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(54) HIGHLY REFLECTING ANODISED AL SURFACES WITH TAILORED DIFFUSE AND SPECULAR CONTENT

STARK REFLEKTIERENDE ANODISIERTE AL-OBERFLÄCHEN MIT MASSGESCHNEIDERTEM DIFFUSEM UND SPIEGELNDEM GEHALT

SURFACES EN AL ANODISÉ HAUTEMENT RÉFLÉCHISSANTES À CONTENU DIFFUS ET SPÉCULAIRE ADAPTÉ

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- **VISWESWARA CHAKRAVARTHY GUDLA ET AL:** "High frequency anodising of aluminium-TiO₂ surface composites: Anodising behaviour and optical appearance", **SURFACE AND COATINGS TECHNOLOGY**, vol. 277, 1 September 2015 (2015-09-01), pages 67-73, XP055333860, AMSTERDAM, NL ISSN: 0257-8972, DOI: 10.1016/j.surfcoat.2015.07.035
- **Visweswara Chakravarthy Gudla ET AL:** "Effect of High Frequency Pulsing on the Interfacial Structure of Anodized Aluminium-TiO₂", **Journal of the Electrochemical Society**, 1 January 2015 (2015-01-01), pages 303-310, XP055333973, DOI: 10.1149/2.0311507jes Retrieved from the Internet: URL:<http://jes.ecsdl.org/content/162/7/C303.full.pdf#page=1&view=FitH> [retrieved on 2017-01-11] cited in the application

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method to obtain a reflective anodised aluminium surface on an object. The present invention relates in particular to a method to obtain a reflective, anodised aluminium surface having a white appearance.

BACKGROUND OF THE INVENTION

[0002] Whereas most colours can be produced by absorption, this is not the case for white, since it is a combination of all visible wavelengths of light. White appearance of aluminium cannot be seen analogous to the coloured appearance of dyed aluminium, as it conceptually is very different.

[0003] White surfaces are ubiquitous in a huge number of applications (window frames, panels, doors, lamps, etc.), and while a white surface can be achieved using paint or even white plastics, a white wear-resistant aluminium surface would often be the number one choice if such a surface would be available.

[0004] White aluminium surfaces can be produced by embedding titanium dioxide (TiO₂) or other white pigments into an anodic film. The white pigments opacify the films primarily by diffusely reflecting light. This reflection occurs because the white pigment scatters or bends light strongly. If there is enough white pigment in an anodic film almost all visible light striking it will be reflected, and the anodic film will appear opaque, white, and bright.

[0005] The scratch and UV-resistance of an anodised surface is significantly higher than that of a traditional painted surface. Hence, anodised surfaces are usually preferred to painted surfaces when it comes to both practical applications and long-lasting decorative purposes. Therefore white anodized surfaces are preferred and have high value compared to the white painted aluminium.

[0006] Embedding white pigments into an anodic film is not a straight-forward operation, considering that the pigments are typically magnitudes larger than the nano-scaled pores that are created in an anodizing process. It is known from EP 2 649 224 B1 to obtain a radiation scattering surface finish on an object by providing the object with a top layer, comprising aluminium or an aluminium alloy, the top layer comprising added discrete inclusions of a second material being different from aluminium and the first alloy, and subsequently anodising said top layer to form an anodic oxide layer and to generate from the inclusions discrete radiation scattering elements. In an embodiment said radiation scattering elements are selected from particles of titanium, tin, zirconium, iron, titanium oxide, tin oxide, zirconium oxide, and iron oxide. The process described will secure that pigments, such as white pigments, are embedded into an anodic alumina film, which together will provide the scat-

tering mechanism that finally generates a surface that is being perceived as white.

[0007] An anodising method using high-frequency switching anodising (HSA) is disclosed in "Anodizing method for aluminum alloy by using high-frequency switching electrolysis" H.Tanaka, M.Fujita, T.Yamamoto, H.Muramatsu Suzuki Motor Corporation; H.Asoh, S.Ono, Kogakuin University.

