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(54) **ANODIZATION METHOD FOR CORROSION PROTECTION OF ALUMINIUM ALLOY ELEMENTS USED IN AN AIRCRAFT STRUCTURE**

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(57) **ABSTRACT**

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An anodization method for corrosion protection of an aluminium or aluminium alloy element used in an aircraft structure, comprising the following steps: a) subjecting the element to a degreasing step by means of an alkaline bath for removing contaminating elements; b) subjecting the element to a subsequent first washing in water; c) subjecting the element to an acid pickling step by dipping the element in an acid solution and then extracting the element from the acid solution and subjecting the element to a subsequent washing in water; subjecting the washed element to a subsequent electrochemical treatment step in a tank by dipping the element in a solution of tartaric acid (C₄H₆O₆) and sulphuric acid (H₂SO₄); e) subjecting the element to a subsequent washing in water; f) dipping the element in a bath in which a solution of chromium, with an oxidation number of +3, and zirconium ions and fluorides is present, in order to carry out a first post-anodization sealing step; g) extracting the element from the bath of step f) and subjecting it to a subsequent final washing and a subsequent dipping in a tank of boiling water (second sealing step), and then drying the element.

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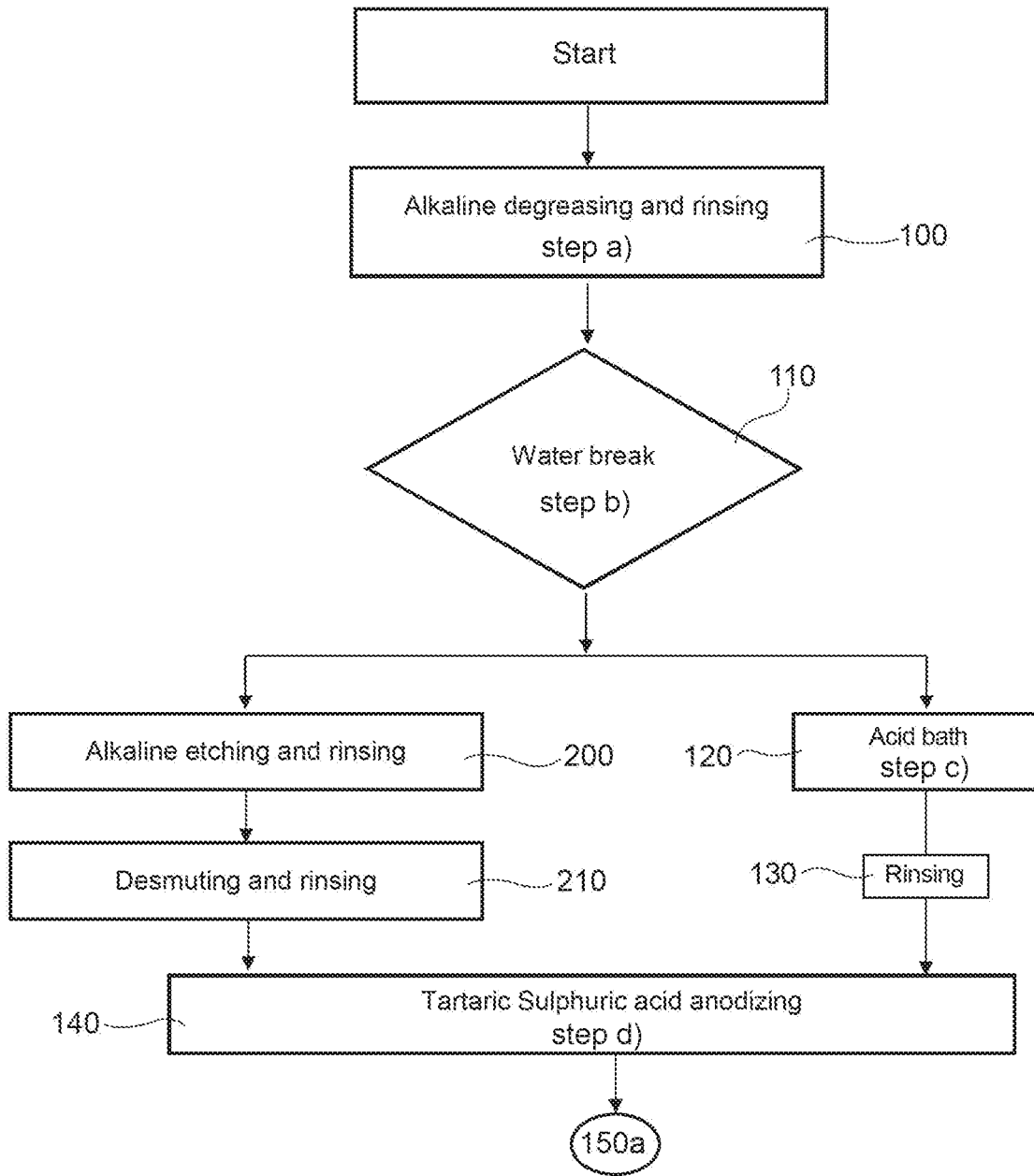


