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(54) **MIXED METAL OXIDE COATINGS FOR TITANIUM ALLOYS**

(57) The present invention relates to a method for preparing a titanium alloy having a mixed metal oxide (MMO) on its surface, to a titanium alloy having a MMO on its surface, particularly obtained or obtainable by said method of preparation, a shaped part destined to be sub-

jected to mechanical stress comprising a titanium alloy having a MMO on its surface, and a method for protecting a titanium alloy having a MMO on its surface by application of a voltage.

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**Description****TECHNICAL FIELD**

5 **[0001]** The present invention belongs to the field of coatings and methods for protecting, particularly from corrosion and biofouling, titanium alloys destined to be immersed in aqueous environments. In particular it relates to a method for preparing a titanium alloy having a mixed metal oxide (MMO) on its surface, to a titanium alloy having a MMO on its surface, particularly obtained or obtainable by said method of preparation, a shaped part destined to be subjected to mechanical stress comprising a titanium alloy having a MMO on its surface, and a method for protecting a titanium alloy  
10 having a MMO on its surface by application of a voltage.

**STATE OF THE ART**

15 **[0002]** Titanium alloys may be used in equipment and structures destined to be immersed, for instance in aqueous environments and in particular in seawater, such as ship and boat hulls, a propeller, a shaft, a rudder, other aquatic or marine equipment such as heat exchangers, drilling platforms, dry dock equipment, oil production rigs, aquaculture equipment and netting and pipes, which are immersed in water, or have water running through them.

**[0003]** However, the surface of titanium alloys in such environments is prone to biofouling (or biological fouling), i.e., the accumulation of aquatic organisms, such as algae (including green and/or brown), microorganisms, or small animals  
20 such as barnacles, mussels, sponges and the like, which tend to grow, in aqueous environments and is seawater in particular, and get adhered to the immersed titanium alloy surfaces. Biofouling poses problems on, e.g., ship and boat hulls, because it increases frictional resistance during movement through water. As a consequence, speed is reduced and fuel consumption increased. On static objects such as legs of drilling platforms, and rigs for oil and gas production, refining and storage, causes problems because the resistance of thick layers of fouling to waves and currents can cause  
25 unpredictable and potentially dangerous stresses in the object, and also because fouling makes it difficult to inspect the objects for defects, such as stress cracking and corrosion. It is also a nuisance in pipes such as cooling water intakes and outlets, because the effective cross-sectional area is reduced by fouling, with the consequence that flow rates are reduced. This requires routine cleaning or the use of chemicals that in many cases are harmful to the environment. Further, cleaning the biofouling of such titanium alloy surfaces it is not an easy task, especially since most of the time,  
30 the surfaces need to remain immersed during the cleaning operation.

**[0004]** Several methods have been described and are currently used to protect structures or shaped parts immersed in aqueous environments such as seawater. For instance, it is common to use cathodic protection. Cathodic protection may involve subjecting the structure or shaped parts to be protected to cathodic polarization and connecting it to a sacrificial material that acts as anode, by which the oxidation reactions occur on the anode, and the life of material acting  
35 as cathode is prolonged, by reducing the degree of corrosion. Impressed current cathodic protection is another method used, which involves sacrificial anodes connected to an external power source. The external power source, often a DC power supply, provides the current necessary to drive the electrochemical reaction required for cathodic protection to occur.

**[0005]** Protection by anodization of such structures, in particular for the oxidation of species in the aqueous environment to achieve an antifouling effect, has also been described.

**[0006]** For instance, for pure titanium structures, JP2003328164A discloses a method for preventing the adhesion of the marine organisms to the titanium ship having a structure to electrically insulate screw propellers and their shaft from the hull comprises maintaining reference electrodes for bringing the hull of the titanium ship into contact with seawater at a potential of 1.2 to 1.4 V (based on a saturated KCl Ag/AgCl reference electrode).

45 **[0007]** However, it has been found that the application of such voltages in a titanium alloy having titanium oxide on its surface, the conductivity is too slow to allow sufficient current density on the surface to obtain a sufficiently strong anti-fouling effect. In particular, in European patent application No. 22382464 it was shown that to obtain antifouling effects for pure titanium, potentials of above 6 V<sub>Ag/AgCl</sub> were required.

**[0008]** On the other hand such anodic potentials (of above 6 V<sub>Ag/AgCl</sub>) are workable in titanium structures due to the highly resistant properties of pure titanium. However, it has been found that working with titanium alloys, structures immersed in aqueous environment subjected to potentials of around 6 V<sub>Ag/AgCl</sub> or above, are above the breakdown potential of the titanium alloy passivation layer, which for grade 5 titanium alloy has been found to be at around 3 V<sub>Ag/AgCl</sub>. Consequently, working at such voltages results in the damage of the titanium alloy structure.

55 **[0009]** In the electrochemistry field it is known to use coatings on the surfaces of metallic electrodes to improve their properties. For instance, back in 1969 British Patent GB 1147442 described a fuel cell electrode comprises a core of titanium which has been degreased and pickled and coated with platinum by electrodeposition or with platinum or platinum nickel alloy by a chemical compound decomposition process and the platinum coating has been oxidized, e.g., to a depth of 5 to 25% of its thickness, by heating in an oxidizing atmosphere or by electrolysis. This publication describes

that in addition to providing chemical resistivity, oxides of platinum metals have the particular advantage that the threshold value at which they are capable of dissociating an electrolyte is lower than that of the pure metal, so that the overall electric energy that needs to be supplied to the electrode is considerably reduced.

**[0010]** The inclusion of such precious metal (oxide)s, such as ruthenium and iridium, may be used to cover the surface of metals to form what is called in the art 'Dimensionally Stable Anodes' or DSA. These have also been used for oxygen or chlorine evolution, by oxidation of water, hydroxide or chloride respectively, which may be present in the aqueous environment and in seawater in particular, whereby the surface of the metal act as anode, protecting the metal which they cover. The generation of oxygen and/or chlorine on the surface, may act as a biocide and prevent the appearance of biological fouling. A problem with these approaches is the high price of precious metals, which for its application on large surfaces, the hull of a ship, becomes difficult to sustain economically.

**[0011]** An alternative to precious metals for the elaboration of DSA's are coatings based on oxides of metals other than precious metals, such as tin oxide ( $\text{SnO}_2$ ) doped with antimony (Sb), what may also be referred to as a mixed metal oxide (MMO). Oxides of such alternative metals have been applied to titanium pure electrodes. Reference is made, e.g., to the following publications.

**[0012]** Montilla *et al.* (Preparation and Characterization of Antimony-Doped Tin Dioxide Electrodes. Part 1. Electrochemical Characterization. F. Montilla, E. Morallon, A. De Battisti, and J. L. Vázquez. The Journal of Physical Chemistry B 2004 108 (16), 5036-5043. DOI: 10.1021/jp037480b), disclose antimony and antimony-platinum doped tin dioxide electrodes supported on titanium prepared by thermal decomposition and describe that the introduction of platinum in the oxide coating increases the service life by 2 orders of magnitude.

**[0013]** Shao *et al.* (Dan Shao, Wei Yan, Lu Cao, Xiaoliang Li, Hao Xu, High-performance Ti/Sb-SnO<sub>2</sub>/Pb<sub>3</sub>O<sub>4</sub> electrodes for chlorine evolution: Preparation and characteristics, Journal of Hazardous Materials, Volume 267, 2014, Pages 238-244, ISSN 0304-3894, <https://doi.org/10.1016/j.jhazmat.2013.12.064>), disclose a cost-effective Ti/Sb-SnO<sub>2</sub>/Pb<sub>3</sub>O<sub>4</sub> electrode which was found to have strong chlorine evolution ability with high current efficiency. During the electrolysis process, it was found that the conversion of Pb<sub>3</sub>O<sub>4</sub> into  $\beta$ -PbO<sub>2</sub> happened gradually on the electrode surface, which not only inhibited the leakage of hazardous Pb<sup>2+</sup> ion but also increased the anti-corrosion capacity of the electrode effectively.

**[0014]** Sun *et al.* (Yi Sun, Shaoan Cheng, Zhen Yu, Longxin Li, Chaochao Li, Jiawei Yang, Elucidating deactivation mechanisms of Pd-doped and un-doped Ti/SnO<sub>2</sub>-Sb electrodes, Journal of Alloys and Compounds, Volume 834, 2020, 155184, ISSN 0925-8388, <https://doi.org/10.1016/j.jallcom.2020.155184>) disclose the Pd-doping of Ti/SnO<sub>2</sub>-Sb (ATO) increasing the service life of ATO electrode by 53 times. However, Pd-doped ATO electrode was deactivated due to the gradual dissolution of doped Pd atoms resulting in the change of coating structure and the loss of coating protection.

**[0015]** Tin used in these approaches is known to form a structure with oxygen known as cassiterite ( $\text{SnO}_2$ ). This oxide has a low electrical conductivity. However, the inclusion of antimony, which dissolves easily in tin oxide, gives it the appropriate properties. As described in Sun *et al.* (referenced above) and in Chaplin (Chaplin, B. P. (2014). Critical review of electrochemical advanced oxidation processes for water treatment applications. Environ. Sci.: Processes Impacts, 16(6), 1182-1203. <https://doi.org/10.1039/c3em00679d>), it is believed that the presence of Sb(V) in the vacancies in the structure provides an extra valence electron that greatly improves conductivity. On the other hand, Sb(III) present on the surface and grain boundaries would offer active sites for the generation of hydroxyl radicals.

**[0016]** A problem with these approaches is that the protective and catalytic layer of MMO, with time, tends to dissolve in the aqueous environment. Further, such coatings have been described to be applied on pure titanium materials and have not been applied to titanium alloys.

## SUMMARY OF THE INVENTION

**[0017]** It has now been found that a surface treatment on a titanium alloy comprising titanium oxide on its surface for the formation of a mixed metal oxide (MMO) on the surface of the titanium alloy, not only can be achieved but also provides the titanium alloy with a modified surface, which is protected with respect to bio-fouling and corrosion when immersed in an aqueous environment, such as seawater.

