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(57) **ABSTRACT**

A method for producing a superhydrophobic coating with self-cleaning properties on a metallic substrate involves providing a metallic substrate that titanium and an electrolyte solution that includes a fluoride salt. At least part of a surface of the metallic substrate is contacted with the electrolyte solution. The metallic substrate is anodized in order to produce a nanoporous layer having nanotubes including titanium dioxide on the metallic substrate. A superhydrophobising coating is applied onto the nanoporous layer comprising nanotubes including titanium dioxide, wherein the electrolyte solution includes a further water-soluble salt selected from the group comprising ammonium sulphate, sodium sulphate, sodium bisulphate, potassium sulphate, potassium bisulphate and mixtures thereof.

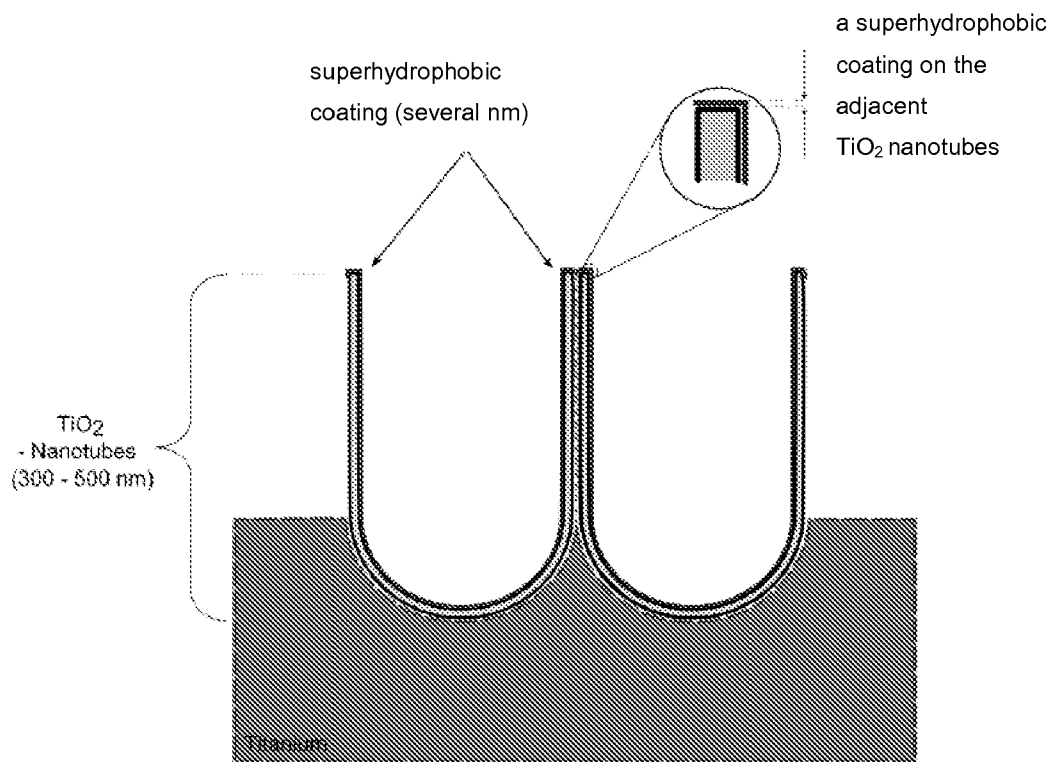


Fig. 1

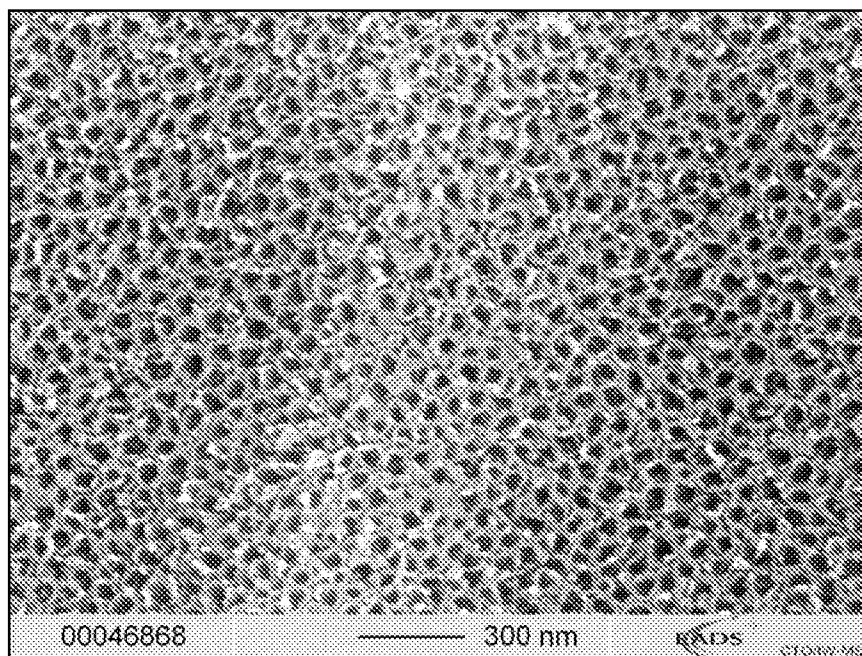


Fig. 2

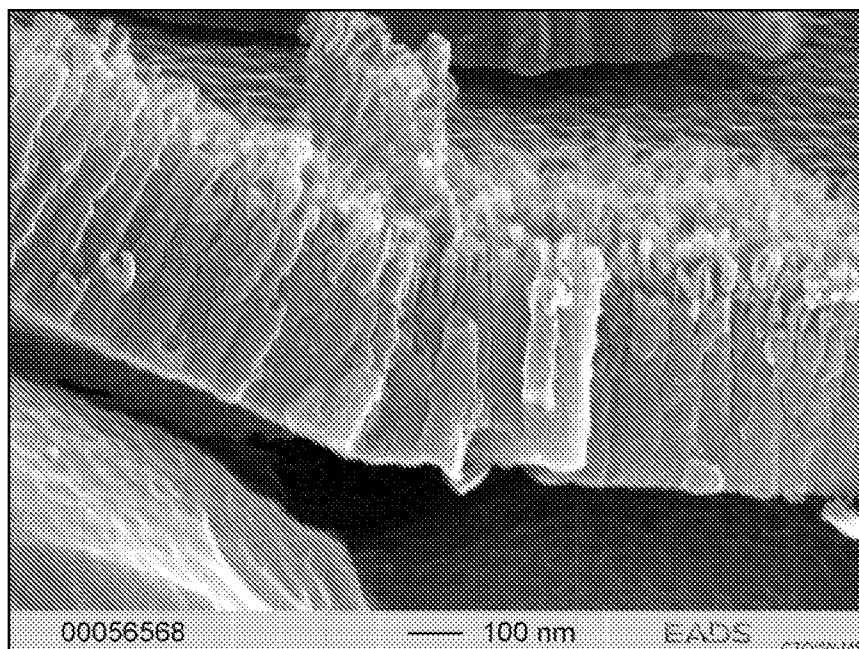
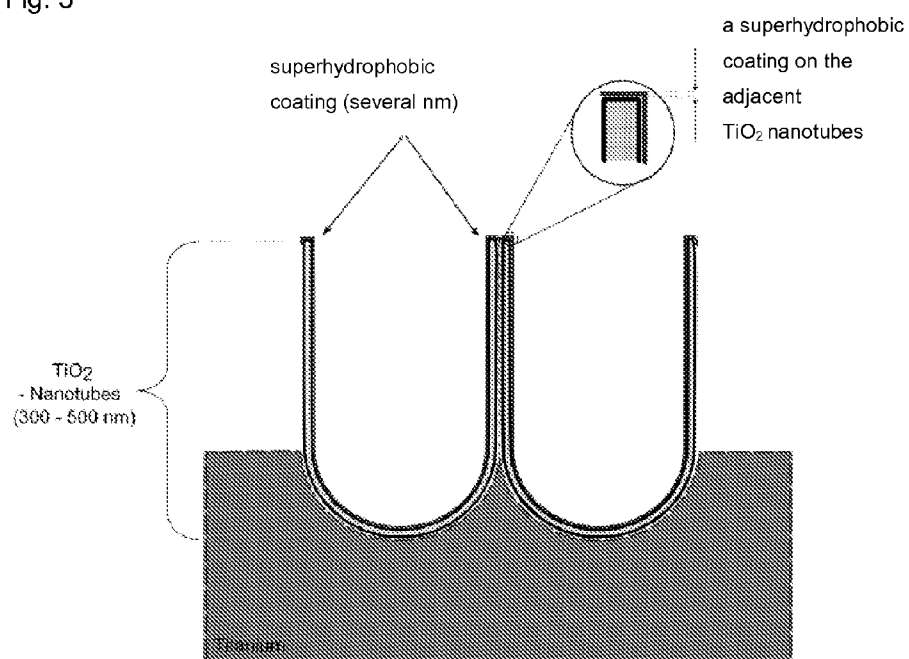


Fig. 3



SELF-CLEANING AND SUPERHYDROPHOBIC SURFACES BASED ON TiO₂ NANOTUBES

BACKGROUND AND SUMMARY OF THE INVENTION

[0001] Exemplary embodiments of the invention relate to a method for producing a superhydrophobic coating having self-cleaning properties on a metallic substrate, a metallic substrate having a superhydrophobic coating and self-cleaning properties that can be obtained using such a method, the use of an electrolyte solution comprising ammonium sulphate and ammonium fluoride for producing a superhydrophobic coating having self-cleaning properties on a metallic substrate, as well as the use of the metallic substrate in order to prevent icing up in aircraft or in order to prevent contamination and/or erosion in aircraft.

[0002] In aircraft, such as for example airplanes or helicopters, lift or flow elements such as wing, engine or tail systems are exposed to the most varied airflows. The airflow over the surfaces concerned can be influenced in an unfavorable manner if such elements ice up, so that the aerodynamics of an aircraft becomes affected and, particularly in the case of icing up, in a worst-case scenario, stalling and loss of lift may result. Moreover, icing up or contamination of these systems may also lead to an increased all-up weight. Moreover, as a result of contamination for example by insects, the realization of a laminar wing may be severely restricted.

[0003] Various approaches are known especially with regard to the de-icing of flow elements of an aircraft. For example, de-icing may be carried out as early as on the ground, where ice accretions are removed by way of a chemical or thermal treatment.

[0004] During the flight of an aircraft, further techniques are employed in order to avoid ice formation. Thus, for example, the leading edge of a wing may be heated using hot bleed air from the engines so as to carry out in this way a de-icing operation or in order to keep the wing free of ice. The use of bleed air from engines, however, can reduce the effective power of engines by approximately 3% and must not be activated during the take-off phase.