FIG. 1A

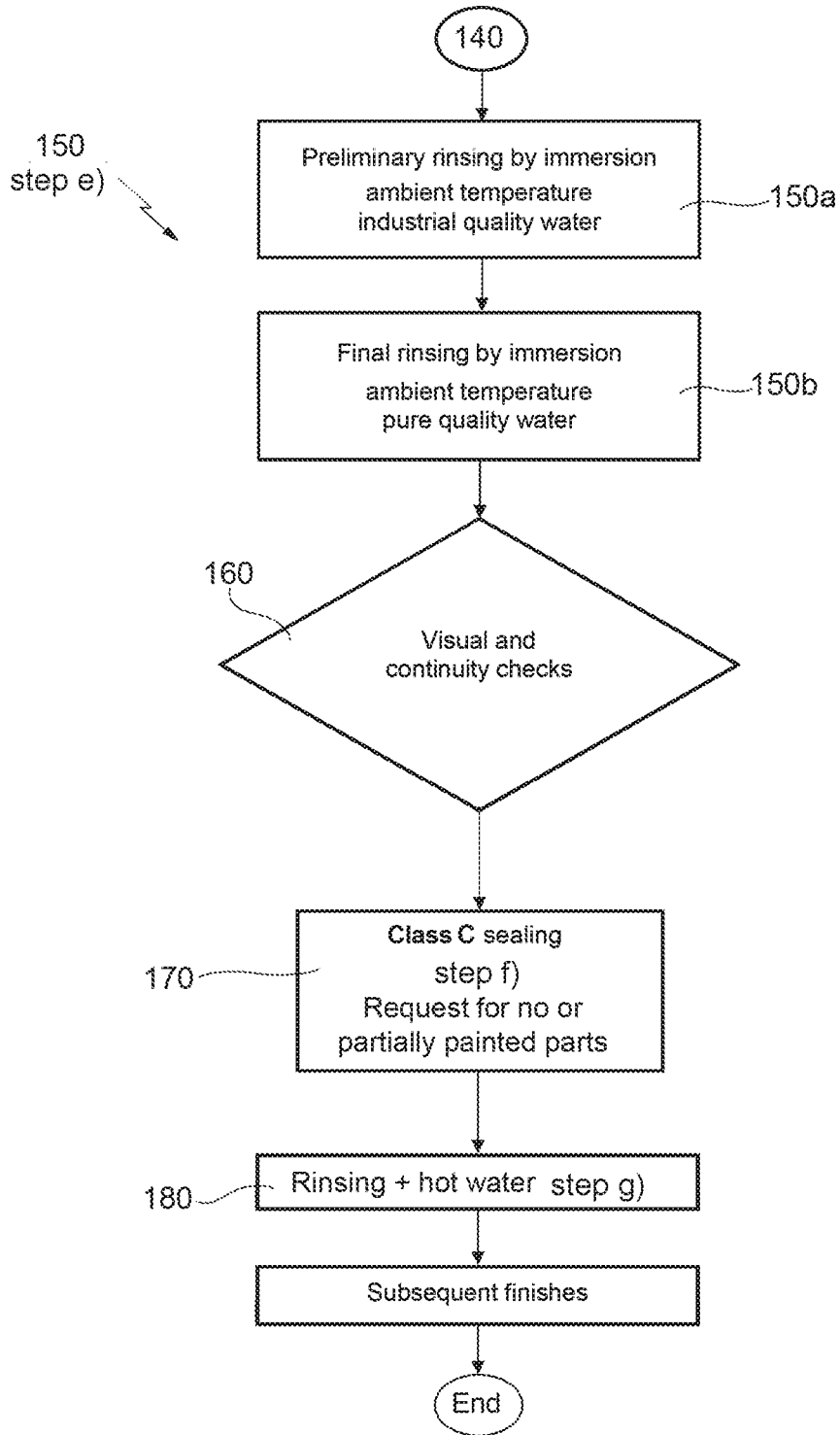
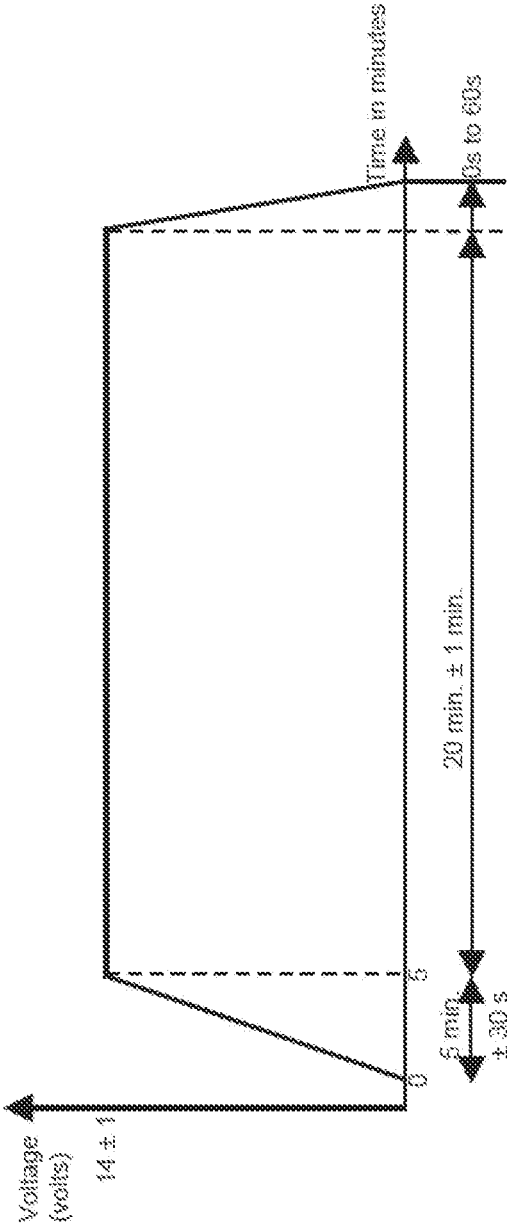