[0008] Multi-pass friction stir processing (FSP) to impregnate TiO₂ particles into the surface of an aluminium alloy and subsequent anodising in a sulphuric acid electrolyte is disclosed by V.C. Gudla, F. Jensen, A. Simar, R. Shabadi, R. Ambat, Friction stir processed Al-TiO₂ surface composites: Anodising behaviour and optical appearance, Appl. Surf. Sci. 324 (2015) 554-562.

[0009] High frequency anodising of friction stir processed Al-TiO₂ surface composites using a high frequency pulse and pulse reverse pulse technique at a fixed frequency in a sulfuric acid bath is disclosed by V. C. Gudla, F. Jensen, K. Bordo, A. Simar, R. Ambat, Effect of High Frequency Pulsing on the Interfacial Structure of Anodized Aluminium-TiO₂, Journal of The Electrochemical Society, 162 (7) C303-C310 (2015).

[0010] Anodizing of aluminium-TiO₂ may also be seen in "High frequency anodising of aluminium-TiO₂ composites: Anodising behaviour and optical appearance" by Gudla et al, Surface and coatings tech. Vol. 277, pp 67-73, September 2015.

[0011] Multi-pass friction stir processing (FSP) to impregnate metal oxide (TiO₂, Y₂O₃ and CeO₂) particles into the surface of an aluminium alloy and subsequent anodising in a sulphuric acid electrolyte is disclosed by V. C. Gudla, F. Jensen, S. Canulescu, A. Simar, R. Ambat, Friction stir processed Al - metal oxide surface composites: anodization and optical appearance, 28th international conference on surface modification technologies, June 16th - 18th, 2014, Tampere University of Technology, Tampere, Finland.

[0012] US 2009/0236228 A1 relates to an anodizing method and apparatus.

[0013] US 2006/0037866 relates to an anodic oxide film and anodizing method.

[0014] US 2008/0087551 relates to a method for anodizing aluminum alloy and power supply for anodizing aluminum alloy.

[0015] JP2004-035930 relates to an aluminum alloy material and anodization treatment method therefor.

[0016] JP2008-0085574 relates to a method for anodizing an aluminum member.

[0017] JP2007-154301 relates to an aluminum alloy anodic oxidation method and power source for aluminum alloy anodic oxidation.

[0018] Other technology may be seen in US20150118512.

[0019] Existing technologies for creating a white anodic film are mainly limited to matt surfaces. Furthermore, existing technologies rely on a fundamentally different light scattering mechanism provided by a structured sur-

face that scatters light diffusely and that does not provide the same degree of whiteness as obtained through the present invention.

[0020] Thus, there is a need for developing a process technology capable of processing aluminium generating visually appealing, wear-resistant, white alumina surfaces.

OBJECT OF THE INVENTION

[0021] It is an object of embodiments of the invention to provide beautiful, wear-resistant anodised aluminium (Al) surfaces with novel optical appearances through a white anodized alumina surface layer (Al₂O₃). Furthermore, the appearance of the surfaces can be tuned the entire way from matt-etched white to a very bright glossy white.

SUMMARY OF THE INVENTION

[0022] It has been found by the present inventor(s) that by providing an object with a top layer comprising aluminium or an aluminium alloy, the top layer comprising embedded discrete particles of titanium or titanium oxide, and anodising said top layer in an aqueous solution of an organic acid applying a time varying signal comprising a high frequency signal in the form of a square wave signal having a frequency between 500 Hz and 5 kHz, a decoratively appealing, wear-resistant white alumina surface is obtained.

[0023] So, in a first aspect the present invention relates to a method according to claim 1.

LEGENDS TO THE FIGURE

[0024]

Fig. 1 (a) shows almost parallel growth of DC formed anodic pores, making it hard to reach the regions underneath particles;

Fig. 1 (b) shows branched pores formed during high frequency anodising; and

Fig. 2 illustrates the process disclosed in example 1.

Detailed disclosure of the invention

Specific embodiments of the invention

[0025] In an embodiment of the invention the embedded discrete particles are titanium oxide particles.

