(54) **METHOD FOR PICKLING PRODUCTS OF A METAL ALLOY CONTAINING IRON AND OF TITANIUM AND ALLOYS THEREOF**

VERFAHREN ZUM BEIZEN VON EISEN ENTHALTENDEN METALLEGIERUNGEN UND TITAN UND SEINEN LEGIERUNGEN

PROCEDE DE DECAPAGE DE PRODUITS CONSTITUES D'UN ALLIAGE DE METAUX CONTENANT DU FER ET DE PRODUITS REALISES EN TITANE OU EN ALLIAGES DE TITANE

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(56) References cited:
**EP-A- 0 415 807   EP-A- 0 517 234
WO-A-97/43463   DE-A- 3 937 438**

• **CHEMICAL ABSTRACTS, vol. 84, no. 20, 17 May 1976 Columbus, Ohio, US; abstract no. 139369e, ISARAI R.: "pickling of austenitic stainless steel" page 256; XP002024602 & JP 50 133 125 A (DAIDO STEEL) 22 October 1975**

EP 0 960 221 B1

Description

[0001] The present invention relates to a method for pickling products made of stainless steel, which avoids the use of nitric acid as an oxidising agent.

[0002] The present invention can also be applied for pickling of titanium and alloys thereof.

[0003] It is known that pickling is the process used to remove the layer of oxidation that forms as a result of heat treating of steel.

[0004] In order to achieve an effective pickling process for stainless steels and titanium, a mixture of nitric acid (HNO_3) and hydrofluoric acid (HF) is normally used, at a temperature that generally varies between 60 and 75°C.

[0005] However, the use of nitric acid causes serious environmental control problems, which result from the following:

- a considerable presence in the vapours over the pickling bath of nitrogen oxides (NO_x), which are developed by the pickling bath itself;
- the formation of exhausted solutions which generate nitrate-rich sludge to be disposed of;
- the high cost of disposal for waste products containing nitrates.

[0006] To overcome the above difficulties, a number of different methods have been drawn up in which reduction or elimination of the use of nitric acid in chemical pickling processes has been foreseen, and which are based on the use of a number of oxidants, added to the bath as reactive agents, among which, for example, it is possible to include permanganates, persulphates, ferric chloride, hydrogen peroxide (H_2O_2), or mixtures thereof. In the pickling bath hydrofluoric acid is always used, in combination with various mineral acids (generally mixtures of acids), among which: sulphuric acid, hydrochloric acid, phosphoric acid.

[0007] In particular, a method exists that foresees a reduction in the amount of nitrogen oxides NO_x that are developed by the bath. Said method is generally based on the use of hydrogen peroxide, which not only makes it possible, if necessary, to reduce the total amount of nitric acid in the bath and required for the process, but also to oxidise the nitrogen oxides to the highest state of oxidation.

[0008] However, this method has the disadvantage that it only partially solves the problems mentioned above, as it only allows a reduction of the NO_x content in the vapours, not its elimination, and it leaves the problem of nitrates in the exhausted baths unsolved. For these only partial improvements, more or less complex variations in the basic pickling process (that is to say HF/HNO_3 mixtures) are necessary.

[0009] Another method is known, the purpose of which is to eliminate the presence of nitric acid altogether, using sulphuric acid, ferric sulphate and hydrogen peroxide alongside the hydrofluoric acid, the presence of which remains practically unchanged in the processes examined here.

[0010] However, the above method also shows the following problems:

a) complex management, deriving from the complexity of the analytical control of hydrogen peroxide in the baths (this reagent is in fact unstable);

b) difficulty in maintaining the dissolution kinetics (these are strongly dependent on the redox potential of the vehicle) within the necessary values; and

high running costs, also deriving from the high cost of the reagents, in particular stabilised hydrogen peroxide solution.

[0011] From Chemical Abstracts, vol. 84, No. 20, 17 May 1976 Columbus, Ohio, US; abstract No. 139369e, ISARAI R.: "Pickling of austenitic stainless steel" page 256; XPOO202 4602 of JP A-50133125, is known a pickling method similar to that of the invention. However, this method, since there is not provided a potentiostatical control of the anodic reaction, cannot assure the desired process kinetics and quality of the final product.

[0012] The aim of the present invention is therefore to solve the above mentioned problems, providing a method for pickling products made of stainless steel, and products made of titanium and alloys thereof, in the absence of nitric acid as an oxidising agent, wherein the product to be pickled is submerged in the pickling solution which forms the anolyte of an electrolytic cell in which the anolyte is made up of an aqueous solution of sulphuric acid, of hydrofluoric acid and optionally of phosphoric acid and hydrochloric acid, and with the catholyte made up of an aqueous solution of sulphuric acid, the oxidising agent in the pickling solution being the ferric ion, or the ions titanium(III) and titanium(IV), formed in the anode by oxidation of the ferrous ion, or of the ion titanium(II), resulting from dissolution of the surface layers of the product to be pickled, and the anodic reaction being potentiostatically controlled.