FIG. 1B



Graph: Anodizing electrolytic cycle

FIG. 2

**ANODIZATION METHOD FOR CORROSION
PROTECTION OF ALUMINIUM ALLOY
ELEMENTS USED IN AN AIRCRAFT
STRUCTURE**

CROSS-REFERENCE TO RELATED
APPLICATIONS

[0001] This patent application claims priority from Italian patent application no. 102018000007314 filed on Jul. 18, 2018, the entire disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

[0002] The present invention relates to an anodization method for corrosion protection of aluminium or aluminium alloy elements used in an aircraft structure.

BACKGROUND OF THE INVENTION

[0003] As is known, in order to protect aluminium or aluminium alloy elements used in an aircraft structure, anodization methods have been developed to provide a thin (a few microns) protective layer of metal oxide, which protects the underlying aluminium/aluminium alloy from corrosion. This layer of metal oxide also facilitates the subsequent painting of the aircraft structures and also increases the surface electrical resistance of the aircraft structure. Typically, the known anodization processes comprise a plurality of steps, including:

[0004] a) subjecting the element to a degreasing step by means of an alkaline bath for removing contaminating elements, such as for example oils, fats, lubricants, protective layers, dusts and residues in general—then subjecting it to a first washing in water;

[0005] b) subjecting the element to an acid pickling step. Then extracting the element from the acid solution and subjecting the element to a subsequent washing in water. This step contributes to the removal of natural oxide, thermal oxides, traces of materials deposited as a result of mechanical processing, scratches, discolourations, mild corrosion;

[0006] c) subjecting the washed element to a subsequent electrochemical treatment step by dipping the element in a chromic acid solution (using chromium with an oxidation number of +6—hexavalent chromium) and applying an electric potential to this element;

[0007] d) subjecting the element to a subsequent second washing in water;

[0008] e) dipping the element in a bath in which a solution of a chromium compound with an oxidation number of +6 (hexavalent chromium) is present, in order to carry out a post-anodization sealing step;

[0009] f) extracting the element from the bath of step e) and subjecting it to a third final washing.