**[0018]** Accordingly, the instant invention relates to a method for preparing a titanium alloy having a mixed metal oxide (MMO) on its surface comprising:

- a) providing a titanium alloy comprising titanium oxide on its surface; and
- b) applying a surface treatment to a surface of the titanium alloy, wherein the surface treatment comprises forming a MMO on the surface of the titanium alloy.

**[0019]** The instant invention also relates to a titanium alloy having a mixed metal oxide on its surface, in particular, obtained by or obtainable by a method of preparation as described herein. Such titanium alloy may also be referred to herein as MMO surface modified titanium alloy, or MMO activated titanium alloy.

**[0020]** It has been particularly found that a titanium alloy with a MMO on its surface as described herein requires the

application of a relatively low anodic voltage, of below  $3 V_{Ag/AgCl}$ , to achieve anti-biofouling properties when immersed. The breakdown potential of the protective oxide layer of a titanium alloy such as grade 5 titanium alloy, has been found to be at an anodic voltage of around  $3 V_{Ag/AgCl}$ . The breakdown potential may be defined as the surface potential at which the surface's passive film breaks down. This leads to active electrochemical reaction, causing corrosion or re-passivation of the surface in the working conditions. Accordingly, by being able to work at voltages below  $3 V_{Ag/AgCl}$ , a method as described herein advantageous allows obtaining an antibiofouling effect working at voltages below or under the breakdown potential of titanium alloys.

**[0021]** Such voltages have also been found to slow down the dissolution of the MMO into the aqueous environments. This advantageously requires a reduced energy consumption, increases the active live time of the MMO modified titanium alloy surface, and provides the possibility of tackling biofouling in titanium alloy structures immersed in aqueous medium, e.g., in seawater, in particular for prolonged periods of time.

**[0022]** Accordingly, the present invention also relates to a method for protecting a titanium alloy surface which comprises the steps of:

- i) immersing a titanium alloy having a mixed metal oxide (MMO) on its surface in an aqueous medium, in particular in seawater;
- ii) applying a voltage below  $3 V_{Ag/AgCl}$  to the surface such that the surface acts as an anode.

**[0023]** Without being bound to any theory, it is believed, that the formation of a MMO on the surface of a titanium alloy favours the electrical conductivity of the surface of the titanium alloy acting as anode and favours the electrocatalytic properties for the oxidation of species, such as water, hydroxide and in particular chloride ions present in aqueous environments such as seawater, upon the application of a voltage onto the titanium alloy surface having MMO such that the surface acts as an anode. In particular, the high conductivity facilitates the flow of electrons through the surface of the coating, generated during oxidation reactions in the electrolyte, i.e., the aqueous environment and seawater in particular. This is achieved even at voltages of below  $3 V_{Ag/AgCl}$ , which result in

- the advantageous anti-fouling effect
- preventing detrimental effects of higher voltages on the titanium alloy and
- adverting costs of higher voltages.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0024]** To complete the description and in order to provide for a better understanding of the invention, a set of drawings is provided. Said drawings form an integral part of the description and illustrate an embodiment of the invention, which should not be interpreted as restricting the scope of the invention, but just as an illustration of some aspects of the invention as described herein. The drawings comprise the following figures:

Figure 1 shows a titanium alloy propeller immersed in seawater upon application of a voltage of  $7 V_{Ag/AgCl}$  (A) and (B) and the same propeller after removal from the seawater (C), for which clear signs of corrosion can be observed. Figure 2 shows intensities (A) and current densities ( $A/m^2$ ) of MMO surface modified grade 5 titanium alloy (A) and grade 5 titanium alloy without modification (B) according to example 1 below. Figure 3 shows both intensity (A) and density ( $A/m^2$ ) curves for the surface modified and the non-modified grade 5 titanium alloy, superimposed for potential ranges below  $2.2 V_{Ag/AgCl}$  (in particular in ranges from 0.0 to  $1.2 V_{Ag/AgCl}$  in A), from 1.2 to  $1.8 V_{Ag/AgCl}$  in B) and from 1.8 to  $2.20 V_{Ag/AgCl}$  in C)). Figure 4 shows the overlap of the current density ( $A/m^2$ ) graphs obtained for the MMO modified grade 5 titanium alloy of Example 1 and the MMO modified grade 2 titanium alloy of Example 2. Figure 5 shows a grade 5 titanium alloy sheet free of biofouling after 6 months of being immersed in seawater, upon constant application of an anodic voltage of  $1.7 V_{Ag/AgCl}$ .

## DETAILED DESCRIPTION OF THE INVENTION

**[0025]** The instant invention relates to a method for preparing a titanium alloy having a mixed metal oxide (MMO) on its surface, comprising:

- a) providing a titanium alloy comprising titanium oxide on its surface;
- b) applying a surface treatment to a surface of the titanium alloy, wherein the surface treatment comprises forming a MMO on the surface of the titanium alloy.

**[0026]** Titanium alloys suitable for a method as described herein include titanium alloys suitably used for equipment and structures destined to be immersed in or to be in contact with an aqueous environment, and in particular seawater. Such equipment and structures may include, for instance ship and boat parts typically immersed in or in constant contact with water such a hull of a boat or a ship, a propeller, a shaft, a rudder, other aquatic or marine equipment such as heat exchangers, drilling platforms, dry dock equipment, oil production rigs, aquaculture equipment and netting and pipes. Such equipment and structures may be particularly selected from ship and boat parts and more in particular may be the hull of a boat or ship.

**[0027]** Titanium alloys that can be used for such equipment and structures are known in the art. In contrast with titanium grades 1, 2, 3 and 4, which are regarded as commercially pure titanium's (with more than 98.5 wt.% titanium and which may include impurities to different degrees), titanium alloys comprise elements other than titanium, as alloying elements, as functional elements or as impurities, including inevitable impurities. Generally, in titanium alloys alloying elements are present in higher amounts than functional elements and impurities, and functional elements, if present, may be present in higher amounts than impurities. Some impurities may be kept to a minimum, their presence being defined typically only as a maximum wt.%. In the present specification such elements other than titanium may be collectively referred to as "other elements".

**[0028]** As a mode of example, a suitable titanium alloy may comprise from 70 to 98.5 wt.% of titanium based on the total weight of the titanium alloy, and the remaining up to 100 wt.% of other elements including alloying elements, functional elements, and inevitable impurities. In particular, the titanium alloy may comprise from 75 to 97.5 wt.% of titanium, more in particular from 80 to 95 wt.% of titanium, yet more in particular from 85 to 92.5 wt.%, and yet more in particular from 87.5 to 91 wt.% of titanium, with the corresponding wt.% remaining up to 100 wt.% of other elements. Other elements including alloying elements, functional elements, and inevitable impurities may be selected from aluminum, vanadium, tin, molybdenum, niobium, tantalum, zirconium, manganese, iron, chromium, cobalt, nickel, copper, palladium, silicon, oxygen, nitrogen and carbon. Some impurities, such as the presence of interstitial elements (such as interstitial oxygen, nitrogen and carbon), may be particularly controlled, for example some titanium alloys are referred to as ELI (extra-low interstitial), to refer to the extra-low amount of interstitial elements.

**[0029]** Some preferred titanium alloys may comprise, aluminum and/or vanadium and optionally other elements such as tin, palladium, chromium, zirconium, nickel, molybdenum, niobium and ruthenium and optionally impurities (e.g., oxygen, iron, carbon). It may be preferred for the titanium alloy to comprise both aluminum and vanadium.

**[0030]** In several embodiments, the amount of aluminum in the titanium alloy may be from 2 to 10 wt.% of aluminum, in particular from 2.5 to 7.5 wt.% aluminum, more in particular from 3 to 7 wt.% of aluminum.

**[0031]** In several embodiments, the amount of vanadium may be from 1 to 10 wt.% of vanadium, in particular from 1.5 to 7 wt.% of vanadium, and more in particular from 2 to 5 wt.% of vanadium.

**[0032]** In several embodiments, the titanium alloy comprises from 70 to 98.5 wt.% of titanium, and further comprises from 2 to 10 wt.% of aluminum and from 1 to 10 wt.% of vanadium, the wt.% based on the total weight of the titanium alloy. In particular embodiments, the preferred or particular ranges of titanium, aluminum and vanadium, and the presence of other elements as described above also apply.

**[0033]** As a mode of example, a titanium alloy may be selected from grade 5 titanium alloy, grade 6 titanium alloy, grade 9 titanium alloy, grade 18 titanium alloy, grade 19 titanium alloy, grade 20 titanium alloy, and grade 21 titanium alloy. Preferably, a grade 5 titanium alloy may be used.

**[0034]** In contrast with titanium grades 1, 2, 3 and 4 which are pure titanium's, grades 5, 6, 9, 18, 19, 20 and 21 are a titanium alloys having defined compositions. Such titanium alloys are known in the art and are readily available.

**[0035]** Grade 5 titanium alloys are considered alpha-beta alloys, with aluminum stabilizing the alpha phase and vanadium stabilizing the beta phase, and may be defined according to the ASTM standard ASTM B265. Grade 5 titanium alloy typically comprises from 88 to 91 wt.% titanium, from 5.5 to 6.8 wt.% aluminum, from 3.5 to 4.5 wt.% vanadium, with a maximum amount of 0.40 wt.% of iron, although a maximum of 0.25 wt.% of iron may be preferred, and a maximum amount of 0.2 wt.% of oxygen. The alloy composition of grade 5 titanium alloy also gives it the name of Ti-6Al-4V or Ti 6-4, owing to the percentages of Al (about 6 wt.%) and V (about 4 wt.%) present in the titanium alloy. Grade 5 titanium alloy is one of the most commonly used titanium alloys and represents about 50% of the worldwide titanium consumption.