[0013] According to another aspect of the invention, the catholyte of the cell is preferably made up of an aqueous solution of sulphuric acid and is send out of the cathodic compartment into the pickling solution, to reintegrate the H_2SO_4 that is consumed during the pickling reaction.

[0014] According to the invention, the pickling bath forms the anolyte of the cell, and is maintained at a temperature preferably comprised between 45 and 85°C, and it is made up of an aqueous solution of sulphuric acid, of hydrofluoric acid and optionally of hydrochloric and phosphoric acid, with the following composition expressed as a percentage by weight:

- free HCl between 0 and 50 g/l
- free H_3PO_4 between 0 and 200 g/l
- free H_2SO_4 from 50 to 250 g/l

- free HF from 5 to 50 g/l
- Fe_{tot} in solution $\geq$ 50 g/l

[0015] Furthermore, the products containing iron for which the method according to the present invention is applicable are selected from the group comprising:

- Stainless, laminated or in any case hot and/or cold worked steel, in particular austenitic, ferritic, duplex and super-stainless steel;
- Ni-based super-alloys.

[0016] Furthermore, the products containing titanium for which the method according to the present invention is applicable are selected from the group comprising:

- CP (commercial purity) Titanium of various grades;
- Titanium alloys.

[0017] The present invention will be more clearly illustrated in the following detailed description of a preferred embodiment thereof, given merely as a nonlimiting example, with reference to the enclosed figures, in which:

figure 1 shows a diagram of an embodiment of the pickling bath according to the present invention; and
figure 2 shows a diagram of the variation in weight of the metal product according to the concentration of acids and iron ions in the pickling bath according to the present invention.

[0018] The method object of the present invention is based on the replacement of nitric acid and on the theory that this acid performs two basic operations:

a) it increases the total acidity of the bath; and
b) it raises the redox potential of the vehicle, according to the oxidising properties of said acid.

[0019] The overall action of the nitric acid can thus be obtained using various reagents capable of guaranteeing these two specific actions, even separately. The reagents selected to control the total acidity are therefore mineral acids and oxidising agents.

[0020] Finally, as regards the use of oxidising agents, the method according to the present invention does not resort to direct addition of reagents into the bath, but uses electro-chemical treatment of the solution which generates the desired oxidising agent directly in the pickling bath.

[0021] Specifically, the method object of the present invention is based on the used of a pickling bath that does not contain nitric acid, but contains in its place a mineral acid (for example sulphuric acid) and as an oxidant contains only the ferric ion Fe^{3+} (or, in the case of titanium, the ions Ti^{3+} and Ti^{4+}). The ferric ion is not added in the form of a reagent, but is obtained directly in the pickling solution by anodic oxidation in an electrolytic cell of the ions Fe^{2+} that are generated during the pickling process itself (dissolution of the steel). In the case of titanium, anodic oxidation of the Ti^{2+} ions to Ti^{3+} and Ti^{4+} ions is carried out in the cell.

[0022] A diagram of a preferred embodiment of the method according to the invention is illustrated in figure 1. According to the method of the invention, an electro-chemical cell of the membrane type is used, worked by controlling the anodic potential or using a galvanostatic control. The cell anolyte (in which the reaction generating Fe^{3+} ions takes place) is made of the same solution as the pickling bath, whereas the catholyte used is a solution of sulphuric acid that is destined to be sent to the pickling bath.

[0023] The mineral acids used as anolyte are mixtures of hydrofluoric, sulphuric, hydrochloric and phosphoric acid.

[0024] According to the invention, the method provides a self-balancing system, that is to say one that is capable of controlling the process kinetics and the final quality of the product. The pickling kinetics are in fact directly controllable according to the speed of production of Fe^{3+} ions in the cell.

[0025] Control of the concentration of Fe^{3+} ions in the pickling bath (which can be done easily by setting the cell working parameters) also allows close control of the most critical process parameter (that is to say the redox potential value of the system), also giving obvious advantages for the final quality of the product.

[0026] The use of anodic oxidation in a cell to generate the oxidant results in a considerable saving in working costs, due to the higher cost of the oxidising reagents added to the bath according to normal methods.

[0027] Finally, the choice of the Fe^{3+} ion as an oxidant does not involve stability problems in the bath, as is the case in certain reagents (in particular hydrogen peroxide solution requires the use of expensive stabilising agents).

[0028] The principles that have resulted in definition of the solutions used to apply the method according to the present invention are based on the following considerations:

a) Pickling (both using traditional processes in HF/HNO_3 solutions and using H_2O_2-based processes) must necessarily involve the presence of an oxidant that keeps the redox potential at the necessary levels;
b) The presence of oxidants involves the passage of ferrous ions from Fe^{2+} (produced during the pickling reaction) to Fe^{3+} (or of Ti^{2+} to Ti^{3+} and Ti^{4+});
c) The ferric ions Fe^{3+} are notoriously oxidant with respect to the steel to be pickled (in fact, according to the reversible electro-chemical potentials scale it can be seen that: E_{rev}=-447 mV SHE (Standard Hydrogen Electrode) for the pair Fe/Fe^{2+}; E_{rev}=+771 mV SHE for the pair Fe^{2+}/Fe^{3+}); in a similar way the