[0005] Further, inflatable elastic mats may be used for de-icing, by means of which any formed ice is supposed to be blasted off. However, such inflatable mats require a certain amount of time until a change of geometry can be achieved as a result of the internal pressure, which will lead to the ice crystals being blasted off. Further, the surface quality of mat systems is extremely limited.

[0006] There is the further possibility of reducing the accretion of ice by means of heating mats on the leading edges of control elements and wings and/or to release any formed ice. Such systems require a lot of power and can therefore, especially in small aircraft and in unmanned aircraft, be integrated only with difficulty.

[0007] It is further known to melt ice using chemicals. Thus there is the possibility of applying a chemical melting liquid onto the critical flow elements through fine bores or outlet nozzles on the flow elements, in order to melt ice crystals thereby. In this way, any accretion of ice will be avoided, however, the maximum duration of use is limited by the size of the tank. Further, the additional weight of the de-icing liquid in the tank is to be regarded as a disadvantage.

[0008] The term de-icing refers to an active removal of ice and snow from the wing. On the ground, this is carried out e.g.

by spraying on de-icing liquids at 70-80° C., during the flight for example by using warm branched-off air or by means of electric heaters in the wing edges.

[0009] In this connection it is to be noted that the known de-icing measures either require substantial effort on the ground or an enormous amount of energy during the flight. On the ground special de-icing vehicles are required, which means that appropriate logistics, such as availability of de-icing vehicles, service schedules or maintenance of the de-icing vehicles have to be in place. Further, the use of these de-icing vehicles raises concerns in terms of environmental aspects, because de-icing liquids are often based on ethylene glycol or propylene glycol, which are controversial with regard to environmental aspects. In addition, the operation of de-icing vehicles leads to considerable fuel consumption due to their size and weight.

[0010] Further, also the contamination of surfaces of an aircraft with insects and/or other organic and inorganic materials can lead to higher air resistance. Contamination with organic and/or inorganic contaminants mainly occurs as a result of an interaction of the aircraft surface with its environment and may for example be caused by dirt and gas components in the air or in rainwater, such as SO₂, NO_x, salts and hygroscopic dust, or by residues from chlorides, sulphides, sulphates or acids. Contamination with insects may develop on the ground and in particular during take-off and landing, when insects collide with the aircraft and get stuck thereto. Such adherent impurities that settle on the surface lead to a rougher surface, as a result of which the airflow is disturbed, which can lead to higher fuel consumption. In particular in the case of wings with laminar airflow, insect contamination may have a considerable negative influence on the flow dynamics as well as on friction losses. The same effects can also be observed in the case of surfaces which are subject to erosion by air, rain and/or sand.

[0011] A further measure consists in providing a superhydrophobic surface on a structure. A method for producing such a coating is disclosed in U.S. patent document 2006/0147634 A1. This method, however, has the disadvantage that toxic and harmful compounds such as hydrofluoric acid are used during the production of such coated structures, so that it constitutes a health risk.

[0012] Therefore, exemplary embodiments of the present invention are directed to a method for producing a superhydrophobic coating having self-cleaning properties on a metallic substrate. Exemplary embodiments of the invention are also directed to a substrate with a superhydrophobic coating and with self-cleaning properties, which allows high resistance to icing up and/or contamination and/or erosion. It is also desirable to reduce or even completely avoid the use of toxic and/or harmful compounds such as hydrofluoric acid during the production of coated substrates.

[0013] A solution according to the invention consists in a method for producing a superhydrophobic coating with self-cleaning properties on a metallic substrate, comprising:

[0014] a) providing a metallic substrate comprising titanium,

[0015] b) providing an electrolyte solution comprising a fluoride salt,

[0016] c) contacting at least part of the metallic substrate surface with the electrolyte solution from step b),

[0017] d) anodising the metallic substrate from step c) for producing a nanoporous layer comprising nanotubes including titanium dioxide on the metallic substrate, and

[0018] e) applying a superhydrophobising coating onto the nanoporous layer comprising nanotubes including titanium dioxide, wherein the electrolyte solution comprises a further water-soluble salt selected from the group comprising ammonium sulphate, sodium sulphate, sodium bisulphate, potassium sulphate, potassium bisulphate and mixtures thereof.

[0019] The invention allows the production of metallic substrates having a superhydrophobic coating and self-cleaning properties. Moreover, the present invention allows the production of metallic substrates having a superhydrophobic coating and self-cleaning properties without the use of hydrofluoric acid. The obtained metallic substrate having a superhydrophobic coating and self-cleaning properties has a high resistance to icing up and/or contamination and/or erosion.

[0020] According to a further aspect of the present invention, a metallic substrate having a superhydrophobic coating and self-cleaning properties obtained by the method is provided. It is preferred that the surface of the metallic substrate having a superhydrophobic coating and self-cleaning properties has a contact angle to water of more than 140°.

[0021] According to a further aspect of the present invention, such a method provides for the use of an electrolyte solution comprising 50 to 250 g/l, in particular 120 to 140 g/l of ammonium sulphate and 0.5 to 10 g/l, in particular 4 to 6 g/l of ammonium fluoride. According to a further aspect of the present invention, the use of a metallic substrate having a superhydrophobic coating and self-cleaning properties so as to prevent icing up in aircraft is provided. According to a further aspect of the present invention, the use of a metallic substrate having a superhydrophobic coating and self-cleaning properties so as to prevent contamination and/or erosion in aircraft is provided.

