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(54) **METHOD OF ANODIZING A PART MADE OF ALUMINUM ALLOY**

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(57) **ABSTRACT**

The invention provides a method of anodizing a part made of aluminum alloy. According to the invention, the method comprises the following steps in succession:

providing an aqueous anodizing bath essentially comprising sulfuric acid at a concentration lying in the range 55 g/l to 85 g/l, and excluding the presence of any phosphoric acid or any boric acid;

maintaining said bath at a constant temperature essentially lying in the range 15° C. to 27° C.;

dipping said part into said bath;

applying a voltage to said part dipped in said bath, the voltage lying essentially in the range 5 V to 30 V, with low current density on said part; and

maintaining said part in said bath until a coating of desired thickness has been obtained, which thickness lies substantially in the range 1 μm to 3 μm.

METHOD OF ANODIZING A PART MADE OF ALUMINUM ALLOY

[0001] The present invention relates to treating aluminum alloy parts, in particular parts for use in making aviation components, and more specifically the invention relates to a method of anodizing a part made of aluminum alloy.

BACKGROUND OF THE INVENTION

[0002] In order to avoid using chemicals containing hexavalent chromium, proposals have already been made for methods of anodizing aluminum and its alloys by using an aqueous anodizing bath containing sulfuric acid and boric acid. A good illustration of such a sulfuric-boric anodization method is given in document U.S. Pat. No. 4,894,127. In that known method, an aqueous electrolytic bath is used that essentially comprises sulfuric acid at a concentration lying in the range 30.5 grams per liter (g/l) to 52 g/l, and boric acid at a concentration lying in the range 5.2 g/l to 10.7 g/l.

[0003] Such an anodization method is relatively effective in applying a coating of aluminum oxide on an aluminum alloy with a solution of sulfuric acid and boric acid. The resulting anodized coating is at least comparable, and in terms of resistance to corrosion, equivalent to the anodized and sealed coatings made in baths containing an aqueous solution of sulfuric acid and chromic acid. The superiority of the method of document U.S. Pat. No. 4,894,127 over other prior methods of sulfuric-boric anodization lies in the thinness of the coatings obtained, in particular coatings having a thickness of 1 micrometer (μm) to 3 μm, which is particularly advantageous in the field of aviation. Nevertheless, the compositions specified for implementing such a method are very broad, and that can lead to characteristics being obtained that present a wide range of variation in the resulting layers. Furthermore, it is difficult to control the thickness of the oxide obtained at the end of treatment. It should be observed that in the context of that known method, a voltage is applied to the part which is dipped in the electrolytic bath, which voltage increases linearly from 5 volts (V) to 20 V, with current density over said part remaining close to 100 amps per square meter (A/m^2).

[0004] Mention can also be made of document EP-A-0 048 909 describing another anodizing method using an anodizing bath which is essentially constituted by sulfuric acid and phosphoric acid, in particular with the following respective concentrations [50 g/l; 50 g/l], [63 μl; 37 g/l], and [75 g/l; 25 g/l]. The presence of sulfuric acid may nevertheless turn out to be undesirable in certain situations, if it is desired to obtain coatings of small thickness, in particular coating less than 3 μm thick.

[0005] Reference may also be made to document U.S. Pat. No. 4,861,440 describing the use of an anodizing bath containing sulfuric acid and at least one carboxylic acid, with the sulfuric acid at high concentration (112 g/l to 150 g/l).

[0006] Other anodizing techniques also exist using an aqueous anodizing bath essentially comprising sulfuric acid to the exclusion of any other acid, with the sulfuric acid at high concentration, in general about 200 g/l.

[0007] Thus, document U.S. Pat. No. 4,554,216 describes an anodizing method using a bath comprising sulfuric acid at a concentration of 166 g/l to 230 g/l. The aqueous bath is at low temperature (0° C. to 5° C.), and the part dipped in said bath is subjected to high current density (200 A/m^2 to 300 A/m^2).

[0008] It is common practice in the field of aviation to use anodizing methods with electrolyte baths comprising sulfuric acid at a concentration lying in the range 180 g/l to 250 g/l. Existing techniques are always restricted to this high range of concentrations for sulfuric acid in anodizing baths because of selection is based on the curve plotting variations in electrical conductivity as a function of sulfuric acid concentration. That curve plotting variations in conductivity is substantially in the form of a downwardly open parabola, presenting a maximum in the zone corresponding to concentrations of sulfuric acid lying in the range 180 g/l to 220 g/l. Specialists have therefore invariably relied on seeking maximum electrical conductivity for the electrolytic bath. It is known that such high electrical conductivity is favorable to rapid growth in the thickness of the oxide. That explains why high concentrations (not less than 200 g/l) have always been selected for the sulfuric acid present in the electrolytic bath.