**[0036]** Grade 6 titanium alloy, comprises about 3 wt.% of aluminum and about 2.5 wt.% of tin.

**[0037]** Grade 9 titanium alloy, comprises about 3 wt.% of aluminum and about 2.5 wt.% of vanadium.

**[0038]** Grade 18 titanium alloy comprises about 3 wt.% aluminum, 2.5 wt.% vanadium and 0.04 to 0.08 wt.% palladium.

**[0039]** Grade 19 titanium alloy comprises about 3 wt.% aluminum, about 8 wt.% vanadium, about 6 wt.% chromium, about 4 wt.% zirconium, and about 4 wt.% molybdenum.

**[0040]** Grade 20 titanium alloy comprises about 3 wt.% aluminum, about 8 wt.% vanadium, about 6 wt.% chromium, about 4 wt.% zirconium, about 4 wt.% molybdenum and from 0.04 to 0.08 wt.% palladium.

**[0041]** Grade 21 titanium alloy comprises about 15 wt.% molybdenum, about 3 wt.% aluminum, about 2.7 wt.% niobium, and about 0.25 wt.% silicon.

**[0042]** A method described herein comprises providing titanium alloys comprising titanium oxide on its surface. Titanium

alloys comprising titanium oxide on the surface are readily available as, typically, a layer of titanium oxide will be formed on the surface of a titanium alloy upon exposure to atmospheric oxygen. Titanium alloys comprising titanium oxide on its surface may accordingly be provided commercially. Thus, titanium alloys may comprise a layer of titanium oxide is generated by natural passivation of the titanium alloy. In particular, titanium alloys may comprise titanium (IV) oxide  $\text{TiO}_2$  (also known as rutile) and/or titanium (II) oxide ( $\text{TiO}$ ), in particular  $\text{TiO}_2$  or both  $\text{TiO}_2$  and  $\text{TiO}$ , more in particular, if both  $\text{TiO}_2$  and  $\text{TiO}$  are present,  $\text{TiO}_2$  may be present in a higher amount than  $\text{TiO}$ .

**[0043]** Titanium alloys comprising other metals, such as aluminum, which also tend to oxidate naturally upon contact of atmospheric oxygen, may also have oxides of such metals on their surface. For instance, titanium alloys comprising aluminum as alloying element may also comprise aluminum oxide, in particular aluminum (III) oxide ( $\text{Al}_2\text{O}_3$ ) on the surface of the titanium alloy. Such alloys, may typically have a mixture of titanium oxide and aluminum oxide on its surface. A mixture of titanium oxide and such other metal oxides is not a MMO since the two metal oxides coexists independently, without sharing the same crystal network.

**[0044]** The titanium oxide layer, optionally comprising other metal oxides, such as aluminum oxide, may cover the titanium alloy surface in whole or in part, but typically covers the surface of the titanium alloy in whole.

**[0045]** The titanium oxide and, if present, of other oxides such as aluminum oxide on the surface of the titanium alloy, and the thickness of the titanium oxide layer may be characterized by X-Ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and/or Energy Dispersive X-ray spectroscopy (EDX) as described below for the characterization of the MMO formed on the surface of the titanium alloy.

**[0046]** The titanium oxide, and if present other oxides such as aluminum oxide, may form a layer typically covering the whole surface of the titanium alloy. Such layer, including titanium oxide and optionally other oxides of metals present in the titanium alloy, such as aluminium oxide, may be referred to as the titanium oxide layer.

**[0047]** In a method described herein the surface treatment comprises forming a mixed metal oxide (MMO) on the surface of the titanium alloy.

**[0048]** The term mixed metal oxide (MMO) generally refers to an oxide of more than one metal, including oxides of multiple metals or a metal oxide of one metal doped with another metal. Mixed metal oxides have interstitial spaces which allow for increased electrical conductivity of the titanium alloy surface on which they are formed. Mixed metal oxides are distinct from mixtures of metal oxides in that in mixtures of metal oxides each metal has its own crystal structure and in contrast, in mixed metal oxides the two metals share the same crystal network.

**[0049]** Generally, a mixed metal oxide may be formed on the surface of the titanium alloy on top of the titanium oxide present on the surface of the titanium alloy, e.g., forming a MMO layer on top of the titanium oxide layer (optionally in combination with other metal oxides such as aluminium oxide), or may be formed within the titanium oxide layer present on the surface of the titanium alloy, e.g., providing a mixed layer of MMO and titanium oxide and optionally other metal oxides that may be present in the titanium oxide layer. The MMO may also be formed within the layer of the titanium oxide and further on top of the titanium oxide layer, e.g., providing a mixed layer of MMO and titanium oxide (optionally in combination with other metal oxides such as aluminium oxide) and a layer MMO on top of the mixed layer.

**[0050]** A MMO formed in a method as described herein may be a mixed metal oxide of two or more metals selected from tin, antimony, lead, nickel, cobalt, and precious metals. A precious metal may be particularly selected from ruthenium (Rh) and iridium (Ir).

**[0051]** A MMO formed in a method as described herein may be preferably selected from a tin-antimony oxide, tin-antimony-lead oxide, a nickel-cobalt oxide and/or a precious metal oxide of two or more precious metals. A MMO may be preferably selected from tin-antimony oxide, tin-antimony-lead oxide, a nickel-cobalt oxide, and may preferably be a tin-antimony oxide or tin-antimony-lead oxide, to reduce the costs of the titanium alloy having a MMO on its surface.

**[0052]** The formation of MMO on the surface of the titanium alloy, reduces the amount of titanium oxide present on the surface of the titanium alloy, by the presence of the MMO within the titanium oxide layer as described above. The formation of the MMO on the surface of the titanium alloy may also reduce or eliminate the presence of titanium oxide on the surface by the formation of, e.g., a mixed layer of MMO and titanium oxide as also described above or a MMO layer on top of the titanium oxide layer or on top of the mixed layer. The formation of the MMO on the surface of the titanium alloy therefore replaces the presence of titanium oxide (in whole or in part) on the surface of the titanium alloy and provides the titanium alloy surface with high electrical conductivity and electrocatalytic properties for the oxidation of species which have been found to be advantageous for antifouling applications.

**[0053]** The amount of MMO formed on the surface of the titanium alloy surface may be determined by methods known in the art, such as gravimetric analysis. For instance, the weight of the titanium alloy prior to the surface treatment may be measured and compared to the weight of the titanium alloy after the surface treatment by which a MMO is formed on the surface of the titanium alloy. The amount of weight increase will correspond to the amount of MMO formed on the surface of the titanium alloy.

**[0054]** The composition of the surface of the titanium alloy and the presence (or absence) of titanium oxide, other metal oxides (such as aluminum oxide) and/or mixed metal oxides formed in a method described herein, may be monitored by methods known in the art.

**[0055]** For instance, X-Ray Diffraction (XRD) may be used to determine of the most predominant crystal phases on the surface of the titanium alloy and the % amounts thereof. XRD may be performed by methods known in the art, using a commercially available apparatus (e.g., an X-ray diffractometer X'pert PROMRD, from PANalytical, Holland B.V.), as described in for instance Shao *et al.* cited above.

**[0056]** X-ray photoelectron spectroscopy (XPS) may be used to obtain, on the one hand, the elemental composition of the different elements that present in the modified surface and on the other hand the state of oxidation in which these elements are found. XPS may be performed by methods known in the art, using a commercially available apparatus.

**[0057]** Energy Dispersive X-ray spectroscopy (EDX) may be used to also determine the elemental composition of the titanium alloy surface. EDX may be performed by methods known in the art, using a commercially available apparatus.

**[0058]** Accordingly, by comparing the XRD, XPS and/or EDX of the starting titanium alloy with those of the surface modified titanium alloy it can be established that the titanium oxide present on the surface of the titanium alloy is replaced by the mixed metal oxides formed in a method as described herein. If titanium oxide is replaced in whole, e.g., by the formation of a MMO layer which does not contain titanium oxide on top of the titanium oxide layer the signals relating to the presence of titanium oxide can no longer be observed in the, e.g., XRD and XPS diffractogram.

**[0059]** The formation of a mixed metal oxide onto the surface of the titanium alloy may be performed by methods known in the art. Known methods include forming a mixed metal oxide on the surface of the titanium alloy from a metal oxide precursor. Accordingly, in a method as described herein the surface treatment of step b) may comprise forming the MMO using a metal oxide precursor. In particular, a MMO formed on the surface of the titanium alloy contains more two or more metals providing from two or more metal oxide precursors.

**[0060]** In particular, a MMO may be formed by applying two or more metal oxide precursors onto the surface of the titanium alloy and forming the mixed metal oxide from the two or more metal oxide precursors.

**[0061]** It has been found that using metal oxide precursors advantageously facilitates the formation of a MMO on the titanium alloy surface, and in particular its integration within and/or on top of the titanium oxide layer. Accordingly, it may be preferred for the mixed metal oxide to be formed from a metal oxide precursor. This may be achieved, by for instance, thermal decomposition or electrochemical methods such as electrodeposition. Such methods are known in the art and it is within the scope of a person skilled in the art to choose adequate conditions for thermal decomposition or electrodeposition of a mixed metal oxide of choice, in terms of the choice of one or more metal oxide precursor, concentration of solutions of metal oxide precursors and reaction parameters (e.g., time, temperature, intensity and voltage as applicable). As a mode of example thermal decomposition or electrodeposition may be carried out as detailed in the following.

**[0062]** Thermal decomposition methods may be preferably used. Thermal decomposition may comprise applying two or more metal oxide precursors to the surface of the titanium alloy, using one or more deposition steps, and heating the titanium alloy with the two or more metal oxide precursors on its surface to form a MMO on the surface of the titanium alloy to provide a MMO modified titanium alloy. In particular, in a deposition step, firstly the surface of the titanium alloy to be modified may be contacted with a solution containing two or more the metal oxide precursors, such as a salt of the metals that are to form the MMO, in particular a metal chloride, e.g., by dipping the surface to be modified into the solution or by applying such solutions onto the surface of the titanium alloy where the MMO is to be formed, by brushing, spraying, rolling, flow coating, or pouring. Secondly, the solvent of the solution is allowed to dry and, thirdly, the treated surface is heated to elevated temperatures for the decomposition of the one or more salts and the formation of the mixed metal oxide. Drying of the solvent may be performed by methods known in the art. As a mode of example, the titanium alloy with the solution of the metal oxide precursor on its surface may be left to dry, air dried and/or dried by heating, e.g., in an oven. In a particular embodiment, the surface may be left to dry and be subsequently heated in an oven, e.g., at a temperature from 250 to 450 °C, in particular from 300 to 400 °C, for 1 to 15 minutes, in particular for 5 to 10 minutes.