[0026] Titanium dioxide (TiO₂) exhibits a light refractive index much different than sealed anodic alumina, making it an ideal pigment for obtaining good light scattering. As such, pigments with other chemical compositions can be used, if they possess properties similar to those of titanium dioxide.

[0027] In an embodiment of the invention the particle size of the embedded discrete particles is in the range

100-500 nm, preferably in the range 150-400 nm, such as 200-300 nm. The size of TiO₂ particles should preferably be 200-300 nm to secure light scattering of all visible wavelengths, making the surface perceived as white.

[0028] In an embodiment of the invention the aluminium or aluminium alloy comprises at least 95% by weight of aluminium, preferably at least 96% by weight of aluminium, such as at least 97% by weight of aluminium, such as at least 98% by weight of aluminium, more preferably at least 99% by weight of aluminium.

[0029] A pure aluminium alloy is required for the anodic film to become as optically transparent as possible. Alloying elements such as Fe, Mn and Cu must be kept to an absolute minimum, knowing that these elements will give rise to a certain degree of light absorption, which will compromise the anodic film whiteness. Using an alloy with a composition equivalent to a 6060 (or even purer), has proven to give good results.

[0030] In an embodiment of the invention the discrete particles of a metal or metal oxide are embedded by a solid state process.

[0031] Non-limiting examples of solid state processes include a solid state process selected from the group consisting of friction stir processing (FSP), additive friction stir processing (AFSP), and powder metallurgy.

[0032] Friction stir processing (FSP) is a solid state process known for its ability to modify microstructures and provide improved properties over conventional processing technologies. The development of friction stir processing (FSP) is based on the friction stir welding (FSW) technology. FSW works by plunging a spinning tool into the joint of two materials and then traversing the rotating tool along the interface. The friction caused by the tool heats up the materials around the pin to a temperature below the melting point. The rotation of the tool "stirs" the material together and results in a mixture of the two materials. In FSP a specially designed rotating pin is first inserted into the material to be processed with a proper tool tilt angle and then moved along the programmed paths. The pin produces frictional and plastic deformation heating within the processing zone. As the tool pin moves, materials are forced to flow around the pin. Material flows to the back of the pin, where it is extruded and forged behind the tool. It is evident that FSW and FSP share the same mechanism, however, have completely different purposes in practical applications. The goal of FSW is to join two plates together, whereas FSP aims at modifying the microstructure of a single or multiple workpieces.

[0033] Additionally, FSP has emerged as an advanced tool to produce surface composites by embedding second phase particles into the matrix. It is exactly this feature that is utilized in this patent application as to embed white pigments into the aluminium bulk, considering that the FSP process has the required advantages of:

i) Maintaining a sufficiently low temperature to avoid

a critical reaction between pigment and aluminium;

ii) Being able to remove excess heat via a Heat Sink, again to avoid a reaction between pigment and aluminium;

iii) Securing a homogenous and individual distribution of pigments within the aluminium matrix; and

iv) Leaving the pigments in a functional state.

[0034] Whereas Friction Stir Processing (FSP) is a very time-consuming batch process, Additive Friction Stir Processing (AFSP) has emerged to create a continuous process, where particles are fed to the material through a hollow spinning tool. Not only is this a much faster (and non-batch) process, it also allows for much higher particle loadings.

[0035] Even though AFSP is the preferred technique for embedding white pigments into an aluminium matrix, other techniques are also available. An further example of solid state processing (route 2) is powder metallurgy, where pigments are mechanically alloyed into the aluminium powder. The composite powder is subsequently compressed and shaped in a normal powder metal route such as forging, cold isostatic pressing (CIP), hot isostatic pressing (HIP), direct profile extrusion, direct rolling of sheets, cold spraying, thermal spraying etc.

[0036] In another embodiment of the invention the discrete particles of a metal or metal oxide are embedded by a liquid state process, such as e.g. Stir Casting or Investment Casting.

[0037] In another embodiment of the invention the discrete particles of a metal or metal oxide are embedded by a vapour state process such as e.g. Physical Vapour Deposition (PVD) or Chemical Vapour Deposition (CVD).