[0022] In an exemplary embodiment of the present invention, the metallic substrate is a titanium alloy. Preferably, the alloy additionally comprises at least one further metal selected from the group comprising V, Fe, Sn, Ni, Nb, Mo, Zr, Y, Hf, Ta, Ce, Tb, Nd, Gd, Dy, Ho and Er and/or additionally at least one further element selected from the group comprising Zn, Mn, Ag, Li, Cu, Si, Al or Ca.

[0023] In an exemplary embodiment of the present invention, the metallic substrate additionally comprises Al and V.

[0024] In an exemplary embodiment of the present invention, the fluoride salt is selected from the group comprising ammonium fluoride, ammonium bifluoride, potassium fluoride, sodium fluoride, calcium fluoride, magnesium fluoride and mixtures thereof, the fluoride salt is preferably ammonium fluoride.

[0025] In an exemplary embodiment of the present invention, the further water-soluble salt is ammonium sulphate.

[0026] In an exemplary embodiment of the present invention, the anodisation of the metallic substrate is carried out in an electrolyte solution comprising 50 to 250 g/l, in particular 120 to 140 g/l of ammonium sulphate and 0.5 to 10 g/l, in particular 4 to 6 g/l of ammonium fluoride at a temperature in a range from 10 to 60° C., in particular 20 to 30° C. and a voltage of preferably 2 to 50 volts, in particular 10 to 20 volts for 5 to 480 minutes, in particular 20 to 40 minutes.

[0027] In an exemplary embodiment of the present invention, the nanotubes including titanium dioxide have a diameter in a range of 10 to 300 nm, preferably 20 to 220 nm, more preferably 30 to 180 nm, even more preferably 30 to 140 nm

and in particular 30 to 100 nm. For example, the nanotubes including titanium dioxide have a diameter in a range of 30 to 60 nm.

[0028] In an exemplary embodiment of the present invention, the superhydrophobic coating having self-cleaning properties on the metallic substrate has a layer thickness between 100 nm and 10 µm, preferably between 200 nm and 1 µm, more preferably between 250 nm and 800 nm, even more preferably between 280 nm and 600 nm and in particular between 300 nm and 500 nm.

[0029] In an exemplary embodiment of the present invention, the superhydrophobising coating comprises a fluoro-alkyl functional silane.

[0030] In an exemplary embodiment of the present invention, the contacting of the metallic substrate surface with the electrolyte solution and/or the application of the superhydrophobising coating onto the nanoporous coating is carried out by means of dipping, spinning, flooding, brushing or spraying.

[0031] The term “superhydrophobic coating” or “superhydrophobising coating” is understood to refer to a coating that has water-repellent properties. In particular, “superhydrophobic coating” or “superhydrophobising coating” is understood to refer to a coating that has a contact angle to water of more than 140°. Due to the repulsive interaction between the superhydrophobic material and the liquid, liquid drops with a small contact surface are formed, so that these liquids easily run off from the surface. Further, “superhydrophobic coating” or “superhydrophobising coating” is understood to refer to a coating that has repellent properties in relation to dirt and gas components in the air or in rainwater, such as SO₂, NO_x, salts and hygroscopic dust, or from residues of chlorides, sulphides, sulphates or acids and/or insects. Due to the small contact surface between the superhydrophobic material and these impurities, it is harder for them to adhere to the surface. If the metallic substrate includes such a superhydrophobic coating, then this will already reduce ice formation or adherence of impurities and/or erosion.

[0032] Further, the superhydrophobic coating also has self-cleaning properties. The term “self-cleaning properties” is understood to mean properties which lead, in particular under UV radiation, to a decomposition of adhering organic components by virtue of the titanium dioxide contained in the nanoporous layer. If the metallic substrate has such a superhydrophobic coating with self-cleaning properties, then also adhering contaminants, in particular organic ones, can be removed from the coated substrate surface by triggering suitable mechanisms.

[0033] A “metallic substrate” is to be understood to mean, within the context of the present invention, any substrate that is continuously made from metal or that includes a metallic layer at least on its surface.

[0034] In terms of the present invention, the terms “metal” and “metallic” do not only comprise pure metals, but also mixtures of metals and metal alloys.

[0035] The method according to the invention can be applied to metallic substrates comprising titanium, although the range of application of the present invention is not limited to this metal. Preferably, a method according to the invention is applied to a metallic substrate that consists of titanium.

[0036] Alternatively, the metallic substrate comprises a titanium alloy.

[0037] The amount of titanium in the alloy is at least 50% by weight in relation to the overall mass of the alloy, for

example between 50 and 98% by weight or 60 and 98% by weight. For example, the alloy includes titanium in an amount of 85 to 95% by weight in relation to the overall mass of the alloy.

[0038] According to one embodiment of the present invention, the titanium alloy additionally comprises one further metal that is selected from the group comprising V, Fe, Sn, Ni, Nb, Mo, Zr, Y, Hf, Ta, Ce, Tb, Nd, Gd, Dy, Ho and Er.

[0039] Titanium alloys that can especially benefit from the present invention are e.g. titanium alloys containing vanadium and aluminium. In particular, the method according to the invention is suitable for producing superhydrophobic coatings having self-cleaning properties for protecting substrates made from titanium as well as alloys thereof.

[0040] For example, the titanium alloy additionally comprises at least Al as a further element. Preferably, the titanium alloy comprises Al as a further element in an amount of for example 1 to 10% by weight or 3 to 9% by weight in relation to the overall mass of the alloy. Alternatively, the titanium alloy comprises V as a further metal in an amount of for example 0.5 to 8% by weight or 1 to 6% by weight in relation to the overall mass of the alloy.