**[0063]** Such a deposition step is typically repeated one or more times. In several embodiments, from 2 to 50 deposition steps may be performed, more in particular from 3 to 40 deposition steps may be performed, and yet more in particular 5 to 30 deposition steps may be performed, yet more in particular from 10 to 25 deposition steps may be performed, and yet more in particular from 15 to 20 deposition steps. Generally, the higher the number of deposition steps, the higher the amount of MMO formed on the titanium alloy surface, and higher the thickness of the layer of MMO being ultimately formed on the titanium alloy. The amount of MMO or thickness of the MMO layer will also determine the useful life time of the MMO modified surface. As used herein the useful life time or active life span of the MMO modified titanium alloy surface, refers to the time that the MMO modified titanium alloy surface can be actively used, by application of a voltage, to prevent biofouling, without observing damage of the MMO modified titanium alloy surface. The higher the amount/thickness, the longer will be the useful life time of the MMO modified surface. From 10 to 25 deposition steps, in particular from 15 to 20 deposition steps, have been found to be optimal in terms of the conductivity conferred to the titanium alloy surface and active life span of the MMO modified titanium alloy surface.

**[0064]** After the one or more deposition steps, heating the treated surface to elevated temperatures may be typically performed in, e.g., an oven, in particular at a temperature from 500 to 700 °C, more in particular 550 to 650 °C, and yet more in particular at a temperature of about 600 °C.

**[0065]** Heating is typically performed until, as described above, the presence of titanium oxide on the surface of the

titanium alloy, has been replaced in part or in whole, preferably in whole, by the formation of the MMO within the titanium oxide layer and/or on top of the titanium oxide layer. This can be monitored by, e.g., taking a control sample from the oven at several time intervals and monitoring the amount of titanium oxide and/or mixed metal oxide on the surface by the XRD and/or XPS methods indicated above. Such methods may also be used to determine the amount of MMO

formed on the surface of the titanium alloy and/or the thickness of the layer of the MMO formed.

**[0066]** Heating may be stopped once the desired amount/thickness of mixed metal oxide has been formed on the surface of the titanium alloy.

**[0067]** As a mode of example, the heating at elevated temperatures may be performed for from 15 minutes to 3 hours, in particular from 30 minutes to 2 hours, and more in particular for 45 to 1.5 hours, and yet more in particular for about 1 hour. A treatment of these lengths ensure the formation of MMO to provide the titanium alloy surface with the desired properties.

**[0068]** Accordingly, the instant invention may relate to a method as described herein, wherein the surface treatment of step b) is performed by thermal decomposition, in particular wherein the thermal decomposition comprises the steps of:

- b1) immersing the titanium alloy comprising titanium oxide on its surface of step a) in a solution of two or more metal oxide precursors in a solvent, to provide a titanium alloy treated with the two or more metal oxide precursors;
- b2) drying the titanium alloy treated with the precursor of the metal oxide of step (b1);
- b3) repeating steps (b1) to (b2) from 2 to 49 times; and,
- b4) repeating step (b1) and heating the sample to a temperature from 500 to 700 °C in particular from 550 to 650 °C for from 15 minutes to 3 hours, in particular from 30 minutes to 2 hours and more in particular from 45 minutes to 1.5 hours, thereby forming a mixed metal oxide onto the surface of the titanium alloy.

**[0069]** Electrodeposition methods may also be used. Accordingly in a method as described herein the surface treatment of step b) is performed by electrodeposition. In particular, electrodeposition may comprise immersing the titanium alloy having titanium oxide on its surface in a solution of two or more metal oxide precursors, connected to an activated titanium anode, cathodically polarizing the titanium alloy by applying a current (e.g., having an intensity from 100 to 800 mA, in particular from 150 to 600 mA, and more in particular from 200 to 500 mA) to induce the formation of the mixed metal oxide onto the titanium alloy surface. Activated titanium anodes are known in the art.

**[0070]** Accordingly, the instant invention may relate to a method as described herein, wherein the surface treatment of step b) is performed by electrodeposition, in particular wherein the electrodeposition comprises:

- b1) connecting the titanium alloy having titanium oxide on its surface to an activated titanium anode,
- b2) immersing the titanium alloy having titanium oxide on its surface connected to the activated titanium anode in a solution of two or more metal oxide precursors in a solvent,
- b3) cathodically polarizing the titanium alloy having titanium oxide on its surface by applying a current, in particular a current of from 100 to 800 mA, more in particular from 150 to 600 mA, and more in particular from 200 to 500 mA, thereby forming the mixed metal oxide on the surface of the titanium alloy.

**[0071]** The current may be applied for a period of time sufficient to obtained a desired amount of deposited mixed metal oxide. As a mode of example, the current may be applied for a period of time of, e.g., from 0.5 to 5 minutes, in particular from 1 to 4 minutes.

**[0072]** Suitable amounts of MMO formed on the surface of the titanium alloy, e.g., by thermal decomposition or electrodeposition, may be from 1 to 20 g/m<sup>2</sup>, in particular from 1.5 to 15 g/m<sup>2</sup>, and more in particular from 2 to 10 g/m<sup>2</sup>.

**[0073]** The thickness of a MMO layer formed on top of the titanium oxide layer or on top of a mixed titanium oxide layer and MMO layer, may be from 0.001 microns to 1 micron, in particular from 0.01 to 0.5 microns, yet more in particular from 0.02 to 0.1 microns.

**[0074]** The amount/thickness of the MMO formed on the surface of the titanium alloy, e.g., by thermal decomposition or electrodeposition, may be monitored as described above by XRD and/or XPS.

**[0075]** Precursors of a metal oxide may be selected from a metal salt, in particular from metal halides, more in particular from metal chlorides, and may preferably be a mixture of two or more metal chlorides. In particular, two or more metal oxide precursors may be selected from tin chloride, antimony chloride, lead chloride, nickel chloride, cobalt chloride, and/or precious metal chloride.

**[0076]** Depending on the metal oxides to be applied onto the surface of the titanium alloy a person skilled in the art would know to choose appropriate metal oxide precursors. For instance, if the mixed metal oxide is a tin-antimony-lead oxide, the precursor of the metal oxide may be a mixture of tin (IV) chloride (SnCl<sub>4</sub>), antimony (III) chloride (SbCl<sub>3</sub>), and lead (IV) chloride (PbCl<sub>4</sub>).

**[0077]** Solutions of the two or more metal oxide precursors in a solvent may be typically used for both thermal decomposition and electrodeposition. The solvent may be selected from, for instance, low alkyl alcohol, e.g., selected from C1



to C4 primary alcohols, preferably ethanol, other suitable solvents may include ethylene glycol. Preferably the solvent may be ethanol or ethylene glycol. The solvent may include, e.g., an acid, such as HCl.

**[0078]** For thermal decomposition, a solution of the metal oxide precursors, e.g., the metal chlorides, may have a concentration from 0.05 to 1.5 % w/v of each metal oxide precursor in the solvent, e.g., ethanol, based on the weight amount of metal oxide precursor per volume of solvent, namely a 1% w/v being 1 g of metal oxide precursor per 100 ml of solvent. In particular the concentration of each metal oxide precursor may be from 0.1 to 1.25 % w/v.

**[0079]** For electrodeposition a solution of the metal oxide precursor, e.g., a metal chloride, may have a concentration from 0.01 to 2 M, of each metal oxide precursor in the solvent, e.g., ethylene glycol, in particular from 0.05 to 1.5 M, more in particular from 0.1 to 1.2 M.

**[0080]** The surface treatment may include further steps prior to or after forming a mixed metal oxide on the surface of the titanium alloy.

**[0081]** For instance, the surface of the titanium alloy may be roughened and/or cleaned prior to forming the mixed metal oxide onto the surface of the titanium alloy. In several embodiments, the titanium alloy surface may be roughened and subsequently cleaned. Such steps may improve, e.g., electrodeposition and the adhesion of the metal oxide precursor onto the surface of the titanium alloy and subsequently improve the formation of the mixed metal oxide upon the thermal decomposition.

**[0082]** Accordingly, in several embodiments, a method described herein, prior to applying the surface treatment of step b), comprises:

- i) roughing the surface to be treated; and
- ii) cleaning the roughened surface.

**[0083]** The surface of the titanium alloy may be roughened by methods known in the art such as sanding with a sand paper or sandblasting. The surface of the titanium alloy may be cleaned by methods known in the art, such as using water with detergents and/or an appropriate solvent, e.g., ethanol, acetone. After cleaning the surface may be dried, e.g., using an air dryer.

**[0084]** The instant invention further relates to titanium alloy having a MMO on its surface (also referred to herein as MMO modified titanium alloy). In particular, the MMO modified titanium alloy may be obtained or obtainable by a process as described herein. The MMO modified titanium alloy comprises a mixed metal oxide on the surface of the titanium alloy, accordingly the mixed metal oxide present on the surface of the titanium alloy may be referred to or regarded as a mixed metal oxide coating.

**[0085]** The considerations and preferred embodiments regarding the MMO defined above in the context of the method of preparation of a titanium alloy with a MMO on its surface, also apply to a titanium alloy having a MMO on its surface as such, in particular with respect to the mixed metal oxide.

**[0086]** The nature of the metal oxides, that are present in the surface of the MMO modified titanium alloy, including, for instance, the absence of titanium oxide or the presence of MMO on the surface of the titanium alloy, may be established as described above, by using known techniques such as XRD and XPS. In particular embodiments, a MMO modified titanium alloy as described herein does not contain titanium oxide on its surface as evidenced, e.g., by XRD and/or XPS. These techniques may be also used to establish the amount of metal oxides which are present on the surface of the MMO modified titanium alloy. What has been described above for the method of preparation, in particular with respect to the amount and/or thickness of the metal oxides including titanium oxide and MMO present on the surface of the titanium alloy obtained by or obtainable by the method of preparation, also apply to the MMO modified titanium alloy as described herein.