high valence titanium ions (Ti^{3+} and Ti^{4+}) are oxidant with respect to the titanium to be pickled, as we have E_{rev} = -1630 mV SHE for the pair Ti/Ti^{2+}, whereas we have E_{rev}= -502 mV SHE and E_{rev} = -368 mV SHE for the pairs Ti^{4+}/Ti^{3+} and Ti^{3+}/Ti^{2+}, respectively;

d) From the above points a), b) and c) it can be seen that there is the possibility of using the types Fe^{3+} (of Ti^{4+} and Ti^{3+}) directly as an oxidising reagent in the solution, instead of nitric acid or hydrogen

e) The total acidity of the solution, in the absence of nitric acid, can be raised using lower cost mineral acids, such as H_2SO_2, HCl and H_3PO_4, either alone or in combination (see points f and g);

f) The hydrochloric acid performs in part the functions of the hydrofluoric acid (it is a strong de-passivating, or activating agent), but at a lower cost.

g) The total acidity cannot be re-established with hydrochloric acid alone, as the ion Cl⁻ would be too aggressive on the surface of the steel, preventing, or complicating unnecessarily, the normal final passivation treatment; the choice of a balanced mixture of the two acids HCl and H_2SO_4 helps to improve control of the electro-chemical working potentials and the dissolution kinetics; when the bath is not required to be excessively aggressive it is possible to use a progressively lower concentration of HCl, even reducing the content to zero, with HF and H_2SO_4, or alternatively mixtures of HF, H_2SO_4 and H_3PO_4; phosphoric acid acts using a mechanism similar to that of sulphuric acid.

[0029] On the basis of the above and according to the method of the present invention, the pickling bath can conveniently use the following reagents:

- acids: HF and mixtures of HCl/H_2SO_4/H_3PO_4 at variable concentrations, including mixtures with HCl and/or H_3PO_4 at concentration zero;
- oxidants: ferric ion Fe^{3+} (alternatively, for titanium, Ti^{4+} and Ti^{3+}).

[0030] In view of the particular oxidant chosen (Fe^{3+} and/or Ti^{3+} and Ti^{4+}), the method object of the invention foresees electro-chemical treatment of the solution, by which it is possible to obtain direct formation of the oxidising agent and control of the correct concentration levels directly within the bath.

[0031] The principles and criteria used to prepare an electro-chemical cell that can be used to apply the method of the present invention will now be defined with reference to figure 1. For the sake of simplicity, reference will be made to a pickling cell for metal alloys containing iron, as treatment of titanium is the same.
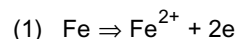
a) Anolyte

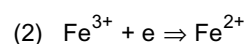**[0032]** The same pickling solution is used, and is con-

tinuously circulated (but discontinuous treatment can also be foreseen) from the bath by pumping;

b) Anodic reaction: $Fe^{2+} \Rightarrow Fe^{3+}$

[0033] This reaction produces the Fe^{3+} that serves to maintain the concentration of the oxidising agent Fe^{3+} in the pickling bath constant. The pickling mechanism in the presence of Fe^{3+} as an oxidant takes place using the following reactions:
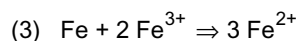
$$(1) \quad Fe \Rightarrow Fe^{2+} + 2e$$

(primary oxidation semi-reaction to dissolve the metallic iron);
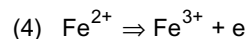
$$(2) \quad Fe^{3+} + e \Rightarrow Fe^{2+}$$

(reduction semi-reaction).

[0034] The resulting reaction (in the bath), that is to say the sum of the two semi-reactions (1)+(2) is:

$$(3) \quad Fe + 2\,Fe^{3+} \Rightarrow 3\,Fe^{2+}$$

[0035] From the reaction (3) it is found that the quantity of Fe^{3+} ions that must be generated in the cell over a period of time is equivalent to double the quantity of iron that is in solution during pickling.
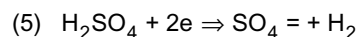
is carried out:

$$(4) \quad Fe^{2+} \Rightarrow Fe^{3+} + e$$

[0036] It should be noted that reaction (4) is the inverse reaction to (2). The ion Fe^{3+} reduces to Fe^{2+} during (2) in the bath and oxidises again in the cell from Fe^{2+} in (4). The oxidising capacity of the system is thus guaranteed by passage of the anodic current in the cell in reaction (4), in which the ion Fe^{3+} is a go-between and, according to the present method, no other reagents are added as oxidants.

c) Cathodic reaction

[0037] For the reaction in the cathodic part of the cell it has been found that the most practical solution is that of using a solution of sulphuric acid as a catholyte, because of the fact that the pickling process in reference foresees the use of sulphuric acid in the bath.