[0009] Known techniques of sulfuric anodic oxidation nevertheless suffer from three drawbacks comprising difficulty in monitoring the thickness of the coating, while obtaining porosity that is always high because of the high concentration of sulfuric acid together with roughness that is uncontrolled. Controlling the thickness or the weight of the coating is indeed difficult, since two phenomena are taking place concurrently during the anodizing process, namely an electrolytic phenomenon which corresponds to growing an interface layer, and a chemical phenomenon of dissolving the barrier layer formed both at the interface between the substrate and the coating that has been formed and at the surface of the porous layer in contact with the electrolyte. The porosity of the resulting coating layer, which is known to depend on the chemical composition of the electrolyte, and in particular on its sulfuric acid concentration, is thus always high, thereby giving an effect that is unfavorable on the whole on the characteristics of the resulting layer.

[0010] The person skilled in the art knows that anodization performed in an acid medium (pH<2.5) is essentially porous, and that if it is desired to avoid high porosity on treated parts, it is necessary to make use of anodizing techniques in a medium that is more neutral, in order to obtain barrier anodization with a non-porous layer.

[0011] The technological background of the invention is also illustrated by the following documents: U.S. Pat. No. 3,563,867, U.S. Pat. No. 6,149,795, U.S. Pat. No. 4,968,398, and JP-A-2000/026997.

OBJECTS AND SUMMARY OF THE INVENTION

[0012] An object of the present invention is to propose an anodizing method that provides better performance, that is essentially related to sulfuric anodic oxidation techniques but that allows better monitoring of the thickness or the weight of the coating, while not obtaining high porosity on the treated parts.

[0013] In accordance with the invention, this problem is solved by a method of anodizing a part made of aluminum alloy, the method comprising the following successive steps:

- **[0014]** providing an aqueous anodizing bath essentially comprising sulfuric acid at a concentration lying in the range 55 g/l to 85 g/l, and excluding the presence of any phosphoric acid or any boric acid;

- **[0015]** maintaining said bath at a constant temperature essentially lying in the range 15° C. to 27° C.;

- **[0016]** dipping said part into said bath;

- **[0017]** applying a voltage to said part dipped in said bath, the voltage lying essentially in the range 5 V to 30 V, with low current density on said part; and

- **[0018]** maintaining said part in said bath until a coating of desired thickness has been obtained, which thickness lies substantially in the range 1 μm to 3 μm.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Particular features relating to the above-specified steps of the anodizing method of the invention are described in greater detail below, and provision can be made in particular for the aqueous anodizing bath also to contain an acid alcohol having one to three acid functions in order to limit dissolution of the resulting coating layer, for the purpose of having perfectly uniform porosity throughout the thickness of the layer while not losing electrical conductivity in the bath which favors good growth of said layer.

[0020] The anodizing method of the invention is described in greater detail below, setting out the various ranges associated with each of the parameters of the method, each time giving preferred values as they have been determined in testing carried out by the Applicant.

[0021] The first step of the anodizing method of the invention consists-in providing an aqueous anodizing bath essentially comprising sulfuric acid at a concentration lying in the range 55 g/l to 85 g/l, and excluding the presence of any phosphoric acid or boric acid. Certain authors prefer the specified concentrations to be given in weight percentages: specifically, the above-mentioned limits given in g/l correspond to concentration values lying in the range 5.36% to 8.2% by weight.

[0022] It is important to observe that the above-mentioned range of concentrations is well below the concentrations used in the above-mentioned known sulfuric anodization techniques, which concentrations lie in the range 180 g/l to 220 g/l. It has therefore been necessary to overcome a prejudice, to avoid seeking maximum electrical conductivity for the electrolytic bath, and consequently to depart from the range that has always been recommended for high concentrations of sulfuric acid.

[0023] The sulfuric acid concentration of the bath is preferably lies essentially in the range 57 g/l to 67 g/l, with a highly preferred value being situated in the vicinity of 62 g/l (i.e. slightly more than 6% by weight).

[0024] The second preparatory step of the anodizing method of the invention consists in maintaining the above-mentioned aqueous anodizing bath at a constant temperature which lies essentially in the range 15° C. to 27° C. The bath is preferably maintained at a constant temperature close to 22° C.

[0025] The aluminum alloy part for treatment is thus dipped into the aqueous anodizing bath as prepared in this way.

[0026] Fundamentally, a voltage essentially lying in the range 5 V to 30 V is then applied to said part dipped in said bath, with the current density on said part being low.

[0027] The voltage applied to the part dipped in the bath may be fixed to a constant value throughout the duration of the anodizing treatment, said constant value then lying in the range −5 V to 30 V. Under such circumstances, it is advantageous to select a constant value for the voltage lying in the range 7 V to 20 V.