**[0087]** The instant invention particularly relates to titanium alloy having a MMO on its surface, wherein the mixed metal oxide is selected from a tin-antimony oxide, tin-antimony-lead oxide, a nickel-cobalt oxide, and/or a precious metal oxide. Such titanium alloy having a MMO on its surface may particularly be obtainable by or obtained by a method as described herein.

**[0088]** The present invention also relates to a shaped part destined to be subjected to mechanical stress, comprising a titanium alloy having a MMO on its surface as described herein, in particular obtained by or obtainable by a method as described herein. Shaped parts comprising a titanium alloy having a MMO on its surface may be formed from the MMO modified titanium alloy or may be formed from a titanium alloy and may be subsequently subjected to a surface treatment as described herein to form a MMO on the surface of the shaped part. Appropriate shaped parts may include parts such as ship and boat hulls, a propeller, a shaft, a rudder, other aquatic or marine equipment such as heat exchangers, drilling platforms, dry dock equipment, oil production rigs, aquaculture equipment and netting and pipes, which are typically immersed in water, or have water running through them.

**[0089]** It has been found that a titanium alloy with a modified surface as described herein requires the application of a current at a relatively low voltage, of under  $3 V_{Ag/AgCl}$ , to achieve the anti-biofouling properties when immersed in, e.g., an aqueous environment such as seawater. This advantageously requires a reduced energy consumption, and

prevents damage of titanium alloys sensitive to high voltages. In particular, working at such potentials allows working below the breakdown potential of the passivation layer of titanium alloys which for grade 5 titanium alloy has been found to be around  $3 V_{\text{Ag/AgCl}}$ .

**[0090]** Accordingly, the present invention also relates to a method for protecting a titanium alloy having a MMO on its surface from biofouling, which comprises the steps of:

- i) immersing the titanium alloy having a MMO on its surface as described herein (in particular obtained or obtainable by a method of preparing a titanium alloy with MMO on its surface as described herein), in an aqueous medium, in particular in seawater; and
- ii) applying a voltage under  $3 V_{\text{Ag/AgCl}}$  to the surface such that said surface acts as an anode.

**[0091]** A method for protecting a titanium alloy may also comprise the steps of preparing a titanium alloy having a mixed metal oxide (MMO) on its surface as described above.

**[0092]** Accordingly, a method for protecting a titanium alloy may comprise:

- a) providing a titanium alloy comprising titanium oxide on its surface;
- b) applying a surface treatment to a surface of the titanium alloy, wherein the surface treatment includes forming a mixed metal oxide (MMO) on its surface, to provide a titanium alloy having a mixed metal oxide (MMO) on its surface and
- i) immersing the titanium alloy having a mixed metal oxide (MMO) on its surface in an aqueous medium, in particular in seawater;
- ii) applying a voltage under  $3 V_{\text{Ag/AgCl}}$  to the surface such that the surface of the titanium alloy having a MMO acts as an anode.

**[0093]** Immersing as used herein includes the partial or total immersion of the surface modified titanium alloy in the aqueous environment. Immersing may also refer to the contact of the inner surface of a tubing or a pipe with an aqueous medium flowing through it.

**[0094]** MMO modified titanium alloys as described herein are chiefly destined to be used in aqueous environments, and seawater in particular. Accordingly, in a method as described herein immersing in the aqueous environment may generally take place during the purposed use of the titanium alloy. The aqueous environment may preferably seawater. Different seawaters may have different properties and some may be more propense to biofouling than other, due to changes in temperature, in sea life and in types and concentrations of solutes. As a mode of example, the seawater may be the Mediterranean Sea, the Atlantic Ocean, the Pacific Ocean, the Nordic Sea, etc. Generally, titanium alloy surfaces immersed in waters of the Mediterranean Sea may be more propense to biofouling than if immersed in other seawaters. In several embodiments, the titanium alloy the having a mixed metal oxide (MMO) on its surface may be immersed in waters of the Mediterranean Sea.

**[0095]** Applying a voltage under  $3 V_{\text{Ag/AgCl}}$  may be performed by methods known in the art. As a person skilled in the art will understand a voltage under  $3 V_{\text{Ag/AgCl}}$ , means a voltage which is below 3V with respect to a Ag/AgCl reference electrode, that contacts the aqueous medium in which the surface onto which the voltage is applied is immersed.

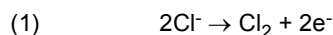
**[0096]** In particular, applying the voltage to the surface may be achieved by connecting the surface to voltage source in any appropriate means known in the art.

**[0097]** A voltage under  $3 V_{\text{Ag/AgCl}}$  may particularly be from 0.5 to  $2.75 V_{\text{Ag/AgCl}}$ , in particular from 0.75 to  $2 V_{\text{Ag/AgCl}}$ , more in particular from 1 to  $1.6 V_{\text{Ag/AgCl}}$ , yet more in particular from 1.1 to  $1.5 V_{\text{Ag/AgCl}}$ , and yet more in particular from 1.2 to  $1.4 V_{\text{Ag/AgCl}}$ .

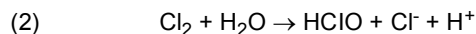
**[0098]** It has been found that working at such voltages in an aqueous environment such as seawater as described herein, a current density can be generated that is sufficient to provide an anti-biofouling effect. Accordingly, a method as described herein allows to achieve anti-biofouling whilst preventing damage to the titanium alloy, which typically occurs at voltages above  $3 V_{\text{Ag/AgCl}}$ .

**[0099]** The voltage is applied such that the surface of the titanium alloy having a MMO acts as an anode. This mode of operation may be also referred to as anodic polarization, in the present case, of the titanium alloy surface having a MMO. This allows the oxidation of species (e.g.,  $\text{Cl}^-$ ,  $\text{OH}^-$  and  $\text{H}_2\text{O}$ ) present in the aqueous medium, in particular seawater, to generate oxidated species (e.g.,  $\text{Cl}_2$  and/or  $\text{O}_2$ ) which prevent, reduce or remove biofouling.

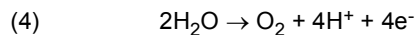
**[0100]** The oxidation of chloride to chlorine taking place in the anode is the following:



**[0101]** Chlorine may further evolve to hypochlorite, which is very reactive contributes to the antifouling effect:



**[0102]** Other reactions taking place in the anode may include the oxidation of water:



**[0103]** Since the oxidized species are generated from species originally found in the aqueous medium as such, the products derived from the reactivity of such species against the biological material responsible of the biofouling are not harmful to the environment. Accordingly, such methods of protection of the titanium surface having MMO against biofouling, advantageously do not generate waste products which are harmful to the environment.

**[0104]** Furthermore, it has been found that the application of voltages under  $3 V_{\text{Ag/AgCl}}$  on a titanium alloy surface having MMO as described herein, allows the flow of a current with sufficient density to prevent, reduce or remove biofouling and at the same time avoid the degradation of the MMO and ultimately the degradation of the titanium alloy.

**[0105]** It has been particularly found that at voltages as described herein (under  $3 V_{\text{Ag/AgCl}}$ ) the antibiofouling properties of the titanium alloy surface having MMO are obtained with current densities of  $5 \text{ mA/m}^2$  and above, in particular of at least  $10 \text{ mA/m}^2$ . The higher the density of the current density generally the higher the antibiofouling effect. However, the higher the current density the higher the power consumption and the shorter the active life span of titanium alloy surface as anode, because the MMO on the surface tend to degrade with time, and the properties conferred to the surface by the MMO are lost. Accordingly, being able to obtain antibiofouling effects at such low current densities, it is highly advantageous for structures which are destined to be immersed for long periods of time, e.g., for several months or several years, as it allows reducing maintenance costs and extending the life span of the titanium alloy surface as an active anode.

**[0106]** As a mode of example, a range of suitable current densities to achieve the antibiofouling effect may be from  $5 \text{ mA/m}^2$  to  $1 \text{ A/m}^2$  and, in particular from  $7 \text{ mA/m}^2$  to  $500 \text{ mA/m}^2$ , more in particular from  $10 \text{ mA/m}^2$  to  $250 \text{ mA/m}^2$ , yet more in particular of  $15 \text{ mA/m}^2$  to  $150 \text{ mA/m}^2$ , and yet more in particular from  $20 \text{ mA/m}^2$  to  $100 \text{ mA/m}^2$ .

**[0107]** The voltage may be applied permanently or in pulses, it may be preferred to apply the voltage in pulses. A pulse may be defined as a period of time for which a voltage is applied. Permanent application of voltages may be of interest for surface modified titanium alloys conforming structures which are permanently immersed in an aqueous environment, e.g., for preventing, reducing or removing biofouling. The use of pulses may be appropriate for reducing the energy consumption and ultimately reducing the costs of the protection of the titanium alloy surface. Pulses may also be appropriate, e.g., for executing a specific cleaning operation, to facilitate the removal of biofouling, including, e.g., constant voltage pulses, alternate pulses or periodic pulses. In several embodiments, the pulses may be applied by alternating anodic application of the pulses, so that the titanium alloy having MMO on the surface acts as anode, and cathodic application, so that the titanium alloy having MMO on the surface acts as cathode. Alternating anodic and cathodic application of the pulses may also be preferred to reduce the consumption of energy. As a mode of example, the application of pulses as described in the European patent application No. 22382464 may also applied to a method as described herein.

**[0108]** Such voltages can be applied by methods known in the art, by providing the titanium alloy having MMO on its surface with appropriate means for voltage application and anodic polarization in particular. In a typical arrangement, the titanium alloy having MMO on its surface will act as an anode and will be connected to a reference electrode (typically a  $\text{Ag/AgCl}$  reference electrode) and to a metal acting as a cathode, which are also immersed in the aqueous environment, by means known in the art. Said electrodes, may be connected to a power source, e.g., a battery or a generator such as fuel powered motor for the generation of electricity. As a mode of example, the application of voltages as described in the European patent application No. 22382464 may also applied to a method as described herein. In particular, the titanium alloy having a MMO on its surface may be divided in two electrically isolated areas, by which one area may be anodically polarized and the other area may be cathodically polarized.