[0038] The cathode reaction is therefore the following:

$$(5) \quad H_2SO_4 + 2e \Rightarrow SO_4 = + H_2$$

[0039] The catholyte is sent into the bath in an hourly

amount equal to the sulphuric ion content necessary to combine with the ion Fe^{2+} generated by reaction (1), according to the following reaction:

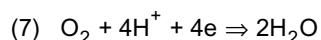$$(6) \quad Fe^{2+} + SO_4 = \Rightarrow FeSO_4$$

d) Anodic control

[0040]   As regards control of the passage of current in the electrolytic cell, two alternatives are possible:
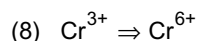
d.1) Potentiostatic control

[0041]   This is performed with a minimum electrode potential of $\geq$ 771 mV SHE which allows the oxidation reaction (4). As regards the maximum value it is preferable to select a value that in particular does not allow development of oxygen, according to the following reaction:

$$(7) \quad O_2 + 4H^+ + 4e \Rightarrow 2H_2O$$

(E_{rev} = +1229 mV SHE)
[0042]   The co-presence of reaction (7) and (4) would, in fact, decrease the efficiency of the cell, attenuating the undesired water hydrolysis reaction by developing oxygen. The chosen potential E is thus in the range of between 771 and 1229 mV SHE. For potential values of this kind, among other things, there is no formation of chrome with valence 6 (often toxic), according to the simplified reaction:

$$(8) \quad Cr^{3+} \Rightarrow Cr^{6+}$$

(reversible potential E_{rev} = +1350 mV SHE).
[0043]   In practice it can be of use to position at values even relatively higher than 1229 mV, taking advantage of the fact that the oxygen development reaction takes place with a certain level of overvoltage.

d.2) Galvanostatic control

[0044]   This control is more simple and more economical to perform in the system, but the advantages indicated in point (d.1) above might be lost, in particular there is a risk of excessive oxygen development. However, exact experimental knowledge of the characteristics of the cell and suitable control of the current make it possible to obtain the desired electro-chemical potential in the anode, also using galvanostatic control.

e) Membrane

[0045]   As the anolyte and catholyte solutions are different and, in particular, in order not to decrease the ef-

ficiency of the cell, it is undesirable that there be any transmigration into the catholyte of ferric ions Fe^{3+} formed in the anolyte, the cell is provided with a suitable membrane. It is possible to use membranes of different effectiveness, working temperature and duration.
[0046]   The electro-chemical cell in reference when tested in the system has provided the following performance levels, which are given below in the form of an example:

- efficiency under current: > 90%
- cell potential (ΔV at terminals) $\cong$ 3V
- specific power $\cong$ 6W/dm^2
- anode current density $\cong$ 2A/dm^2
- consumption per mole Fe^{3+} produced $\cong$ 0.081 kWh

[0047]   To the above must be added that the value of the current, when the cell characteristics are known, directly expresses the Fe^{3+} ion formation speed, as per reaction (4). This makes it possible to maintain its concentration in the bath constant, when the characteristic speed of the pickling process is known.
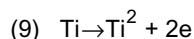[0048]   The system thus results self-balanced, in fact the dissolution reaction (1), that is to say the pickling reaction, cannot proceed at a kinetic level superior to the cell reaction (4), as there would be a deficit in the transfer of electrons for the anodic pickling semi-reaction itself. In a similar manner, if dissolution in (5) decreases its kinetics for any reason, there would be a progressive rise in the concentration of Fe^{3+} ions in the bath (as the supply from reaction (4) is constant), with a corresponding rise in the redox potential of the solution and thus of the overall pickling kinetics.
[0049]   With reference to figure 1, it is shown how the dissolution kinetics of AISI 409 LI stainless steel increase as the Fe^{3+} content increases.
[0050]   Finally, the proposed pickling method follows the speed of reaction (4), which can be controlled easily using the cell parameters.
[0051]   As regards more specifically application of the method according to the present invention for pickling of titanium and alloys thereof, the following must be specified:
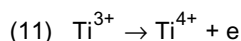
- Titanium is susceptible to pickling in the same conditions as stainless steel, that is to say traditional baths in HNO_3/HF solutions or in baths of the type without nitric acid (generally speaking, because of the higher reactivity of this element, low concentrations and temperatures of around 40-50°C are used);
- Pickling of titanium and alloys thereof shows kinetics and elementary pickling reactions that are entirely the same as regards the electro-chemical cell and method described above. In particular, it is sufficient to bear in mind that in the case of titanium the basic pickling reaction is:

$$(9) \quad Ti \rightarrow Ti^2 + 2e$$

$$(E_{rev} = -1630 \text{ mV SHE})$$

[0052] The role played by the ion Fe^{3+} in reaction (2) can be substituted, if iron is not available or not desired in the bath, by the ions Ti^{3+} and Ti^{4+}, given that for the pair Ti^{3+}/Ti^{2+} $E_{rev} = 502$ mV and for the pair Ti^{4+}/Ti^{3+} $E_{rev} = -368$ mV SHE.

[0053] In the electro-chemical cell, in this case, the following oxidation reactions take place:

$$(10) \quad Ti^{2+} \rightarrow Ti^{3+} + e$$

$$(11) \quad Ti^{3+} \rightarrow Ti^{4+} + e$$

[0054] The anodic cell potential in this case is selected within the range of between -368 mV SHE (oxidation of Ti^{2+} to Ti^{4+}) and 1229 mV SHE (development of oxygen).