[0041] For example, the titanium alloy additionally comprises at least V as a further metal and in addition at least Al as a further element. Preferably, the titanium alloy comprises V as a further metal in an amount of for example 0.5 to 8% by weight or 1 to 6% by weight in relation to the overall mass of the alloy, and Al as a further element in an amount of for example 1 to 10% by weight or 3 to 9% by weight in relation to the overall mass of the alloy.

[0042] In a preferred embodiment, the metallic substrate constitutes a titanium alloy Ti-6Al-4V.

[0043] One requirement of the method according to the invention is that at least part of the metallic substrate surface is brought into contact with an electrolyte solution. In particular, the metallic substrate surface that is brought into contact with the electrolyte solution is the one that is to be protected by the superhydrophobic coating with self-cleaning properties from icing up and/or contamination and/or erosion. For example, the entire surface of the metallic substrate is brought into contact with the electrolyte solution. The electrolyte solution comprises a fluoride salt.

[0044] The fluoride salt is preferably selected from the group comprising ammonium fluoride, ammonium bifluoride, potassium fluoride, sodium fluoride, calcium fluoride, magnesium fluoride and mixtures thereof. For example, the fluoride salt is ammonium fluoride.

[0045] Preferably, the electrolyte solution can be provided in the form of an aqueous solution. The overall amount of fluoride salt in the electrolyte solution may be in a range from 0.5 to 10 g/l. For example, the electrolyte solution includes the fluoride salt in an amount of 4 to 6 g/l.

[0046] According to one embodiment of the present invention, the electrolyte solution includes a further water-soluble salt for improving the conductivity of the electrolyte solution. The further water-soluble salt is preferably selected from the group comprising ammonium sulphate, sodium sulphate, sodium bisulphate, potassium sulphate, potassium bisulphate and mixtures thereof. Preferably, the further aqueous salt is ammonium sulphate.

[0047] The overall amount of further water-soluble salt in the electrolyte solution may be between 50 and 250 g/l. For example, the electrolyte solution contains the further water-soluble salt in an amount of 120 to 140 g/l.

[0048] According to a further embodiment, the electrolyte solution comprises ammonium sulphate and ammonium fluoride. According to a further embodiment of the present invention, the electrolyte solution consists of water, ammonium sulphate and ammonium fluoride.

[0049] Preferably, the electrolyte solution comprises 50 to 250 g/l, in particular 120 to 140 g/l, preferably approx. 130 g/l of ammonium sulphate and 0.5 to 10 g/l, in particular 4 to 6 g/l, preferably approx. 5 g/l of ammonium fluoride.

[0050] Preferably, the electrolyte solution does not contain any hydrofluoric acid.

[0051] The contacting of at least part of the metallic substrate surface with the electrolyte solution may be carried out by means of standard application techniques. Preferably, the electrolyte solution may be applied by way of dipping, spinning, flooding, brushing or spraying.

[0052] According to a further embodiment, the surface of the metallic substrate is pretreated prior to the application of the electrolyte solution. In one embodiment, the substrate is initially cleaned and afterwards etched or pickled in an acidic manner. Suitable means for cleaning are for example ethanol/surfactant mixtures or alkaline detergents such as e.g. P3 Almeco 18 (Henkel Technologies). The etching or acidic pickling of the substrate may be carried out, for example, using an aqueous solution that contains hydrofluoric acid in nitric acid, or using commercially available pickles such as e.g. Turco®5578 (Henkel Technologies). According to another embodiment, following the pickling step, the surface of the substrate is conditioned in an acidic or basic manner by dipping the substrate into an alkaline cleaning bath for a short time.

[0053] According to the invention, the method includes anodising the metallic substrate coated with the electrolyte solution in order to produce a nanoporous layer on the metallic substrate. Preferably, the method includes anodising the entire metallic substrate coated with the electrolyte solution for producing a nanoporous layer on the metallic substrate. Anodisation is an electrochemical process that can be used to produce an oxide layer on titanium as well as alloys thereof by way of anodic oxidation.

[0054] Preferably, anodisation is carried out by means of a three-electrode assembly. Such three-electrode assemblies are per se known, so that they do not need to be illustrated or explained in any detail.

[0055] According to one embodiment, anodisation is carried out at a voltage between 2 volt and 50 volt, for example at a voltage between 10 and 20 volt. Preferably, the anodisation step is carried out at a temperature between 10° C. and 60° C. or between 20° C. and 30° C. For example, anodisation is carried out at room temperature, such as between 21° C. and 25° C.

[0056] Further, anodisation has to be carried out for a period of time that is sufficient to effect the formation of the desired surface structure. Preferably, anodisation is carried out for a period of time of at least 5 min. For example, anodisation is carried out for a period of time of 5 min to 480 min or 20 min to 40 min. Preferably, anodisation is carried out for a period of time of approx. 30 min.

[0057] The anodisation step according to the invention leads to the formation of a nanoporous layer on the metallic substrate.

[0058] It has been determined that the indicated electrolyte solution has advantageous properties. According to the present invention, the anodisation of the metallic substrate

treated with the electrolyte solution leads to the formation of nanotubes including titanium dioxide (TiO₂).