**[0109]** The active life span of a titanium alloy having MMO on its surface acting as anode, will vary depending on the amount of MMO present on the surface of the titanium alloy, the thickness of the MMO layer, the actual working conditions and the aqueous environment in which it is immersed. As a mode of example, the active life span of a titanium alloy having MMO on its surface acting as anode immersed in seawater, may be of up to 25 years, e.g., from 6 months to 20 years, in particular from 1 year to 15 years.

**[0110]** The high conductivity due to the presence of mixed metal oxides replacing the titanium oxides originally present on the titanium alloy surface, facilitates the flow of electrons through the surface of the titanium alloy, generated during oxidation reactions in the electrolyte upon the application of a current.

**[0111]** In this text, the term "comprises" and its derivations (such as "comprising", etc.) should not be understood in

an excluding sense, that is, these terms should not be interpreted as excluding the possibility that what is described and defined may include further elements, steps, etc.

[0112] The invention is obviously not limited to the specific embodiment(s) described herein, but also encompasses any variations that may be considered by any person skilled in the art (for example, as regards the choice of materials, dimensions, components, configuration, etc.), within the general scope of the invention as defined in the claims.

[0113] In the following, the invention will be further illustrated by means of examples. The examples should in no case be interpreted as limiting the scope of the invention, but only as an illustration of the invention.

## EXAMPLES

[0114] Anodic polarization of untreated grade 5 titanium alloy under conditions for antifouling properties useful in pure titanium:

A propeller of untreated grade 5 titanium alloy was subjected to anodic polarization under conditions established to be sufficient for grade 2 titanium alloy to generate chlorine in sea water, as described in the European patent application No. 22382464.

[0115] The propeller was immersed in seawater and an anodic potential of  $7 V_{Ag/AgCl}$  was applied to the propeller.

[0116] Under water the breakage of the grade 5 titanium alloy propeller was immediately observed as it is apparent from the pictures of Figure 1A and B.

[0117] Upon removal of the propeller from the aqueous environment the damage on the propeller was clearly apparent with clear signs of breakage of the titanium alloy Figure 1C.

[0118] Thus, it could be established that conditions suitable for providing pure titanium with antifouling properties, are unsuited for titanium alloys such as grade 5 titanium alloy.

### Example 1: grade 5 titanium alloy

#### *Preparation of MMO modified grade 5 titanium alloy*

[0119] Three samples of commercially available grade 5 titanium alloy sheets of a thickness of 2 mm with a surface area of 6x5 cm were selected. The presence of titanium oxide on the surface of the grade 5 titanium alloy was could be established by XRD.

1. Both faces of each sample were roughened with 320 grit sandpaper until a homogeneous surface was achieved.
2. The samples were cleaned with soap and water, distilled water and ethanol, then dried with a dryer.
3. A surface treatment was applied on to the surface of the samples by placing the samples inside a beaker and adding onto them approximately 1.5 mL of a solution of 1 % w/v  $SnCl_4 \cdot 5H_2O$  and 0.1% w/v  $SbCl_3$  in HCl with ethanol.
4. They samples were dried by being left to dry in the air (variable time and incomplete drying on many occasions) and placing them in an oven at 400°C for 10 minutes.
5. Steps 3 and 4 were repeated 18 additional times.
6. Step 3 was repeated and the samples were placed in an oven at 600°C for one hour to get a total of 20 deposition steps, to provide a surface modified grade 5 titanium alloy.

[0120] The properties of the surface modified grade 5 titanium alloy were analysed as follows.

#### *Gravimetric analysis*

[0121] Before and after performing the surface treatment, the samples were weighed to obtain the effect on the mass of the samples from the surface treatment. Table 1 shows the mass before treatment,  $M_0$ , after, M and the difference of both values.

Table 1

Sample	$M_0$ (g)	M (g)	$\Delta M$ (mg)
1	27.4391	27.4595	20.4
2	27.3648	27.3861	21.3
3	27.4613	27.4877	26.4

**[0122]** As can be derived from table 3 the surface treatment resulted in an increase of the mass of the sample due to the thermal decomposition of the metal oxide precursor (metal chloride) deposited onto the surface of the titanium alloy into metal oxide.

#### 5 *Anodic polarization up to 6 V*

**[0123]** The surface modified grade 5 titanium alloy samples were subjected to an increasing anodic polarization up to  $6 V_{Ag/AgCl}$  using a potentiostat using a Nova 1.7 software, to test the resistance to corrosion of the surface modified grade 5 titanium alloy, by immersing in seawater the surface treated grade 5 titanium alloy samples as working electrodes, and grade 5 titanium alloy samples without a surface treatment as counter electrodes.

**[0124]** The test conditions used were the following:

- Cell: a volume of about 375 mL of seawater
- Maximum potential: 6 V
- Immersed area:  $20 \text{ cm}^2$  (i.e.,  $5 \times 4 \text{ cm}$ )
- Counter electrode: grade 5 titanium alloy without surface treatment
- Reference electrode: Ag / AgCl
- Cable color: Red (anode) and Black (cathode)
- Software: Nova 1.7
- Step: 0,005V
- Scan rate: 0.0001667 V/s

**[0125]** The breakdown potential of grade 5 titanium alloy, without any protection or coating, is known to be of approximately  $2.5 V_{Ag/AgCl}$ , much lower than the maximum potential reached during the test with the surface modified titanium alloy ( $6 V_{Ag/AgCl}$ ). With this test it was intended to verify if the surface treatment applied protected the surface from corrosion (pitting) when the potential was raised above said potential. It was also intended to verify how long it took before the metal oxide on the surface of the titanium alloy was lost and the consequences of the loss, on the surface having the base titanium alloy exposed.

**[0126]** The same test was executed using the test conditions with untreated grade 5 titanium alloy as working anode and using a potential of up to  $3 V_{Ag/AgCl}$ . The untreated grade 5 titanium used was the same as the samples used for MMO modification.

**[0127]** Figure 2A graphically represents the intensities (A) (left) and current densities ( $A/m^2$ ) (right) obtained in the test for MMO modified grade 5 titanium alloy, and Figure 2B shows the same graphs (left and right) for the comparative test for grade 5 titanium alloy without modification.

**[0128]** The curves obtained for the MMO modified grade 5 titanium alloy, show an intensity / density flat plateau, which is due to the potentiostat not registering currents above a certain value, resulting in said flat plateau. Accordingly, the graphs do not show the maximum intensities / densities reached.

**[0129]** In any case it can be clearly observed that the coating is positively affecting the amount of current that is mined through the surface, being both the intensity and the current density, several orders of magnitude higher for the MMO modified titanium alloy (of about 0.6 A and about  $300 A/m^2$  for a potential of about  $2.5 V_{Ag/AgCl}$ ) when compared to the untreated titanium alloy (of about 0.0002 A and  $0.04 A/m^2$  for a potential of  $2.5 V_{Ag/AgCl}$ ). The current intensities and densities recorded indicate that for the MMO modified titanium alloy, around  $1.6 V_{Ag/AgCl}$  a reaction occurs which has been identified as the generation of  $Cl_2$  from the seawater electrolyte. In stark contrast, for the non-modified titanium alloy, even though a small peak occurs at around  $1.6 V_{Ag/AgCl}$  the densities and intensities recorded are so minimal (of 0.0020 A and  $0.24 A/m^2$  that cannot be attributed to any significant reaction. Further, for the non-modified titanium alloy, at around  $2.5 V_{Ag/AgCl}$  an increase of intensity and density is recorded, and further can be seen that at around  $3 V_{Ag/AgCl}$  the intensity and density curves show a failure of the electrode, as can be identified by the backward loop being recorded. For the MMO modified titanium alloy, even though potential goes up to  $6 V_{Ag/AgCl}$ , no such loop is observed at around  $3 V_{Ag/AgCl}$ , which is indicative that the MMO modified titanium alloys are protected from such electrode failures at voltages of around  $3 V_{Ag/AgCl}$  in the electrolyte of most interest (namely seawater).

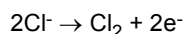
**[0130]** In Figure 3, both curves for the surface modified and the non-modified grade 5 titanium alloy, are shown superimposed for potential ranges below  $2.2 V_{Ag/AgCl}$  (in particular in ranges from 0.0 to  $1.2 V_{Ag/AgCl}$  in A), from  $1.2$  to  $1.8 V_{Ag/AgCl}$  in B), and from  $1.8$  to  $2.20 V_{Ag/AgCl}$  in C)). The curves show a similar initial growth, diverging noticeably from  $1 V_{Ag/AgCl}$ , and completely masking the intensity peak that occurs in grade 5 titanium alloy around  $1.5 V_{Ag/AgCl}$ . In particular, titanium alloy with MMO on its surface the recording of densities starts at  $0.0023 A/m^2$  and increases to  $0.168 A/m^2$ .

**[0131]** This is an indication that working at similar voltages, a titanium alloy with MMO on its surface as described herein displays a higher current intensities and densities at the potential of chlorine generation, which is indicative of

clearly sufficient amounts of chlorine generation for an anti-fouling effect, and at the same time no electrode failure is observed at potentials of around 3 V<sub>Ag/AgCl</sub>, which is indicative of the suitability of MMO modified titanium alloys for anti-fouling applications at voltages below 3 V<sub>Ag/AgCl</sub>.