[0055] The method according to a second embodiment of the invention foresees, for pickling of titanium and alloys thereof, the use of the same baths and acid solutions containing Fe^{3+} that are used for pickling of stainless steel. This method is very convenient, because the majority of titanium coil manufacturers process these coils on the same lines used for stainless steel.

[0056] In this case, in the baths containing solutions of H_2SO_4 (or other mineral acids), HF and iron ions, the titanium is pickled according to the reaction (9) (oxidation reaction), as the oxidising agent is the ion Fe^{3+}, which reduces according to reaction (2), whereas in the electro-chemical cell the concentration of Fe^{3+} is restored by means of reaction (4).

[0057] Finally, as seen above, the ion Fe^{3+} (and the ion Fe^{2+} from which it is formed) does not participate in the overall reaction balance, so there is no consumption of the quantity of iron ions contained in the bath, whereas the oxidising capacity, in terms of electron transfer, is ensured by the passage of current to the cell anode.

[0058] An example of a pickling process carried out according to the method of the present invention will now be given.

EXAMPLE

[0059] The example of a pickling process refers to a coil of hot laminated and peened AISI 304 steel.

[0060] The initial pickling solution is made up of:

Free H_2SO_4 = 150 g/l
Free HF = 30 g/l
Total Fe in solution $\geq$ 50 g/l.

[0061] Initially the solution is made to circulate in the electrolytic cell until reaching the optimum Fe^{3+} value, equivalent to $\geq$ 30 g/l, and a temperature of approximately 65°C.

[0062] After this the pickling process commences (tape sent into the pickling bath) at the line speed foreseen. The line speed, the thickness and the width of the treated tape obviously define the production level per hour, expressed in t/h of pickled tape (e.g. at a speed of 18 metres/minute, tape thickness 3.2 mm and width 1500 mm the production of pickled tape will be approximately 40 t/h). According to the example, the tape is 3.2 mm thick (typical average thickness of hot-laminated products).

[0063] Pickling was carried out continuously in the following conditions:

- Circulation of the pickling solution in the electro-chemical cell with a production of Fe^{3+} ions $\geq$ 48 moles/t of pickled tape;
- Consumption (and therefore reintegration) of acids:

     $H_2SO_4 \geq 1.8$ Kg/t of pickled tape;
     HF ≥ 1.4 Kg/t of pickled tape.

[0064] It will be obvious to those expert in the field that other embodiments differing from the one described above with reference to figure 1 are possible. In particular the pickling bath can be made up of the anodic part of the cell, without the need to create external circulation of the anolyte between the bath and the cell. Furthermore, as regards the catholyte, it is not necessarily essential to resort to solutions using sulphuric acid, as different electrolytes can be chosen (e.g. HCl, mixtures of HCl/H_2SO_4 or others), including the pickling solution itself which is eliminated as waste. Input of the catholyte into the bath may also not be necessary, in particular when electrolytes other than those used in the pickling bath are chosen. All the above variations are alternatives to the one described and illustrated as the preferred embodiment, and are understood to fall within the scope of the present invention.

Claims

1. A method for pickling products made of stainless steel or products made of titanium and alloys thereof, in the absence of nitric acid as an oxidising agent, wherein the product to be pickled is submerged in the pickling solution which forms the anolyte of an electrolytic cell in which the anolyte is made up of an aqueous solution of sulphuric acid, of hydrofluoric acid and optionally of phosphoric acid and hydrochloric acid, and with the catholyte made up of an aqueous solution of sulphuric acid, the oxidising agent in the pickling solution being the ferric ion, or the ions titanium (III) and titanium (IV),

formed in the anode by oxidation of the ferrous ion, or of the ion titanium (II), resulting from dissolution of the surface layers of the product to be pickled, and the anodic reaction being potentiostatically controlled.

2. A method for pickling products made of stainless steel according to claim 1, in which the working electro-chemical potential of the cell anode being between 771 and 1229 mV SHE (Standard Hydrogen Electrode).

3. A method for pickling products made of titanium and alloys thereof according to claim 1, in which the working electro-chemical potential of the cell anode is between -368 and 1229 mV SHE (Standard Hydrogen Electrode).

4. A method for pickling products made of stainless steel, and products made of titanium and alloys thereof according to any one of the preceding claims, in which the pickling operations are carried out in a continuous or discontinuous manner by means of continuous or discontinuous circulation of the anolyte.

5. A method for pickling products made of stainless steel, and products made of titanium and alloys thereof according to the preceding claim, in which the pickling bath containing the anolyte forms the anodic compartment in the electro-chemical cell.

6. A method for pickling products made of stainless steel, and products made of titanium and alloys thereof according to any one of the preceding claims, in which the catholyte of the electrolytic cell is made up of a solution of sulphuric acid and is sent, on leaving the cathodic compartment, into the pickling solution as an anolyte.

7. A method according to the preceding claim, in which the catholyte solution is made up of any electrolyte which can either be sent into the anolyte or not.

