und insbesondere zwischen 240 und 250 A/dm<sup>2</sup> liegt.

3. Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß eine Lösung als Elektrolytlösung verwendet wird, die eine Natriumsulfatkonzentration von bis zur Löslichkeitsgrenze besitzt.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß eine Lösung als Elektrolytlösung verwendet wird, die eine Nickelsulfatkonzentration besitzt, die zwischen 200 und 270 g/l, bevorzugt zwischen 222 und 242 g/l und insbesondere bei etwa 232 g/l liegt.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß eine Lösung als Elektrolytlösung verwendet wird, die eine Borsäurekonzentration von etwa 30 bis 60 g/l und bevorzugt von etwa 50 g/l und eine Schwefelsäurekonzentration von etwa 5 bis 15 g/l und insbesondere etwa 10 g/l besitzt.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Elektrolyse bei einer Temperatur verwirklicht wird, die zwischen 50 und 80°C und bevorzugt bei etwa 70°C liegt.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß eine Blei-Silberanode als unlösliche Anode verwendet wird.

8. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß eine Titananode, die mit einem Edelmetall beschichtet ist, als unlösliche Anode verwendet wird.

9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Objektoberfläche und die Anode im wesentlichen in paralleler Beziehung zueinander angeordnet sind und die Elektrolytlösung zwischen der Oberfläche und der Anode eingespritzt wird.

## Revendications

1. Procédé de dépôt électrolytique d'une couche métallique composée essentiellement d'un alliage nickel-cobalt sur une surface d'un objet (8), en particulier un feuillard en fer, à l'aide d'un bain d'électro-

lyse dans lequel est aménagé au moins une anode (2; 3) dans une solution (5) d'électrolyte qui comprend au moins du sulfate de nickel, du sulfate de cobalt et de l'acide borique, suivant lequel procédé on trempe au moins ladite surface dans la solution d'électrolyte et on applique une tension électrique entre ladite anode et l'objet faisant office de cathode, l'électrolyse étant réalisée dans la solution d'électrolyte à laquelle de l'acide sulfurique a été ajoutée, et caractérisé en ce que la tension qui est appliquée entre la cathode et l'anode, qui est une anode sensiblement insoluble, a une telle valeur que l'on réalise à ladite cathode une densité de courant d'au moins 30 A/dm<sup>2</sup>.

2. Procédé suivant la revendication 1, caractérisé en ce que la tension électrique appliquée a une telle valeur que ladite densité de courant est comprise entre 50 et 300 A/dm<sup>2</sup>, de préférence entre 150 et 300 A/dm<sup>2</sup> et particulièrement entre 240 et 250 A/dm<sup>2</sup>.

3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que comme solution d'électrolyte une solution ayant une concentration de sulfate de soude allant jusqu'à la limite de la solubilité est utilisée.

4. Procédé suivant l'une des revendications 1 à 3 caractérisé en ce que comme solution d'électrolyte une solution ayant une concentration de sulfate de nickel comprise entre 200 et 270 g/l, de préférence entre 222 et 242 g/l et particulièrement d'environ 232 g/l est utilisée.

5. Procédé suivant l'une ou l'autre des revendications 1 à 4, caractérisé en ce que comme une solution d'électrolyte une solution ayant une concentration d'acide borique entre environ 30 et 60 g/l et de préférence d'environ 50 g/l et une concentration d'acide sulfurique entre environ 5 et 15 g/l et particulièrement d'environ 10 g/l est utilisée.

6. Procédé suivant l'une ou l'autre des revendications 1 à 5, caractérisé en ce que l'électrolyse est réalisée à une température comprise entre 50 et 80°C et de préférence à une température d'environ 70°C.

7. Procédé suivant l'une des revendications 1 à 6, caractérisé en ce que comme anode insoluble une anode de plomb-argent est utilisée.

8. Procédé suivant l'une ou l'autre des revendications 1 à 6, caractérisé en ce qu'on utilise comme anode insoluble une anode de titane recouverte d'un métal noble.

9. Procédé suivant l'une des revendications 1 à 8, caractérisé en ce que l'on dispose ladite surface de

l'objet et ladite anode sensiblement en parallèle l'une à l'autre et que l'on injecte la solution d'électrolyte entre ladite surface et l'anode.

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