[0059] According to a preferred embodiment, the nanoporous layer on the metallic substrate therefore has such a structure that comprises a multiplicity of nanotubes including titanium dioxide. Preferably, the layer thickness of the nanoporous layer is adjusted to a layer thickness between 100 nm and 10 μ m. Preferably, the layer thickness of the nanoporous layer is adjusted to a layer thickness between 200 nm and 1 μ m, preferably between 250 nm and 800 nm, more preferably between 280 nm and 600 nm. For example, the layer thickness of the nanoporous layer is adjusted to a layer thickness between 300 nm and 500 nm.

[0060] Additionally or alternatively, the nanotubes including titanium dioxide that are contained in the nanoporous layer are adjusted to a certain pore diameter. Preferably, the pore diameter of the nanotubes including titanium dioxide is adjusted to a diameter between 20 nm and 300 nm, preferably to a diameter between 20 nm and 220 nm or between 30 nm and 180 nm. Particularly preferably, the diameter of the nanotubes is between 30 nm and 140 nm. For example, the diameter of the nanotubes including titanium dioxide is adjusted to a diameter between 30 nm and 100 nm, for example to a diameter between 30 nm and 60 nm.

[0061] The nanotubes including titanium dioxide which are generated during the anodisation process are preferably evenly distributed over the metal surface.

[0062] The anodisation step may be carried out once or several times.

[0063] According to the invention, a superhydrophobising coating is applied to the nanoporous layer. According to a preferred embodiment, the structure of the nanoporous layer comprising nanotubes including titanium dioxide is not modified during the application of the superhydrophobising coating.

[0064] In particular, any coating materials may be used that lead to a superhydrophobising coating, i.e. one that has a contact angle to water of more than 140°.

[0065] In particular, sol-gel coatings, SAMs (Self Assembled Molecules), amphiphilic block copolymers, siloxanes, long-chained hydrocarbons and any further coating materials that form a very thin superhydrophobic layer may be used. For example, superhydrophobising coatings are suitable, by means of which a layer thickness between 0.1 nm and 200 nm can be adjusted, preferably a layer thickness between 1 nm and 100 nm or between 2 nm and 70 nm. Particularly preferred is a layer thickness between 3 nm and 50 nm or between 5 nm and 30 nm.

[0066] Examples of superhydrophobising coatings are amphiphilic block copolymers. Preferably, amphiphilic block copolymers are selected from the group consisting of hydrophilic block copolymers such as e.g. polyethylene oxide (PEO), hydrophobic block copolymers such as e.g. polyethylene (PE), polybutadiene (PB) and mixtures thereof.

[0067] Further examples include siloxanes such as e.g. oligomeric alkyl alkoxy siloxanes or polymeric siloxanes, long-chained hydrocarbons such as e.g. octyl triethoxysilane or silane-siloxane mixtures.

[0068] Preferably, a sol-gel coating is applied onto the nanoporous layer.

[0069] Sol-gel processes are disclosed for example in the following patent documents: DE 10 2009 005 105 A1, U.S. Pat. No. 5,814,137, U.S. Pat. No. 5,849,110, U.S. Pat. No. 5,789,085, U.S. Pat. No. 5,869,141, U.S. Pat. No. 5,958,578,

U.S. Pat. No. 5,869,140, U.S. Pat. No. 5,939,197, U.S. Pat. No. 6,037,060, US 2009/0148711 and WO 2008/052510 A1.

[0070] Suitable sol-gel coatings are for example optionally fluorinated alkyl silane compounds.

[0071] Examples of suitable, optionally fluorinated alkyl silane compounds are tetraalkoxysilanes, alkyl trialkoxysilanes, aryl trialkoxysilanes, alkenyl trialkoxysilanes, glycidioxyalkyl trialkoxysilanes and (meth)acryl trialkoxysilanes as well as mixtures thereof. Particularly preferred are sol-gel coatings that comprise fluoralkyl functional silane. Examples of fluoralkyl functional silanes include fluorinated tetraalkoxysilanes, alkyl trialkoxysilanes as well as mixtures thereof. Particularly preferred are fluorinated alkyl trialkoxysilanes. The sol-gel coating preferably includes (tridecafluoro-1,1,2,2-tetrahydrooctyl)-triethoxysilane. A sol-gel matrix that can be used for the method according to the invention is the commercially available Dynasylan®F 8261 (Evonik Industries).

[0072] The properties of the coating, e.g. the hardness, may be enhanced by adding silicon-free precursors. Examples of these are metal organic compounds such as tetraisopropoxytitanium, triisopropoxyaluminium, tri-sec-butoxyaluminium, tetrabutoxyzirconium and tetrapropoxyzirconium.

[0073] In addition, small particles such as e.g. nanoparticles from metal oxides, metal carbides and metal nitrides may be added to the sol-gel matrix. Suitable materials are for example SiC, Si₃N₄, Al₂O₃, ZrO₂, TiO₂ or SiO₂. For example, nanoparticles can enhance the resistance of the coating. In order to enhance the compatibility with the sol-gel matrix, the particles may, if necessary, be functionalized. Functionalization may be carried out for example by chemomechanical processes during grinding of the particles. A compound suitable for functionalizing nanoparticles is e.g. TODA (3,6,9-trioxadecanoic acid).

[0074] The hydrolysis of the sol-gel forming components may be carried out by adding water.

[0075] The processing properties of the sol-gel material may be adjusted using solvents as well as additives. Suitable solvents are e.g. ethanol, isopropanol, 1-butanol, butoxyethanol, butylacetate, isopropoxyethanol and glycol. The additives may comprise for example wetting agents, levelling agents, anti-foaming agents, dispersing agents, UV stabilizers and silicones as well as condensation catalysts such as e.g. acids or bases. In order to enhance flexibility, the finished sol may moreover be provided with organic polymers.