8. A method according to any one of the preceding claims, in which the catholyte is made up of pickling solution and is subsequently discharged from the cathodic area as waste material.

9. A method for pickling products made of stainless steel, and products made of titanium and alloys thereof according to any one of the preceding claims, in which the pickling bath has a temperature of between 40 and 90°C and is made up of an aqueous solution containing the following components:

- free HCl between 0 and 50 g/l
- free H_3PO_4 between 0 and 200 g/l

- free H_2SO_4 from 50 to 250 g/l
- free HF from 5 to 50 g/l
- Fe_{tot} in solution $\geq$ 50 g/l

and alternatively, for products in titanium and alloys thereof, Ti_{tot} in solution $\geq$ 50 g/l.

10. A method for pickling products made of stainless steel according to any one cf claims 1, 2 and 4-9, in which said products made of stainless steel are chosen from the group comprising:

- Stainless, laminated or in any case hot and/or cold worked steel, in particular austenitic, ferritic, duplex and super-stainless steel; and
- Ni-based super-alloys.

11. A method for pickling products made of titanium and alloys thereof according to any one of claims 1, 3 and 4-10, in which said products containing titanium and alloys thereof are selected from the group comprising:

- CP (commercial purity) Titanium of various grades;
- Titanium alloys.

Patentansprüche

1. Verfahren zum Beizen von Erzeugnissen, die aus nichtrostendem Stahl gefertigt sind, oder von Erzeugnissen, die aus Titan und Legierungen davon gefertigt sind, in Abwesenheit von Salpetersäure als Oxidationsmittel, wobei das zu beizende Erzeugnis in die Beizlösung eingetaucht wird, welche den Anoiyt einer elektrolytischen Zelle bildet, in welcher der Anolyt aus einer wässrigen Lösung von Schwefelsäure, von Fluorwasserstoffsäure und gegebenenfalls von Phosphorsäure und Chlorwasserstoffsäure gebildet ist, und wobei der Katholyt aus einer wässrigen Lösung von Schwefelsäure gebildet ist, wobei das Oxidationsmittel in der Beizlösung das Eisen(III)-Ion oder die Ionen Titan(III) und Titan(IV) sind, die in der Anode durch Oxidation des Eisen(II)-Ions oder des Ions Titan(II) gebildet werden, welche von der Auflösung der Oberflächenschichten des zu beizenden Erzeugnisses herrühren, und wobei die Anodenreaktion potentiostatisch geregelt wird.

2. Verfahren zum Beizen von Erzeugnissen, die aus nichtrostendem Stahl gefertigt sind, nach Anspruch 1, in welchem das elektrochemische Arbeitspotential der Zellenanode zwischen 771 und 1229 mV SHE (Standardwasserstoffelektrode) beträgt.

3. Verfahren zum Beizen von Erzeugnissen, die aus

Titan und Legierungen davon gefertigt sind, nach Anspruch 1, in welchem das elektrochemische Arbeitspotential der Zellenanode zwischen -368 und 1229 mV SHE (Standardwasserstoffelektrode) beträgt.

4. Verfahren zum Beizen von Erzeugnissen, die aus nichtrostendem Stahl gefertigt sind, und von Erzeugnissen, die aus Titan und Legierungen davon gefertigt sind, nach einem der vorangehenden Ansprüche, in welchem die Beizvorgänge auf kontinuierliche oder diskontinuierliche Weise mittels einer kontinuierlichen oder diskontinuierlichen Umwälzung des Anolyts durchgeführt werden.

5. Verfahren zum Beizen von Erzeugnissen, die aus nichtrostendem Stahl gefertigt sind, und von Erzeugnissen, die aus Titan und Legierungen davon gefertigt sind, nach dem vorangehenden Anspruch, in welchem das Beizbad, welches den Anolyt enthält, die Anodenkammer in der elektrochemischen Zelle bildet.

6. Verfahren zum Beizen von Erzeugnissen, die aus nichtrostendem Stahl gefertigt sind, und von Erzeugnissen, die aus Titan und Legierungen davon gefertigt sind, nach einem der vorangehenden Ansprüche, in welchem der Katholyt der elektrolytischen Zelle aus einer Lösung von Schwefelsäure gebildet ist und beim Verlassen der Kathodenkammer in die Beizlösung als Anolyt geleitet wird.

7. Verfahren nach dem vorangehenden Anspruch, in welchem die Katholytlösung aus einem beliebigen Elektrolyt gebildet ist, der entweder in den Anolyt geleitet oder nicht geleitet werden kann.

8. Verfahren nach einem der vorangehenden Ansprüche, in welchem der Katholyt aus der Beizlösung gebildet ist und anschließend als Abfall aus dem Kathodenbereich ausgetragen wird.