[0028] Nevertheless, it has been found to be more advantageous for further improving good control over the growth of the oxide coating to make provision for the voltage applied to the part dipped in the bath to begin by being fixed to a first constant value, and then after a predetermined duration to a second constant value that is higher than the first, said first and second constant values both lying in the range 5 V to 30 V.

[0029] In this respect, it has been found particularly advantageous to select a first constant voltage value lying in the range 5 V to 11 V, with this low value serving to control moderate growth of the oxide layer, and a second constant voltage value lying in the range 15 V to 30 V, in order to obtain the desired properties for the barrier layer. The use of two successive voltage levels, of duration that is essentially a function of the thickness desired for the coating, makes it possible to build the barrier layer more quickly while keeping control over the growth of the coating. The Applicant has performed numerous tests and has observed, in particular on the basis of curves plotting rate of growth, that excellent results are obtained with a first level of 10 V for a duration of about 25 minutes (min), followed by a second level of 20 V for a duration of 15 min.

[0030] As mentioned above, relatively low current density is used on the part which is dipped in the electrolytic bath. The term "low" means in this case that the current density is substantially less than 100 A/m^2.

[0031] In practice, it has been found advantageous to make provision for the current density to be essentially less than 80 A/m^2, and for it to lie preferably in the range 30 A/m^2 to 70 A/m^2. Optimum values for current density with the above-mentioned voltage values lie around 34 A/M^2 to 35 A/M^2.

[0032] In an anodizing method as described above, the part for treatment is maintained in the electrolytic bath until the desired thickness of coating has been obtained, which thickness lies substantially in the range 1 μm to 3 μm.

[0033] In this respect, it is advantageous to observe that relatively low concentrations of sulfuric acid have already been used in hard anodizing techniques, but the coating thicknesses involved have nothing to do with the presently-desired values since those coatings were very thick, being about 250 μm. The other parameters of hard anodizing also lie well outside the ranges provided in the present method (high voltage up to 120 V, high current densities of about 250 A/m^2, and low temperatures lying in the range −5° C. to +5° C.): the present anodizing method therefore cannot be compared with prior hard anodizing techniques.

[0034] In the context of more advanced developments of the above-described anodizing method, it has also been found advantageous to envisage adding an acid alcohol to the aqueous anodizing bath, the acid alcohol having one to three acid functions, and being at a concentration that remains low, lying in the range 12 g/l to 22 g/l.

[0035] This addition of an acid alcohol at low concentration appears to be advantageous in limiting dissolution of the layer and in increasing the wettability of the electrolyte, and thus obtaining good uniformity of porosity throughout the thickness of the layer, and this is achieved without spoiling the electrical conductivity of the electrolytic bath. Acid alcohols are particularly advantageous under such circumstances since they are completely miscible with the electrolyte at ambient temperature. High stability is thus obtained in the rate of dissolution with highly satisfactory maintenance of electrical conductivity.

[0036] The acid alcohol used in the bath is preferably tartaric acid (an acid alcohol having two acid functions, of formula $C_4H_6O_6$) or citric acid (an acid alcohol having three acid functions, of formula $C_6H_8O_7$). The concentration of tartaric acid or of citric acid then preferably lies essentially in the range 12 g/l to 17 g/l, with the optimum concentration observed during testing lying in the vicinity of 17 g/l.

[0037] Selecting tartaric acid and citric acid also appears to be particularly advantageous insofar as it is desirable firstly to have pH stabilized on a low value, and secondly to have a strong oxidizer whose electrochemical activity is high without being aggressive, and thus not generating pitting. It has thus been found that sulfuric-tartaric or sulfuric-citric anodic oxidation appears to be much more desirable than sulfuric-boric anodic oxidation as used in prior techniques, in particular in the technique described in document U.S. Pat. No. 4,894,127. In the present case, excellent stability is obtained in the dissolution of the alumina layer.

[0038] Adding tartaric acid or citric acid to the bath in the context of the present invention makes it possible to obtain dissolution of the alumina layer which is less than that obtained with sulfuric acid on its own, and in addition current density in the bath does not drop off as would be the case with other acids, such as boric acid, because of the action of surface tension.

[0039] It is also important to provide for the part that is to be treated to be subjected to preliminary degreasing/pickling treatment or deoxidation prior to being dipped in the bath.

[0040] In traditional techniques, use has been made of a first step of degreasing, followed by rinsing, then followed by a second step of pickling in an alkaline medium, or more generally in an aqueous solution of sulfuric acid and chromic acid, finally followed by further rinsing. Nevertheless, it has been found to be more advantageous to use a solution capable of performing satisfactory degreasing and pickling directly in a single step, and use may advantageously be made of a solution comprising phosphoric acid having anionic wetting agents added thereto such as the product sold under the reference "NOVACLEAN AL-85" by the German supplier Henkel Surface Technologies. The use of such a product makes it possible to obtain pickling that is uniform, i.e. without the presence of any surface etching.