[0010] This method uses very dangerous compounds, such as H_2CrO_4 , commonly called chromic acid where the chromium has an oxidation number of +6; it is a highly oxidizing species.

[0011] The chemical reaction that occurs is the following:

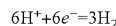
Electrochemical Reaction at the Anode:

[0012]



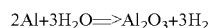
Electrochemical Reaction at the Cathode:

[0013]



Resulting Anodization Reaction:

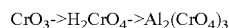
[0014]



Aluminium Chromate Will Also be Formed According to the Following Mechanism:

[0015]

chromic anhydride->chromic acid->aluminium chromate



[0016] Furthermore, on the basis of experimental and epidemiological evidence, chromium with an oxidation number of +6 (hexavalent chromium) has been classified by IARC as a human carcinogen (Class I).

[0017] With regard to the effects on health, several studies have demonstrated that exposure to hexavalent chromium is one of the possible causes of lung cancer, as it is mutagenic and carcinogenic. In fact, the respiratory system is the main target of the toxic and carcinogenic action, and acute and chronic occupational exposure occurs above all by absorption through inhalation. The toxicity of the hexavalent form at the intracellular level appears above all with the numerous molecular and structural alterations caused by the unstable [Cr(V) and Cr(IV)] and stable [Cr(III)] forms resulting from the reduction process.

SUMMARY OF THE INVENTION

[0018] Therefore, there is a need to develop a method which does not use toxic/carcinogenic materials and allows the formation of an oxide layer that provides good protection to the underlying aluminium/aluminium alloy.

[0019] The above object is achieved by the present invention in so far as it relates to an anodization method for corrosion protection of an aluminium or aluminium alloy element used in an aircraft structure, comprising the following steps:

[0020] a) subjecting the element to a degreasing step by means of an alkaline bath (block **100**) for removing contaminating elements;

[0021] b) subjecting the element to a subsequent first washing in water (block **110**);

[0022] c) subjecting the element to an acid pickling step (**120**) by dipping the element in an acid solution and then extracting the element from the acid solution and subjecting the element to a subsequent washing in water;

[0023] d) subjecting the washed element to a subsequent electrochemical treatment step in a tank (**140**) by dipping the element in a solution of tartaric acid ($C_4H_6O_6$) and sulphuric acid (H_2SO_4) and applying an electric potential to said element;

[0024] e) subjecting the element to a subsequent second washing in water (**150**);

[0025] f) dipping (block **170**) the element in a bath in which a solution of chromium, with an oxidation number of

+3, and zirconium ions and fluorides is present, in order to carry out a post-anodization sealing step;

[0026] g) extracting the element from the bath of step f) and subjecting it to a third final washing in water and a subsequent dipping in a tank of boiling water, which provides a second sealing step, and then drying the element (block 180).

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The invention will now be illustrated with reference to the accompanying figures wherein:

[0028] FIGS. 1A and 1B represent a non-limiting embodiment showing the main steps of the method according to the present invention; and

[0029] FIG. 2 specifies one step of the method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0030] With reference to FIGS. 1A and 1B, the anodization method for corrosion protection of an aluminium or aluminium alloy element used in an aircraft structure comprises the following steps:

[0031] a) subjecting the element to a degreasing step by means of an alkaline bath (block 100) for removing contaminating elements, such as for example oils, fats, lubricants, protective layers, dusts and residues in general. Typically, step a) is carried out by dipping the element in the alkaline bath for a time interval of 10-20 minutes. Typically, the alkaline bath has a temperature of approximately 55 ± 5 degrees Celsius.

[0032] b) subjecting the element to a subsequent first washing in water (block 110). Typically, step b) is carried out with water for a time ranging from 2 to 5 minutes at a temperature below 35 degrees Celsius.