9. Verfahren zum Beizen von Erzeugnissen, die aus nichtrostendem Stahl gefertigt sind, und von Erzeugnissen, die aus Titan und Legierungen davon gefertigt sind, nach einem der vorangehenden Ansprüche, in welchem das Beizbad eine Temperatur zwischen 40 und 90°C hat und aus einer wässrigen Lösung gebildet ist, welche die folgenden Bestandteile enthält:

- freie HCl zwischen 0 und 50 g/l
- freie H_3PO_4 zwischen 0 und 200 g/l
- freie H_2SO_4 von 50 bis 250 g/l
- freie HF von 5 bis 50 g/l
- Fe_{gesamt} in Lösung $\geq$ 50 g/l

und alternativ, für Erzeugnisse aus Titan und Legie-

rungen davon, Ti_{gesamt} in Lösung $\geq$ 50 g/l.

10. Verfahren zum Beizen von Erzeugnissen, die aus nichtrostendem Stahl gefertigt sind, nach einem der Ansprüche 1, 2 und 4-9, in welchem die Erzeugnisse, die aus nichtrostendem Stahl gefertigt sind, ausgewählt werden aus der Gruppe umfassend:

- nichtrostenden, laminierten oder jedenfalls warm- und/oder kaltverarbeiteten Stahl, insbesondere austenitischen Stahl, ferritischen Stahl, Duplex-Stahl und extrem nichtrostenden Stahl (super-stainless steel); und

- Superlegierungen auf Ni-Basis.

11. Verfahren zum Beizen von Erzeugnissen, die aus Titan und Legierungen davon gefertigt sind, nach einem der Ansprüche 1, 3 und 4-10, in welchem die Erzeugnisse, die Titan und Legierungen davon enthalten, ausgewählt sind aus der Gruppe umfassend:

- CP-Titan (Titan mit handelsüblicher Reinheit) verschiedener Qualitätsstufen;
- Titanlegierungen.

Revendications

1. Procédé pour le décapage de produits réalisés à partir d'acier inoxydable ou de produits réalisés en titane ou en alliages de titane, en l'absence d'acide nitrique en tant qu'agent oxydant, dans lequel le produit à décaper est immergé dans la solution de décapage qui forme l'anolyte d'une cellule électrolytique, dans laquelle l'anolyte consiste en une solution aqueuse d'acide sulfurique, d'acide fluorhydrique et facultativement d'acide phosphorique et d'acide chlorhydrique, et avec le catholyte consistant en une solution aqueuse d'acide sulfurique, l'agent oxydant dans la solution de décapage étant l'ion ferrique, ou les ions titane (III) et titane (IV), formés dans la cathode par oxydation de l'ion ferreux, ou de l'ion titane (II), résultant de la dissolution des couches de surface du produit à décaper, et la réaction anodique étant contrôlée potentiostatiquement.

2. Procédé pour le décapage de produits réalisés à partir d'acier inoxydable selon la revendication 1, dans lequel le potentiel électrochimique de travail de l'anode de cellule se situe entre 771 et 1299 mV SHE (Electrode d'hydrogène étalon).

3. Procédé pour le décapage de produits réalisés en titane et en alliages de titane selon la revendication 1, dans lequel le potentiel électrochimique de travail
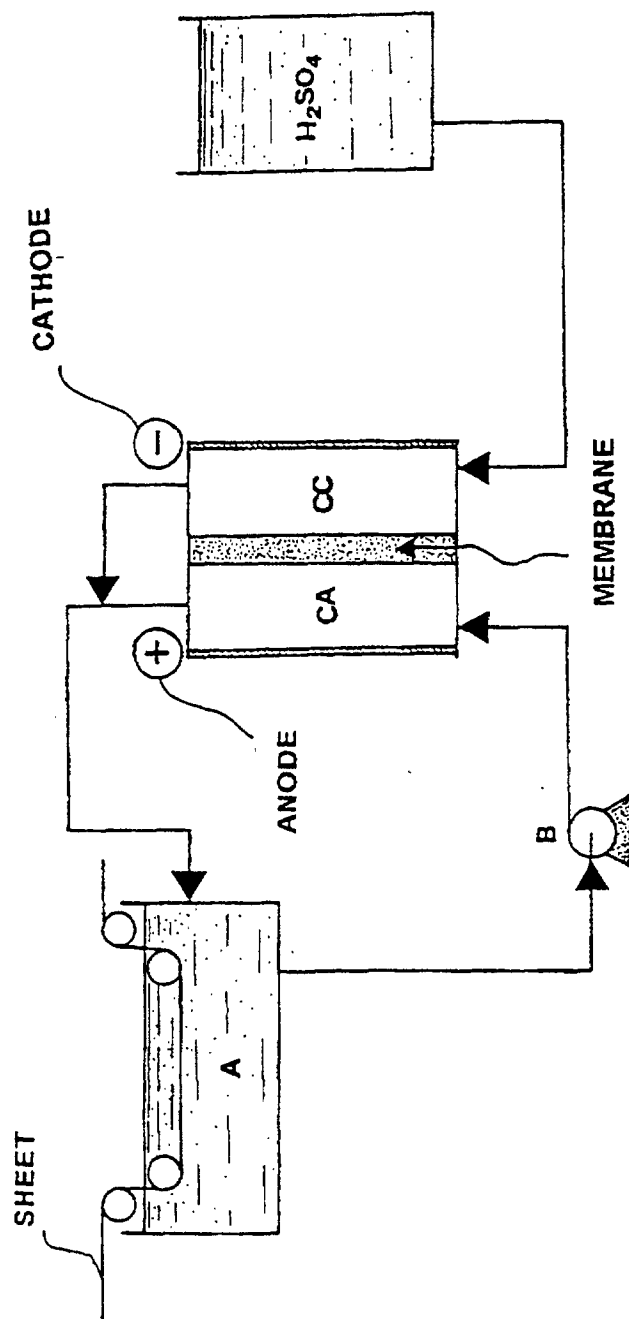
de l'anode de cellule se situe entre -368 et 1229 mV SHE (Electrode d'hydrogène étalon).