#### 5 Estimation of Cl<sub>2</sub> generation:

[0132] Cl<sub>2</sub> generation may be accompanied by other oxidation reactions such as water oxidation as detailed above. However, an estimation of the amount of Cl<sub>2</sub> that is generation may be derived from the integral of the intensity curve, assuming a generation yield of 100% ( $\eta_{Cl} = 100\%$ ). With this assumption, the theoretical amount of chlorine generated can be derived from the number of electrons extracted from sea water. In this case, the load is related to the oxidation reaction of chloride to molecular chlorine:



[0133] The mass of chlorine generated can be determined without subtracting the uncoated intensity, by equation (1), where  $\eta_{Cl}$  is the yield of the generation, Q is the integral of the intensity curve of the MMO modified sample, F is the Faraday constant, and MW<sub>Cl<sub>2</sub></sub> is the molecular weight of Cl<sub>2</sub>.

$$m_{Cl_2} = \frac{Q}{2F} * MW_{Cl_2} \cdot \eta_{Cl}$$

equation (1)

[0134] On the first polarization curve, chlorine generated ( $m_{Cl_2}$ ) with a yield of 100% would be of 5.43 g.

[0135] Irrespective of the actual amount of chlorine generated the antibiofouling effect has been demonstrated in Example 3 below.

#### 30 Example 2: grade 2 titanium alloy

[0136] Three samples of commercially available grade 2 titanium alloy sheets of a thickness of 2mm with a surface area of 6x5 cm were selected.

[0137] Two of the samples were processed as described above for grade 5 titanium alloy, for the formation of MMO on the surface of the titanium alloy, and one sample was processed in the same way, subjecting int to a thermal treatment but without deposition steps, as a control sample.

[0138] The properties of the surface modified grade 5 titanium alloy were analysed as follows.

#### Gravimetric analysis

[0139] As described above for the grade 5 titanium alloy, before and after performing the surface treatment, the samples were weighed to obtain the effect on the mass of the samples from the surface treatment.

[0140] Table 2 shows the mass before treatment, M<sub>0</sub>, after, M and the difference of both values.

Table 2

Sample	M <sub>0</sub> (g)	M (g)	ΔM (mg)
1	27.4154	27.4288	13.4
2	25.7089	25.7211	12.2
3*	21.1542	21.1576	3.4
*control sample			

#### 55 X-Ray Diffraction (XRD) Characterization

[0141] In the control sample, without deposition steps and therefore without the formation of MMO on the surface of the grade 2 titanium, it can be observed that the main crystalline phases observed are titanium and titanium oxides, in

particular titanium (IV) oxide (TiO<sub>2</sub>) and in minor amounts titanium (II) oxide (TiO).

**[0142]** In the sample of MMO modified grade 2 titanium, in addition to the above indicated phases for the untreated grade 2 titanium, in addition the presence of SnO<sub>2</sub> can also be observed, as a consequence of the MMO modification.

#### 5 X-ray photoelectron spectroscopy (XPS)

**[0143]** The elemental composition of the MMO modified titanium was analysed by XPS.

Table 3 shows the elemental composition for both the control and the MMO modified samples.

Sample	Element						
	O	C	Sb	Sn	Ti	Fe	S
1	60.9	16.8	7.2	10	-	4.6	0.5
3*	57.5	20.5	0.9	5.6	11	3	1.6

**[0144]** It can be observed in the control sample that, having been placed in the oven simultaneously with the samples treated with coating, has suffered contamination, with the presence of Sb and Sn, although in a significantly higher concentration is present in the sample with the surface treatment for the formation of MMO.

Table 4 shows the energy peaks associated to the different elements, indicating the oxidation degree of the different elements:

Sample	Element					
	Sb 3d 5/2	Ti 2p	Sn 3d 5/2	Fe 2p	Fe 2p	S2p
1	530.4	-	486.5	711	709.44	169.61
3*	530.53	458.44	486.24	711	709.39	168.69

**[0145]** In the case of the Sb, taking into account that the most intense component, the 3d5/2 coincides with the oxygen peak, the 3d3/2 component has been used for the adjustment and knowing the relation of position (+9.3eV) and of the areas (1:1.5) that it has with respect to the peak 3d5/2 this has been calculated. In this way, the position of 530.5 eV has been obtained, which could correspond to Sb(III). In the case of Sn, its position indicates the presence of Sn(IV) and Ti would be as Ti(IV). In the case of Fe, it is also interfered with by the Sn2p3/2 component and in, in this case, the breakdown of components has been done, setting the most common positions for Fe(II) and Fe(III), 709.4 and 711 eV, respectively.

#### Anodic polarization up to 6 V

**[0146]** The surface modified grade 2 titanium samples were subjected to an increasing anodic polarization up to 6 V<sub>Ag/AgCl</sub> as described above for the MMO modified grade 5 samples, under the same conditions.

**[0147]** Figure 4 shows the overlap of the current density (A/m<sup>2</sup>) graphs obtained for the MMO modified grade 5 titanium alloy and the MMO modified grade 2 titanium alloy.

**[0148]** As in the curves obtained in example 1, the potentiostat does not register currents above certain value and the MMO modified grade 2 alloy also shows a flat plateau which does not correspond to the real intensities reached.

**[0149]** When comparing the curves obtained for both titanium alloys, the plateau in the case of grade 5 titanium alloy sample it is above the grade 2 titanium sample, due to the limitations of each measurement.

**[0150]** Nonetheless, when comparing the evolution of the two curves, it can be observed that they both show a very similar increase in current density up to around 1.7 V<sub>Ag/AgCl</sub>.

**[0151]** This demonstrates that not only a MMO modification can be performed on titanium alloys, but that this modification can be used to provide titanium alloys with sufficient conductivity and catalytic properties for chlorine generation to obtain an antifouling effect with anodized titanium alloys having MMO on its surface.

#### Example 3: protection of grade 5 titanium alloy from biofouling

**[0152]** A grade 5 titanium alloy sheet having all its surfaces modified with a MMO formed as described above for example 1, was immersed in the Mediterranean Sea by attaching the sheet to a boat through a plastic chord. Upon

immersion constant anodic polarization at  $1.7 V_{Ag/AgCl}$ , was applied to the surface of the grade 5 titanium alloy. After 6 months of having the titanium alloy sheet and its plastic chord immersed in water it could be clearly observed, as shown in Figure 5, that biofouling was prevented on the titanium alloy sheet whilst it was found to be abundant on the plastic chord. Furthermore, the titanium alloy did not show any signs of corrosion.

[0153] With this example it was clearly demonstrated that the application of an anodic voltage of under  $3 V_{Ag/AgCl}$  on a MMO modified titanium alloy surface, the titanium alloy was protected from biofouling without suffering corrosion effects.

## Claims

1. A method for preparing a titanium alloy having a mixed metal oxide (MMO) on its surface, comprising:
  - a) providing a titanium alloy comprising titanium oxide on its surface; and
  - b) applying a surface treatment to a surface of the titanium alloy, wherein the surface treatment comprises forming a MMO on the surface of the titanium alloy.
2. The method according to claim 1, wherein the titanium alloy comprises from 70 to 98.5 wt.% of titanium, in particular further comprises from 2 to 10 wt.% of aluminium and/or from 1 to 10 wt.% of vanadium, the wt.% based on the total weight of the titanium alloy, more in particular, the titanium alloy is selected from grade 5 titanium alloy, grade 6 titanium alloy, grade 9 titanium alloy, grade 18 titanium alloy, grade 19 titanium alloy, grade 20 titanium alloy, and grade 21 titanium alloy, and more in particular is a grade 5 titanium alloy.
3. The method according to claim 1 or 2, wherein the MMO comprises two or more metals selected from tin, antimony, lead, nickel, cobalt, and precious metals, wherein a precious metal is preferably selected from iridium and ruthenium, and in particular, the MMO is selected from tin-antimony oxide, tin-antimony-lead oxide, nickel-cobalt oxide, and/or precious metal oxides, wherein the precious metal is preferably selected from iridium and ruthenium.
4. The method according to any one of the preceding claims, where in the surface treatment of step b) comprises forming the MMO using a metal oxide precursor.
5. The method according to claim 4, wherein the surface treatment of step b) is performed by thermal decomposition, in particular wherein the thermal decomposition comprises the steps of:
  - b1) immersing the titanium alloy comprising titanium oxide on its surface of step a) in a solution of two or more metal oxide precursors in a solvent, to provide a titanium alloy treated with the two or more metal oxide precursors;
  - b2) drying the titanium alloy treated with the two or more metal oxide precursors of step (b1);
  - b3) repeating steps (b1) to (b2) from 2 to 49 times; and,
  - b4) repeating step (b1) and heating the sample to a temperature from 500 to 700 °C in particular from 550 to 650 °C for from 15 minutes to 3 hours, in particular from 30 minutes to 2 hours and more in particular from 45 minutes to 1.5 hours, thereby forming a mixed metal oxide onto the surface of the titanium alloy.
6. The method according to claim 4, wherein the surface treatment of step b) is performed by electrodeposition, in particular wherein the electrodeposition comprises:
  - b1) connecting the titanium alloy having titanium oxide on its surface to an activated titanium anode
  - b2) immersing the titanium alloy having titanium oxide on its surface connected to the activated titanium anode in a solution of two or more metal oxide precursors in a solvent,
  - b3) cathodically polarizing the titanium alloy having titanium oxide on its surface by applying a current, in particular a current of from 100 to 800 mA, more in particular from 150 to 600 mA, and more in particular from 200 to 500 mA, thereby forming the mixed metal oxide onto the surface of the titanium alloy.
7. The method according to any one of claims 4 to 6, wherein the two or more metal oxide precursors are selected from metal salts, preferably from metal halides, and preferably is a mixture of two or more metal chlorides and, in particular, the two or more metal oxide precursors are selected from tin chloride, antimony chloride, lead chloride, nickel chloride, cobalt chloride, and/or precious metal chloride.
8. The method according to any one of claims 4 to 7 wherein the solvent of the solution of the metal oxide precursor



is selected from C1 to C4 primary alcohols and from ethylene glycols, preferably the solvent is ethanol or ethylene glycol.

- 5      **9.** The method according to any one of the preceding claims, wherein prior to applying the surface treatment of step b) the method comprises:

- i) roughing the surface to be treated; and
- ii) cleaning the roughened surface.