[0038] As such, any of the above major processing routes can be used, as long as they fulfil the considerations mentioned above. Anodizing secures the conversion of aluminium into aluminium oxide. The pigments which were embedded into the top aluminium layer will become embedded into the aluminium oxide after anodizing.

[0039] The difference in refractive index between the anodic oxide and the white pigments secures scattering of all visible wavelengths that finally makes the anodized surface appear white.

[0040] Anodic films are traditionally formed by passing a direct current (DC) through an electrolyte, with the aluminium part working as the anode and a suitable material serving as the cathode. However, DC anodizing has proven problematic in anodizing the aforementioned composite alloy, due to the regions that are underneath each individual pigment. Anodic pores formed through a DC process are almost completely parallel and do not reach the regions underneath the pigments. This leaves an anodic film with embedded pigments that have a small area of non-anodized aluminium underneath them. In

turn this is a very unfortunate situation, considering the light absorption properties of metallic aluminium, which finally makes the entire anodic film be perceived as dark rather than white.

[0041] High Frequency Anodizing has proven much more advantageous compared to traditional DC anodizing, due to the branching nature of the pores, which extend all the way underneath each individual pigment. This will secure an anodic film entirely depleted of non-anodized aluminium, as shown in Figure 1.

[0042] Like traditional hard anodizing the white anodizing must be carried out at low temperature and in low-aggressive electrolyte to decrease the degree of pore wall attack.

[0043] The electrolyte used in an anodising process is traditionally water based and has an active content of acid. Almost all weak and strong organic acids can function as an electrolyte in the anodizing step of the process according to the invention.

[0044] In an embodiment of the invention the anodising of step b. takes place in an aqueous solution of an organic acid selected from the group consisting of oxalic acid, succinic acid, tartaric acid, malic acid, maleic acid, formic acid, citric acid and acetic acid. In a preferred embodiment of the invention the anodising of step b. takes place in an aqueous solution of an organic acid selected from the group consisting of oxalic acid, formic acid and citric acid, preferably oxalic acid.

[0045] The high frequency signal, which is a time varying signal, may comprise a square wave signal having pulses with amplitudes between -5 V and +5 V in the low period and between +15 V and 100 V in the high period. Moreover, the voltage ramp up/down times of the pulses may be in the range between 0 and 15% of the ideal square wave pulse duration. The frequency of the square wave signal may typically be around 1 kHz.

[0046] The thickness of the anodized film determines how white the surface appears. To secure a total white light scattering effect in the visible spectrum - normally about 100 μm oxide is necessary. Thus in an embodiment of the invention the thickness of the anodized film is in the range 50-300 μm, such as about 75-200 μm, preferably in the range 100-150 μm, such as in the range 80-130 μm.

[0047] The pigment concentration determines how white the surface appears. Thus in an embodiment of the invention the pigment concentration is in the range 2-25 wt%, such as about 5-20 wt%, preferably in the range 10-15 wt%.

[0048] The anodizing parameters will determine the quality of the anodized film. Thus. optical properties can be characterized by a standard spectrophotometer, where the degree of reflected light is measured.

[0049] Hardness can be measured with a standard microhardness testing unit, where a diamond indenter is pressed into the surface. The diagonal (in case of Vickers hardness testing) of the resulting indentation gives a figure for the surface hardness.

[0050] Tribological properties can be found by a standardised wear tester such as a ball-on-disc setup.

[0051] The thick anodic film obtained above may be slightly dissolved in the upper part because of the prolonged exposure to the acid electrolyte, a phenomenon known as "pore wall attack".

[0052] The porous oxide can be stabilized by impregnating it with an agent that fills the anodic pores.

[0053] Thus, in an embodiment of the method according to the invention the method comprises a further step of impregnating the anodised aluminium oxide layer.

[0054] In an embodiment of the invention said impregnation is performed by means of an impregnating substance selected from the group consisting of a silicate, a lacquer, and a sol-gel substance. Non-limiting examples of lacquers and sol-gel substances include acrylics, silanes and silane based sol-gels.