[0076] According to one embodiment, the sol-gel material is produced from (tridecafluoro-1,1,2,2-tetrahydrooctyl)-triethoxysilane and isopropanol, and the hydrolysis is carried out by adding water and 37% hydrochloric acid.

[0077] The superhydrophobic coating can be applied using standard application methods such as dipping, spinning, flooding, brushing or spraying.

[0078] The sol-gel coating can be thermally cured, e.g. at a temperature between 40° C. and 180° C., preferably at a temperature between 60° C. and 120° C. For example, the sol-gel coating is cured at a temperature of approx. 120° C. The coating may be alternatively or additionally cured by radiation, e.g. using UV light, infrared or the like.

[0079] The sol-gel coating is adjusted to a layer thickness between 0.1 nm and 200 nm, preferably to a layer thickness between 1 nm and 100 nm or between 2 nm and 70 nm. Particularly preferably, the layer thickness is between 3 nm

and 50 nm or between 5 nm and 30 nm. By means of multi-layer coating, the layer thickness may, if required, be enhanced further.

[0080] The metallic substrates having a superhydrophobic coating and self-cleaning properties, which are obtained using the method according to the invention, may be used in particular in aircraft such as airplanes and helicopters. The present metallic substrates having a superhydrophobic coating and self-cleaning properties may further also be used in land vehicles, rail vehicles or maritime vehicles.

[0081] The obtained metallic substrates having a superhydrophobic coating and self-cleaning properties have in particular a contact angle to water of more than 140°. Preferably, the obtained metallic substrate having a superhydrophobic coating and self-cleaning properties has a contact angle to water of more than 150°. For example, the obtained metallic substrate having a superhydrophobic coating and self-cleaning properties has a contact angle to water between 140° and 170° or between 150° and 160°.

[0082] In preferred embodiments, the metallic substrate, onto which the superhydrophobic coating with self-cleaning properties according to the invention is applied, is selected from structures of airplanes or helicopters that are loaded with ice and contamination, such as for example wings, engines, rudders, tailplane, windows, rotor blade and the like. In further preferred embodiments, the metallic substrate, onto which the superhydrophobic coating with self-cleaning properties according to the invention is applied, is selected from rotor blades of wind turbines, building facades, bridges, power lines and the like.

[0083] Aircraft, in which the metallic substrates having a superhydrophobic coating and self-cleaning properties according to the invention are used, are protected from erosion and/or contamination by insects and/or organic and inorganic materials such as for example dirt and gas components in the air or in rainwater. The same analogously also applies to icing. Moreover, contamination may initially be caused by organic materials. These adherent impurities are decomposed under UV irradiation by the metallic substrate having a superhydrophobic coating and self-cleaning properties and are removed from the coated substrate surface.

[0084] In a further aspect of the present invention, the use of a metallic substrate having a superhydrophobic coating and self-cleaning properties in order to prevent icing up in aircraft is therefore provided. Further, another aspect of the present invention provides for the use of a metallic substrate having a superhydrophobic coating and self-cleaning properties in order to prevent contamination in aircraft. According to a further aspect of the present invention, the use of an electrolyte solution comprising 50 to 250 g/l, in particular 120 to 140 g/l of ammonium sulphate and 0.5 to 10 g/l, in particular 4 to 6 g/l of ammonium fluoride in a method for producing a superhydrophobic coating with self-cleaning properties on a metallic substrate such as described above is provided.

[0085] The embodiments of the method also apply to the metallic substrate that can be obtained using said method as well as to the uses, and vice versa.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

[0086] FIG. 1 shows a top view of a coated titanium substrate in a scanning electron micrograph.

[0087] FIG. 2 shows a lateral view of a coated titanium substrate in a scanning electron micrograph.

[0088] FIG. 3 shows a schematic view of a metallic substrate having a superhydrophobic coating with self-cleaning properties.

DETAILED DESCRIPTION

[0089] In order to produce a superhydrophobic coating with self-cleaning properties on a metallic substrate, first of all, a titanium alloy (TiAl6V4) was degreased and cleaned using the commercially available alkaline detergent P3 Almeco 18 (Henkel Technologies) at a concentration of 30 g/l at approx. 70° C. for 15 min. Subsequently, the substrate was etched with a concentration of 500 g/l of the commercially available pickle Turco® 5578 (Henkel Technologies) at approx. 95° C. for 5 min., cleaned with deionised water and air-dried.

[0090] For the anodic oxidation, an aqueous electrolyte solution containing ammonium sulphate in a concentration of 130 g/l and ammonium fluoride in a concentration of 5 g/l was provided. The anodisation of the cleaned substrate was carried out in the electrolyte solution using a three-electrode assembly with TiAl6V4 as the cathode with a voltage of 15 volts for 30 min. at approx. 22° C. In the course of this, a substrate with a nanoporous layer having a layer thickness of 300 nm to 350 nm was obtained. The nanoporous layer was evenly spread over the treated substrate and had a multiplicity of nanotubes with a pore diameter of approx. 40 to 50 nm. The anodised substrate was then cleaned with deionised water and was dried with a stream of nitrogen.

[0091] The homogenous distribution of the nanoporous layer on the titanium substrate and the pore diameter of the obtained nanotubes after anodisation are shown in the scanning electron micrograph in FIG. 1.