[0033] c) subjecting the element to an acid pickling step (block 120) by dipping the element for approximately 5-10 minutes in an acidic solution based on ferric sulphate and a mixture of acids maintained at a temperature comprised between 20° C. and 40° C. and then extracting the element from the acidic solution and subjecting the element to a subsequent washing in water (block 130 following block 120) for 4-10 minutes at room temperature and assessing the film of water. Checking by assessing the film of water on the surface of the part during the rinsing ensures the effectiveness of the pretreatment. Step c) contributes to the removal of natural oxide, thermal oxides, traces of materials deposited as a result of mechanical processing, scratches, discolorations, mild corrosion;

[0034] d) subjecting the washed element to a subsequent electrochemical treatment step in a tank (block 140) by dipping the element in a solution of tartaric acid ($C_4H_6O_6$) and sulphuric acid (H_2SO_4) and applying an electric potential, wherein the aluminium/aluminium alloy element behaves as the anode (positive pole) whereas the negative electrode (or cathode) is represented by the tank. Step d) is carried out with a solution having a temperature comprised between 36 and 39 degrees Celsius. The typical concentration of tartaric acid is 72-88 g/l and that of sulphuric acid is 36-44 g/l.

[0035] The chemical reaction occurring in step d) is the following:

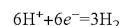
Electrochemical Reaction at the Anode:

[0036]



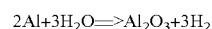
Electrochemical Reaction at the Cathode:

[0037]

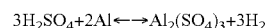


Resulting Anodization Reaction:

[0038]



Aluminium Sulphate, which Contributes to the Protection of the Underlying Metal/Metal Alloy, Will Also be Formed According to the Following Mechanism:



[0039] Step d) is typically performed using the following parameters (see FIG. 2):

[0040] applying the voltage within one minute from the dipping of the element in the solution;

[0041] applying an increasing voltage with a ramp not exceeding 3 volts per minute;

[0042] applying a constant voltage (approximately 14 Volts) for approximately 20 minutes, and thereafter;

[0043] gradually reducing the voltage to a null value in approximately one minute;

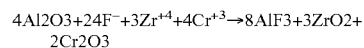
[0044] removing the element from the solution within 3 minutes from the switching off of the voltage

[0045] e) subjecting the element to a subsequent second washing in water (block 150). Typically, step e) comprises an optional rinsing step by dipping in industrial water (block 150a) at room temperature and a subsequent rinsing step by dipping in purified water at room temperature (block 150b).

[0046] Subsequently, the washed element is subjected to visual inspection by an operator (block 160) and, if this step is fulfilled, the following step is carried out:

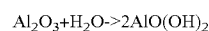
[0047] f) dipping (block 170) the element in a bath in which chromium, with an oxidation number of +3, zirconium ions and fluorides (resulting from salts and fluoro-zirconates/silicates) are present, in order to carry out a first post-anodization sealing step;

[0048] The Chemical Reaction that Occurs is the Following:



[0049] Typically, the dipping time in step f) is comprised between 2 and 3 minutes.

[0050] g) extracting the element from the bath of step f) and subjecting it to a third final washing and a subsequent dipping in a tank of boiling water (temperature above 95 degrees Celsius, pH ranging from 4.5 to 7, for approximately 30 minutes), which provides a second sealing step, according to the following reaction:



[0051] Which results in a volume increase, which is responsible for the "filling" of the pores of the anodic oxide. The reduction in porosity resulting from alumina hydration drastically reduces the adsorption capacity, making the sur-

face insensitive to fingerprints, colour and grease stains, and giving the oxide a greater resistance to corrosion.

[0052] Drying the element (block **180**). Typically, the drying can be carried out in a dust-free environment, for example an oven that reaches a temperature between 45 and 65 degrees Celsius for at least 20 minutes.

[0053] Between step b) and step d) the following further steps may also be carried out, optional to step c), which is carried out anyway:

[0054] rapid alkaline chemical etching (block **200**) with a caustic soda based solution in order to prepare/activate the aluminium/aluminium alloy surfaces for the electrochemical treatment in step d). Typically, this step is carried out by dipping the element in an alkaline solution having a temperature of approximately 60 degrees for 30-60 seconds; and

[0055] Aluminium desmutting and rinsing (block **210**). Typically, this step of clearing the blackening due to the preceding alkaline bath is performed by dipping the element in a clearing solution (based on ferric sulphate and a mixture of acids) at room temperature (approximately 25 degrees) for 5-10 minutes.

[0056] From the above description it appears that the method of the present invention, in particular the sealing (step f), does not use highly toxic, and in particular carcinogenic compounds, such as chromium with an oxidation number of +6. The sealed oxide layer has a sensibly constant thickness of a few microns (typically from 2 to 7 microns) and good adhesion characteristics. The elements are therefore effectively protected from corrosion.