EXAMPLE 1

[0055] Aluminium plates with dimensions 200 mm × 60 mm × 6 mm were used for the FSP trials. Commercial TiO₂ powder in rutile phase was used. The median diameter of the powder particles was 210 nm. Processing the FSP process was performed using a hermle milling machine equipped with a steel tool having 20 mm shoulder diameter, 1.5 mm pin length with a m6 thread. The backwards tilt angle of the tool was maintained at 1°. A groove 0.5 mm deep, 10 mm wide, and 180 mm long in the Al plates which was compactly filled with TiO₂ powder. The filled plates were then covered by the same Al sheet rolled down to a thickness of 0.25mm to prevent loss of TiO₂ powder during the initial FSP pass. Rotational speed of the tool was 1000 rpm and the advancing speed was 200 mm/min for the first pass to insure correct closure of the groove and 1000 mm/min for the next six passes. A surface of 175 mm long × 20 mm wide was processed for each pass with a total processing time of roughly 2 min. All seven passes were performed one over the other without any shift. The samples were then mechanically polished, buffed to a mirror finish and then degreased in a mild alkaline solution at 60°C. The samples were subsequently desmuted by immersing in diluted HNO₃ followed by demineralized water rinsing. Anodising was carried out in a saturated oxalic acid bath maintained at 10°C. A square wave high frequency signal of 1 kHz from 0 to 40V was applied, with a controlled ramp up/down duration which corresponds to 10% of the pulse duration. The process continues until the film thickness has grown to approximately 100 μm. After anodising the surface appears white, with both specular and diffuse reflections. The sample is rinsed and transferred to a hot water sealing tank for closing the open-pored anodic structure. The process is illustrated in Fig. 2.

Claims

1. A method to obtain a reflective anodised aluminium surface on an object, comprising the steps:

- a. Providing the object with a top layer comprising aluminium or an aluminium alloy, the top layer comprising embedded discrete particles of titanium or titanium oxide,
- b. Subsequently anodising said top layer to form an anodic oxide layer, wherein said anodising of step b. takes place by applying a time varying signal comprising a high frequency signal in the form of a square wave signal having a frequency between 500 Hz and 5 kHz, such as around 1 kHz;

characterized in that said anodising of step b. takes place in an aqueous solution of an organic acid.

2. The method according to any one of the preceding claims, wherein the particle size of the embedded discrete particles is in the range 100-500 nm, preferably in the range 150-400 nm, such as 200-300 nm.

3. The method according to any one of the preceding claims, wherein the aluminium or aluminium alloy comprises at least 95% by weight of aluminium, preferably at least 96% by weight of aluminium, such as at least 97% by weight of aluminium, such as at least 98% by weight of aluminium, more preferably at least 99% by weight of aluminium.

4. The method according to any one of the preceding claims, wherein the discrete particles of titanium or titanium oxide are embedded by a solid state process.

5. The method according to claim 4, wherein said solid state process is a process selected from the group consisting of friction stir processing (FSP), additive friction stir processing (AFSP), and powder metallurgy.

6. The method according to any one of claims 1-4, wherein the discrete particles of titanium or titanium oxide are embedded by a liquid state process.

7. The method according to any one of claims 1-4, wherein the discrete particles of titanium or titanium oxide are embedded by a vapour state process.

8. The method according to any one of the preceding claims, wherein the anodising of step b. takes place in an aqueous solution of an organic acid selected from the group consisting of oxalic acid, succinic acid, tartaric acid, malic acid, maleic acid, formic acid, citric acid and acetic acid.

9. The method according to claim 8, wherein the organic acid is selected from the group consisting of oxalic acid, succinic acid, tartaric acid, malic acid, maleic acid, and citric acid.
10. The method according to claim 1, wherein the square wave signal has an amplitude between - 5 V and 100 V, such as between 0 V and 40 V.
11. The method according to claim 1 or 10, wherein the square wave signal comprises ramp up and/or ramp down times between 0 and 15 % of a pulse duration.
12. The method according to any one of the preceding claims, further comprising a further step of impregnating the anodised aluminium oxide layer.
13. The method according to claim 12, wherein said impregnation is performed by means of an impregnating substance selected from the group consisting of a silicate, a lacquer, and a sol-gel substance.