[0092] Subsequently, the substrate was treated with the commercially available fluorosilane Dynasylan® F 8261 (Evonik Industries). To this end, the sol-gel, which consisted of 2% by weight of the fluorosilane Dynasylan® F 8261, 5% by weight of water and 0.2% by weight of hydrochloric acid (37%), was hydrolysed in isopropanol for 2 h. The application of the fluorosilane coating was carried out by way of dip coating for 2 min and subsequent cleaning with deionised water for 30 s. The obtained substrates were cured at 80° C. for 1 h.

[0093] As a result of this process, also the edge areas of the nanotubes containing TiO₂ were treated with a thin layer (several nm) of the fluorosilane coating. In the course of this, a substrate having a nanoporous layer with a layer thickness of 300 nm to 350 nm was obtained.

[0094] The nanoporous layer of nanotubes containing TiO₂ on the titanium substrate and the structure of the obtained nanotubes are shown in the scanning electron micrograph in FIG. 2. As shown in FIG. 2, the nanotubes including TiO₂ are not closed. FIG. 3 shows a schematic view of the titanium substrate having a superhydrophobic coating and self-cleaning properties.

[0095] The foregoing disclosure has been set forth merely to illustrate the invention and is not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to

include everything within the scope of the appended claims and equivalents thereof.

1-15. (canceled)

16. A method for producing a superhydrophobic coating with self-cleaning properties on a metallic substrate, the method comprising:

- a) providing a metallic substrate comprising titanium;
- b) providing an electrolyte solution comprising a fluoride salt;
- c) contacting at least part of a surface of the metallic substrate with the electrolyte solution from step b);
- d) anodizing the metallic substrate from step c) in order to produce a nanoporous layer comprising nanotubes including titanium dioxide on the metallic substrate; and
- e) applying a superhydrophobising coating onto the nanoporous layer comprising nanotubes including titanium dioxide, wherein the electrolyte solution comprises a further water-soluble salt selected from the group comprising ammonium sulphate, sodium sulphate, sodium bisulphate, potassium sulphate, potassium bisulphate and mixtures thereof.

17. The method of claim **16**, wherein the metallic substrate is a titanium alloy and the alloy additionally comprises at least one further metal selected from the group comprising V, Fe, Sn, Ni, Nb, Mo, Zr, Y, Hf, Ta, Ce, Tb, Nd, Gd, Dy, Ho and Er, or in addition at least one further element selected from the group comprising Zn, Mn, Ag, Li, Cu, Si, Al or Ca.

18. The method of claim **16**, wherein the metallic substrate additionally comprises Al and V.

19. The method of claim **16**, wherein the fluoride salt is selected from the group comprising ammonium fluoride, ammonium bifluoride, potassium fluoride, sodium fluoride, calcium fluoride, magnesium fluoride and mixtures thereof.

20. The method of claim **19**, the fluoride salt is ammonium fluoride.

21. The method of claim **16**, wherein the further water-soluble salt is ammonium sulphate.

22. The method of claim **16**, wherein the anodization of the metallic substrate in an electrolyte solution comprising 50 to 250 g/l and 0.5 to 10 g/l of ammonium fluoride is carried out at a temperature in a range of 10 to 60° C. and a voltage of 2 to 50 volt for 5 to 480 minutes.

23. The method of claim **16**, wherein the anodization of the metallic substrate in an electrolyte solution comprising 120 to 140 g/l of ammonium sulphate and 4 to 6 g/l of ammonium fluoride is carried out at a temperature in a range of 20 to 30° C. and a voltage of 10 to 20 volt for 20 to 40 minutes.

24. The method of claim **16**, wherein the nanotubes including titanium dioxide have a diameter in a range of 10 to 300 nm.

25. The method of claim **16**, wherein the nanotubes including titanium dioxide have a diameter in a range of 30 to 140 nm.

26. The method of claim **16**, wherein the nanotubes including titanium dioxide have a diameter in a range of 30 to 100 nm.

27. The method of claim **16**, wherein the superhydrophobic coating with self-cleaning properties on the metallic substrate has a layer thickness between 100 nm and 10 µm.

28. The method of claim **16**, wherein the superhydrophobic coating with self-cleaning properties on the metallic substrate has a layer thickness between 280 nm and 600 nm.

29. The method of claim **16**, wherein the superhydrophobic coating with self-cleaning properties on the metallic substrate has a layer thickness between 300 nm and 500 nm.

30. The method of claim **16**, wherein the superhydrophobising coating comprises a fluoroalkyl functional silane.

31. The method of claim **16**, wherein the contacting of the metallic substrate surface with the electrolyte solution or the application of the superhydrophobising coating on the nanoporous layer is carried out by dipping, spinning, flooding, brushing or spraying.

32. A metallic substrate having a superhydrophobic coating and self-cleaning properties, which is obtain by:

- a) providing a metallic substrate comprising titanium;
- b) providing an electrolyte solution comprising a fluoride salt;
- c) contacting at least part of a surface of the metallic substrate with the electrolyte solution from step b);
- d) anodizing the metallic substrate from step c) in order to produce a nanoporous layer comprising nanotubes including titanium dioxide on the metallic substrate; and
- e) applying a superhydrophobising coating onto the nanoporous layer comprising nanotubes including titanium dioxide, wherein the electrolyte solution comprises a further water-soluble salt selected from the group comprising ammonium sulphate, sodium sulphate, sodium bisulphate, potassium sulphate, potassium bisulphate and mixtures thereof.

33. The metallic substrate as claimed in claim **32**, wherein the surface of the substrate with a superhydrophobic coating and self-cleaning properties has a contact angle to water of more than 140°.

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