[0057] The Applicant performed a series of mechanical fatigue tests on samples subjected to the method of the present invention. The tests were carried out on cylindrical specimens treated according to the method of the present invention in accordance with standard EN6072 provided in the aeronautical field. Results were plotted in a Wohler curve at various load levels.

[0058] By comparing the data, the treatment according to the present method was thus shown not to alter the fatigue resistance of the sample, which complies with the CS 25.571 aeronautical directives. Corrosion tests, which were carried out in a salt spray chamber for ASTM B 117, also performed well. In this case, a salt spray chamber was used, which was capable of providing a controlled saline environment fed by a 5% NaCl salt solution. Tests for permanence in the salt spray for 336 hours were brilliantly passed.

[0059] Tests for adhesion of the paint to the elements treated according to the method of the present invention were also carried out. These tests were carried out in accordance with ISO 2409 standard after dipping in demineralized water at 23 degrees Celsius for 14 days. The test consists in squaring off, after the dipping in water, the paint layer with a six-blade cutter, arranging and pressing a layer of tape against the squared paint and then tearing off the tape quickly. The tests gave a positive result, with a detachment of the coating paint of less than 5%.

1. An anodization method for corrosion protection of an aluminium or aluminium alloy element used in an aircraft structure,

comprising the following steps:

- a) subjecting the element to a degreasing step by means of an alkaline bath (block **100**) for removing contaminating elements;
- b) subjecting the element to a subsequent first washing in water (block **110**);

c) subjecting the element to an acid pickling step (**120**) by dipping the element in an acid solution and then extracting the element from the acid solution and subjecting the element to a subsequent washing in water;

d) subjecting the washed element to a subsequent electrochemical treatment step in a tank (**140**) by dipping the element in a solution of tartaric acid ($C_4H_6O_6$) and sulphuric acid (H_2SO_4) and applying an electric potential to said element;

e) subjecting the element to a subsequent second washing in water (**150**);

f) dipping (block **170**) the element in a bath in which a solution of chromium, with an oxidation number of +3, and zirconium ions and fluorides is present, in order to carry out a post-anodization sealing step;

g) extracting the element from the bath of step f) and subjecting it to a third final washing in water and a subsequent dipping in a tank of boiling water, which provides a second sealing step, and then drying the element (block **180**).

2. The anodization method as defined in claim 1, wherein step c) is carried out by dipping the element in an acid bath for a time interval of 5 to 10 minutes.

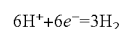
3. The anodization method as defined in claim 1, wherein step c) is carried out by dipping the element in an acid bath having a temperature of 20° C. to 40° C.

4. The anodization method as defined in claim 1, wherein step d) is configured to perform the following chemical reactions:

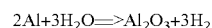
Electrochemical reaction at the anode:



Electrochemical reaction at the cathode:



Resulting anodization reaction:



5. The anodization method as defined in claim 1, wherein step d) is carried out using the following parameters:

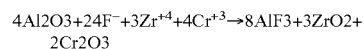
- applying the voltage within one minute from the dipping of the element in the solution;
- applying an increasing voltage with a ramp not exceeding 3 volts per minute;
- applying a constant voltage for approximately 20 minutes, and thereafter;
- gradually reducing the voltage to a null value;
- removing the element from the solution within 3 minutes from the switching off of the voltage.

6. The anodization method as defined in claim 1, wherein step d) is carried out using a solution having a temperature ranging between 36° C. and 39° C.

7. The anodization method as defined in claim 1, wherein step g) is carried out in a tank of boiling water with a temperature higher than 95° C. and a pH ranging between 4.5 and 7 for approximately 30 minutes.

8. The anodization method as defined in claim 1, wherein in step d) the concentration of tartaric acid is 72-88 g/l and the concentration of sulphuric acid is 36-44 g/l.

9. The anodization method as defined in claim 1, wherein step f) performs the following chemical reactions:



10. The anodization method as defined in claim 1, wherein between step b) and step d) the following further steps are also carried out:

alkaline chemical etching (**200**) in order to prepare/activate the aluminium/aluminium alloy surfaces for the electrochemical treatment in step d); and aluminium/aluminium alloy desmutting and rinsing (**210**).

11. The anodization method as defined in claim 1, wherein said boiling water has a temperature higher than 95° C.

12. The anodization method as defined in claim 1, wherein said boiling water has a pH ranging between 4.5 and 7.

13. The anodization method as defined in claim 1, wherein said fluorides result from salts and fluorozirconates/silicates.

* * * * *