Patentansprüche

1. Verfahren zum Erzielen einer reflektierenden anodisierten Aluminiumoberfläche auf einem Objekt, umfassend folgende Schritte:
- a) Versehen des Objekts mit einer Deckschicht, die Aluminium oder eine Aluminiumlegierung umfasst, wobei die Deckschicht eingebettete diskrete Partikel von Titan oder Titanoxid umfasst,
- b) anschließendes Anodisieren der Deckschicht, um eine anodische Oxidschicht zu bilden, wobei das Anodisieren in Schritt b) durch Anlegen eines zeitvariablen Signals erfolgt, das ein Hochfrequenzsignal in der Form eines Rechtecksignals umfasst, das eine Frequenz zwischen 500 Hz und 5 kHz, wie etwa ungefähr 1 kHz, aufweist;
- dadurch gekennzeichnet, dass** das Anodisieren in Schritt b) in einer wässrigen Lösung einer organischen Säure erfolgt.
2. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Partikelgröße der eingebetteten diskreten Partikel in dem Bereich von 100 bis 500 nm, bevorzugt in dem Bereich von 150 bis 400 nm, wie etwa zwischen 200 und 300 nm, liegt.
3. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Aluminium oder die Aluminiumlegierung mindestens 95 Gewichtsprozent Aluminium, bevorzugt mindestens 96 Gewichtsprozent Aluminium, wie etwa mindestens 97 Gewichtsprozent Alu-

minium, wie etwa mindestens 98 Gewichtsprozent Aluminium, weiter bevorzugt mindestens 99 Gewichtsprozent Aluminium umfasst.

- 5 4. Verfahren nach einem der vorhergehenden Ansprüche, wobei die diskreten Partikel von Titan oder Titanoxid durch einen Festphasenprozess eingebettet werden.
- 10 5. Verfahren nach Anspruch 4, wobei der Festphasenprozess ein Prozess ist, der aus der Gruppe ausgewählt wird, die aus Reibschweißverarbeitung (FSP), additiver Reibschweißverarbeitung (AFSP) und Pulvermetallurgie besteht.
- 15 6. Verfahren nach einem der Ansprüche 1 bis 4, wobei die diskreten Partikel von Titan oder Titanoxid durch einen Flüssigphasenprozess eingebettet werden.
- 20 7. Verfahren nach einem der Ansprüche 1 bis 4, wobei die diskreten Partikel von Titan oder Titanoxid durch einen Dampfphasenprozess eingebettet werden.
- 25 8. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Anodisieren in Schritt b) in einer wässrigen Lösung einer organischen Säure erfolgt, die aus der Gruppe ausgewählt wird, die aus Oxalsäure, Bernsteinsäure, Weinsäure, Apfelsäure, Maleinsäure, Ameisensäure, Zitronensäure und Essigsäure besteht.
- 30 9. Verfahren nach Anspruch 8, wobei die organische Säure aus der Gruppe ausgewählt wird, die Oxalsäure, Bernsteinsäure, Weinsäure, Apfelsäure, Maleinsäure und Zitronensäure umfasst.
- 35 10. Verfahren nach Anspruch 1, wobei das Rechtecksignal eine Amplitude zwischen -5 V und 100 V, wie etwa zwischen 0 V und 40 V, aufweist.
- 40 11. Verfahren nach Anspruch 1 oder 10, wobei das Rechtecksignal Hochlauf- und/oder Rücklaufzeiten zwischen 0 und 15 % einer Impulsdauer umfasst.
- 45 12. Verfahren nach einem der vorhergehenden Ansprüche, ferner umfassend einen weiteren Schritt des Imprägnierens der anodisierten Aluminiumoxidschicht.
- 50 13. Verfahren nach Anspruch 12, wobei das Imprägnieren anhand einer Imprägniersubstanz erfolgt, die aus der Gruppe ausgewählt wird, die aus einem Silikat, einem Lack und einer Sol-Gel-Substanz besteht.
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Revendications