4. Procédé pour le décapage de produits réalisés en acier inoxydable, et de produits réalisés en titane et alliages de titane selon l'une quelconque des revendications précédentes, dans lequel les opérations de décapage sont exécutées d'une manière continue ou discontinue au moyen de la circulation continue ou discontinue de l'anolyte.

5. procédé pour le décapage de produits réalisés en acier inoxydable, et de produits réalisés en titane et en alliages de titane selon la revendication précédente, dans lequel le bain de décapage contenant l'anolyte forme le compartiment anodique dans la cellule électrochimique.

6. Procédé pour le décapage de produits réalisés en acier inoxydable, et de produits réalisés en titane et en alliages de titane selon l'une quelconque des revendications précédentes, dans lequel le catholyte de la cellule électrolytique consiste en une solution d'acide sulfurique et est envoyée, après avoir quitté le compartiment cathodique, dans la solution de décapage en tant qu'anolyte.

7. Procédé selon la revendication précédente, dans lequel la solution de catholyte consiste en tout électrolyte pouvant être envoyé ou non dans l'anolyte.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catholyte consiste en une solution de décapage et elle est consécutivement déchargée de la zone cathodique comme matière de déchet.

9. Procédé pour le décapage de produits réalisés à partir d'acier inoxydable, et de produits réalisés en titane et en alliages de titane selon l'une quelconque des revendications précédentes, dans lequel le bain de décapage a une température entre 40 et 90 °C et consiste en une solution aqueuse contenant les composants suivants :

   - HCL libre entre 0 et 50 g/l
   - H_3PO_4 entre 0 et 200 g/l
   - H_2SO_4 de 50 à 250 g/l
   - HF libre de 5 à 50 g/l
   - Fe_{tot} dans la solution > 50 g/l

   et en variante, pour des produits en titane et alliages de titane, Ti_{tot} en solution > 50 g/l.

10. Procédé pour le décapage de produits réalisés à partir d'acier inoxydable selon l'une quelconque des revendications 1,2 et 4-9, dans lequel lesdits produits réalisés en acier inoxydable sont choisis à par-

tir du groupe comprenant :

   - l'acier inoxydable, laminé ou en tout cas travaillé à chaud et/ou à froid; et
   - des super alliages à base de Ni.

11. Procédé pour le décapage de produits réalisés à partir du titane et en alliages de titane selon l'une quelconque des revendications 1,3 et 4-10, dans lequel lesdits produits contenant le titane et les alliages de titane sont choisis à partir du groupe comprenant :

   - du Titane PC (pureté commerciale) de différentes qualités;
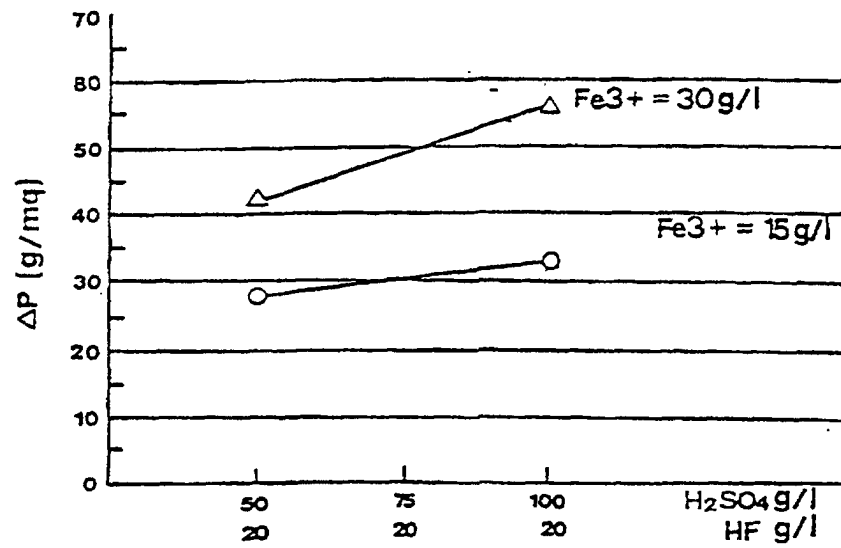   - des alliages de titane.

FIG 1

A : Pickling bath

B: Pump

CA: Anodic compartment

CC: Cathodic compartment

Temperature   T = 45°C
Time   t = 60 s
Material   :   AISI 409 LI

FIG 2