[0041] Finally, it is advantageous to make provision for the treated part to be subjected to subsequent treatment for sealing the coating.

[0042] Sealing of the coating must perform two functions, namely promoting both adhesion and resistance to corrosion. Sealing is conventionally performed by soaking in hot water at a temperature of not less than 97° C., or in a dilute solution of potassium bichromate. It is preferable to use a solution of deionized water at a temperature lying in the range 85° C. to 98° C., with soaking being performed for a duration which is a function of the thickness of the coating that has been obtained. In a variant, it is also possible to use sodium molybdate ($MoNa_2O_4$, $2H_2O$) or manganese sulfate (MnO_2S, H_2O), or indeed immersion in a particularly effective sealant based on nickel acetates or on lithium acetates, for example using the respective products "ANOSEAL 1000" or ENVIROSEAL 2500" sold by the above-specified supplier Henkel Surface Technologies.

[0043] Among the numerous tests performed by the Applicant, mention can be made of a first example of sulfuric anodic oxidation with an aqueous anodizing bath comprising sulfuric acid at a concentration of 62 g/l. It was found that the coating layer grew regularly and good control was obtained over small thicknesses without any change to the initial roughness of the substrate.

[0044] Other tests with a sulfuric-citric anodizing bath may also be mentioned, with the sulfuric acid concentration being 62 g/l and the citric acid concentration being 17 g/l. For the other operating conditions, it can be mentioned that the constant temperature at which the bath was maintained was 22° C., and the applied voltage was 10 V for a first period of 25 min followed by 20 V for a second period of 15 min. That produced a low porosity coating of thickness lying in the range 2.8 μm to 3.2 μm.

[0045] As an indication, the tests were performed using the aluminum alloys bearing the references 2024 T 351 and 7175 T 7351.

[0046] After sealing, it was observed that the parts treated in this way still presented highly satisfactory appearance after being exposed for 500 hours to a saline mist. In addition, fatigue weakening characteristics remained very satisfactory compared with known sulfuric-boric or chromic anodic oxidation techniques.

[0047] A high performance anodizing method is thus provided which makes it possible simultaneously to monitor the thickness or the weight of the coating and its roughness, and to obtain low porosity at the surface of the treated parts.

[0048] The invention is not limited to the method described above, but on the contrary encompasses any equivalent anodizing method coming within the general definition given at the beginning of the description.

What is claimed is:

1/ A method of anodizing an aluminum alloy part, the method comprising the following steps in succession:

providing an aqueous anodizing bath essentially comprising sulfuric acid at a concentration lying in the range 55 g/l to 85 g/l, and excluding the presence of any phosphoric acid or any boric acid;

maintaining said bath at a constant temperature essentially lying in the range **15**° C. to 27° C.;

dipping said part into said bath;

applying a voltage to said part dipped in said bath, the voltage lying essentially in the range 5 V to 30 V, with low current density on said part; and

maintaining said part in said bath until a coating of desired thickness has been obtained, which thickness lies substantially in the range 1 μm to 3 μm.

2/ A method according to claim 1, in which the concentration of sulfuric acid in the bath lies essentially in the range 57 g/l to 67 g/l, and is preferably close to 62 g/l.

3/ A method according to claim 1, in which the bath is maintained at a constant temperature close to 22° C.

4/ A method according to claim 1, in which the voltage applied to the part dipped in the bath is fixed on a constant value throughout the duration of the anodizing treatment, said constant value lying in the range 5 V to 30 V.

5/ A method according to claim 4, in which the constant value of the voltage lies in the range 7 V to 20 V.

6/ A method according to claim 1, in which the voltage applied to the part dipped in the bath is initially fixed to a first constant value, and then after a predetermined duration, to a second constant value that is higher than the first, said first and second constant values both lying in the range 5 V to 30 V.

7/ A method according to claim 6, in which the first constant voltage value lies in the range 5 V to 11 V, and the second constant voltage value lies in the range 15 V to 30 V.

8/ A method according to claim 1, in which the current density on the part dipped in the bath remains well below 100 A/m^2.

9/ A method according to claim 8, in which the current density is essentially less than 80 A/m^2, preferably lying in the range 30 A/m^2 to 70 A/m^2.

10/ A method according to claim 1, in which the aqueous anodizing bath also contains an acid alcohol having one to three acid functions, at a concentration lying in the range 12 g/l to 22 g/l.

11/ A method according to claim 10, in which the acid alcohol used in the that is tartaric acid or citric acid, and the concentration of said acid alcohol lies essentially in the range 12 g/l to 17 g/l.

12/ A method according to claim 1, in which the part to be treated is subjected to preliminary degreasing/pickling treatment prior to being dipped in the bath.

13/ A method according to claim 1, in which the treated part is subjected to subsequent treatment of sealing the coating.

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