1. Procédé pour obtenir une surface réfléchissante en aluminium anodisé sur un objet, comprenant les étapes consistant à :
 - a. pourvoir l'objet d'une couche supérieure comprenant de l'aluminium ou un alliage d'aluminium, la couche supérieure comprenant des particules discrètes enrobées de titane ou d'oxyde de titane,
 - b. anodiser ensuite ladite couche supérieure pour former une couche d'oxyde anodique, dans lequel ladite anodisation de l'étape b. a lieu par application d'un signal variable dans le temps comprenant un signal haute fréquence sous la forme d'un signal carré ayant une fréquence comprise entre 500 Hz et 5 kHz, telle qu'environ 1 kHz ;

caractérisé en ce que ladite anodisation de l'étape b. a lieu dans une solution aqueuse d'un acide organique.
2. Procédé selon l'une quelconque des revendications précédentes, dans lequel la granulométrie des particules discrètes enrobées est dans la plage de 100 à 500 nm, de préférence dans la plage de 150 à 400 nm, telle que 200 à 300 nm.
3. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'aluminium ou l'alliage d'aluminium comprend au moins 95 % en poids d'aluminium, de préférence au moins 96 % en poids d'aluminium, tel qu'au moins 97 % en poids d'aluminium, tel qu'au moins 98 % en poids d'aluminium, plus préférentiellement au moins 99 % en poids d'aluminium.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel les particules discrètes de titane ou d'oxyde de titane sont enrobées par un procédé à l'état solide.
5. Procédé selon la revendication 4, dans lequel ledit procédé à l'état solide est un procédé choisi dans le groupe constitué par le traitement par friction-malaxage (FSP), le traitement par friction-malaxage additive (AFSP) et la métallurgie des poudres.
6. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel les particules discrètes de titane ou d'oxyde de titane sont enrobées par un procédé à l'état liquide.
7. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel les particules discrètes de titane ou d'oxyde de titane sont enrobées par un procédé à l'état de vapeur.
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'anodisation de l'étape b. a lieu dans une solution aqueuse d'un acide organique choisi dans le groupe constitué par l'acide oxalique, l'acide succinique, l'acide tartrique, l'acide malique, l'acide maléique, l'acide formique, l'acide citrique et l'acide acétique.
9. Procédé selon la revendication 8, dans lequel l'acide organique est choisi dans le groupe constitué par l'acide oxalique, l'acide succinique, l'acide tartrique, l'acide malique, l'acide maléique et l'acide citrique.
10. Procédé selon la revendication 1, dans lequel le signal carré a une amplitude comprise entre -5 V et 100 V, telle qu'entre 0 V et 40 V.
11. Procédé selon la revendication 1 ou 10, dans lequel le signal carré comprend des temps de montée et/ou de descente compris entre 0 et 15 % d'une durée d'impulsion.
12. Procédé selon l'une quelconque des revendications précédentes, comprenant en outre une étape supplémentaire d'imprégnation de la couche d'oxyde d'aluminium anodisée.
13. Procédé selon la revendication 12, dans lequel ladite imprégnation est effectuée au moyen d'une substance d'imprégnation choisie dans le groupe constitué par un silicate, une laque et une substance sol-gel.

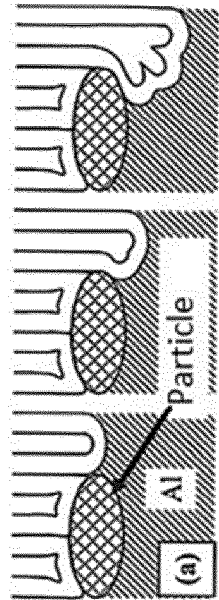


Figure 1a

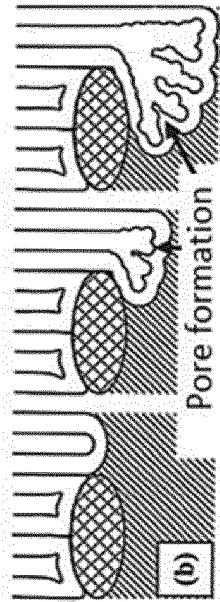


Figure 1b

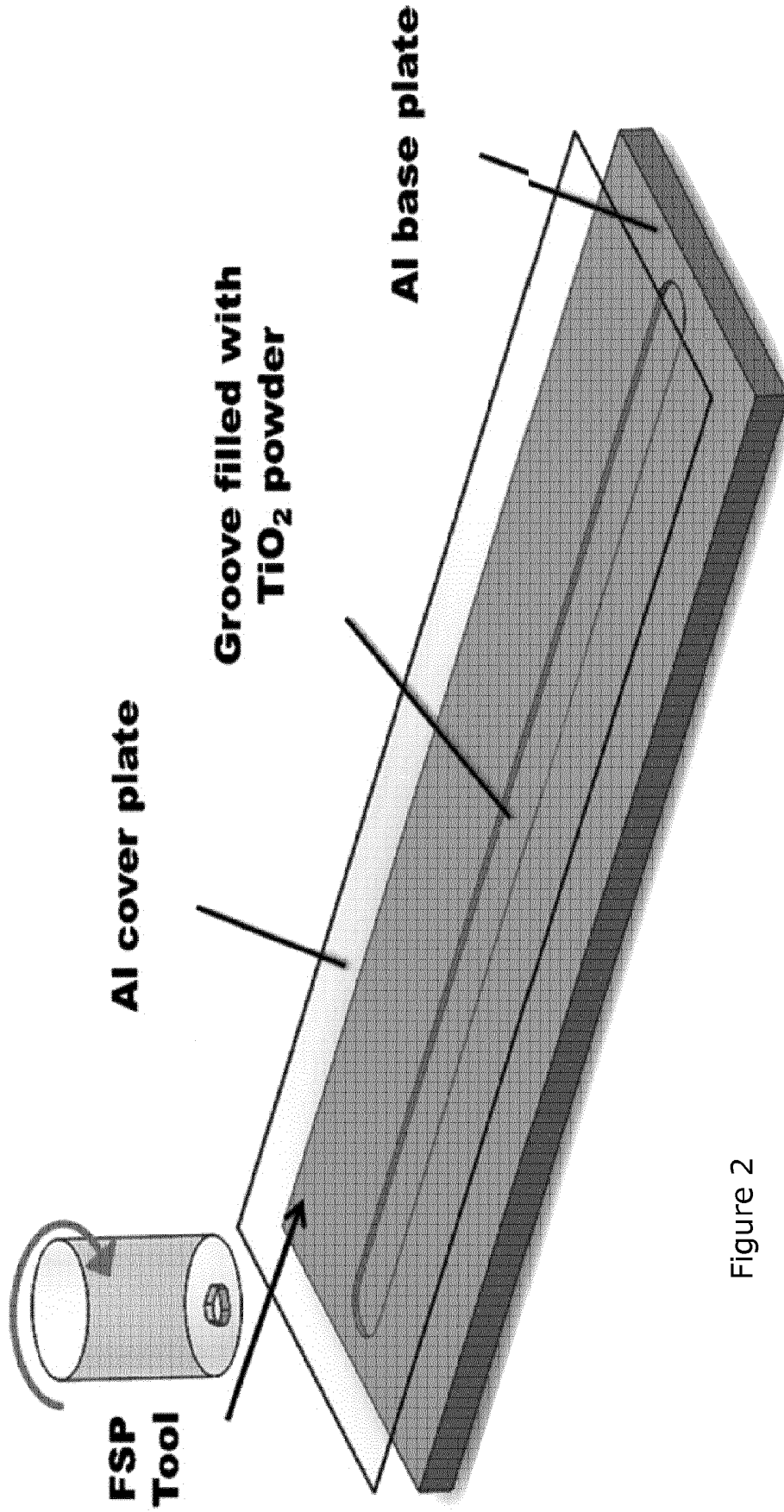


Figure 2

REFERENCES CITED IN THE DESCRIPTION

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