- 10      **10.** A titanium alloy having a mixed metal oxide (MMO) on its surface, wherein the MMO preferably comprises two or more metals selected from tin, antimony, lead, nickel, cobalt, and precious metals, wherein a precious metal is preferably selected from iridium and ruthenium, and in particular, the MMO is selected from tin-antimony oxide, tin-antimony-lead oxide, nickel-cobalt oxide, and/or precious metal oxides, wherein the precious metal is preferably selected from iridium and ruthenium.

- 15      **11.** A titanium alloy having a mixed metal oxide (MMO) on its surface, obtained by or obtainable by the method of any one of claims 1 to 9.

- 20      **12.** A method for protecting a titanium alloy having a MMO on its surface of claim 10 or 11 from bio-fouling, comprising the steps of:

- i) immersing the titanium alloy having a MMO on its surface in an aqueous medium, in particular in seawater; and
- ii) applying a voltage under  $3 V_{Ag/AgCl}$ , to the surface of the titanium alloy having a MMO, such that said surface acts as an anode, in particular the voltage is from 0.5 to  $2.75 V_{Ag/AgCl}$ , more in particular from 0.75 to  $2 V_{Ag/AgCl}$ , more in particular from 1 to  $1.6 V_{Ag/AgCl}$ , yet more in particular from 1.1 to  $1.5 V_{Ag/AgCl}$ , and yet more in particular from 1.2 to  $1.4 V_{Ag/AgCl}$ .

- 30      **13.** Shaped part destined to be subjected to mechanical stress, comprising a titanium alloy having a MMO on its surface of claim 10 or 11.

FIGURE 1

A)



B)



C)

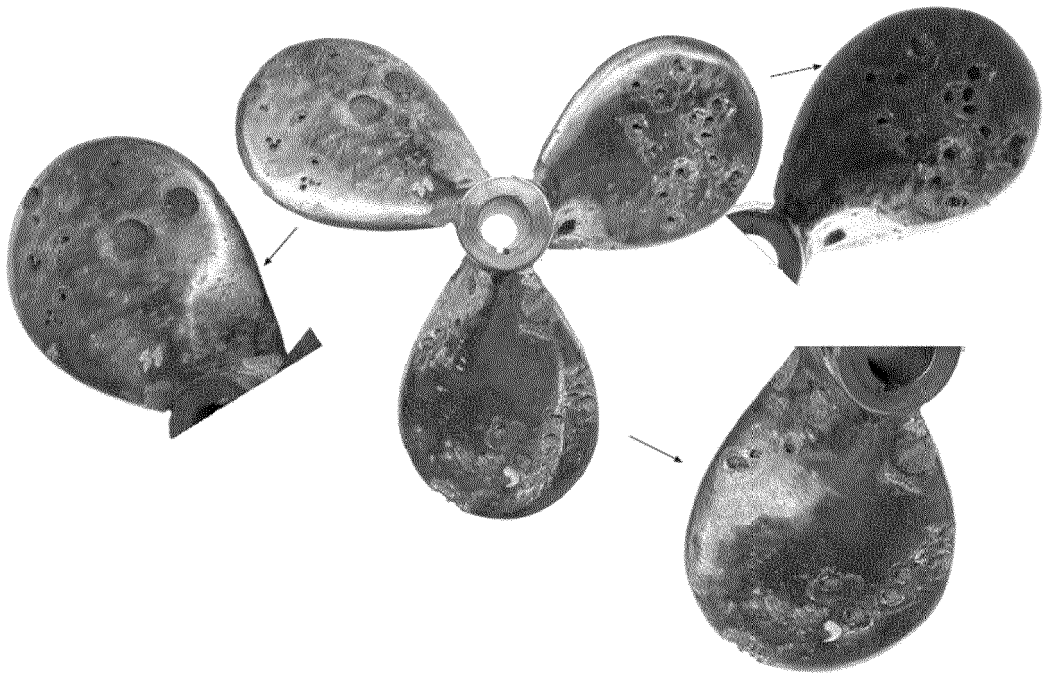


FIGURE 2

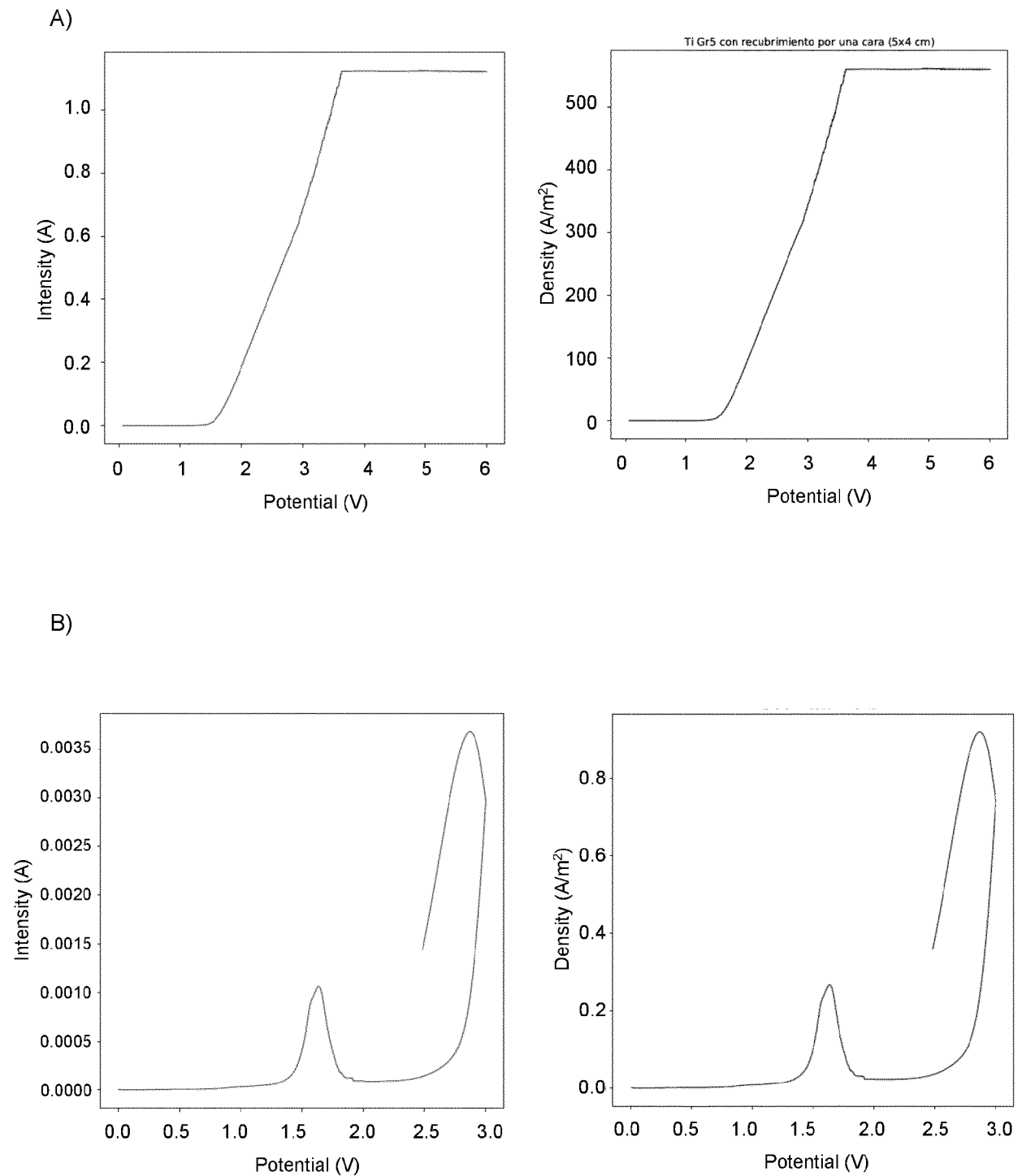
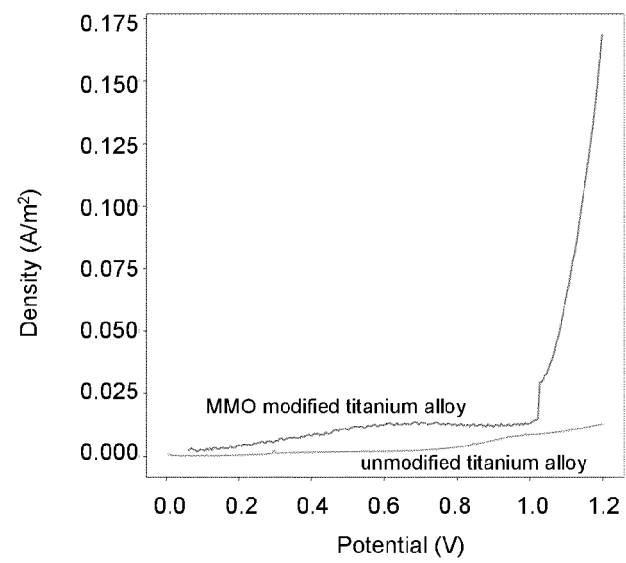
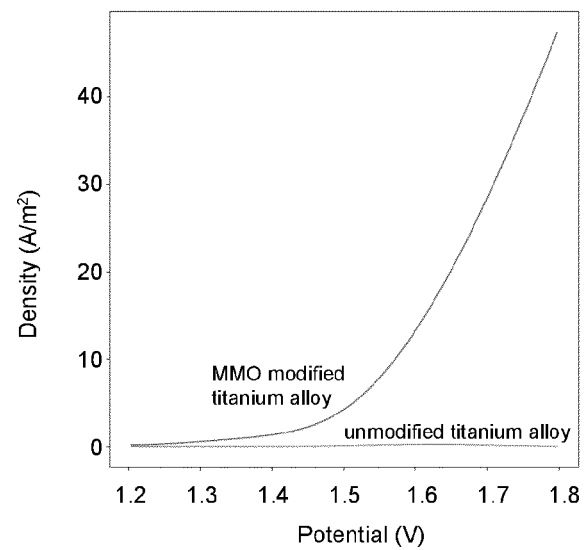


FIGURE 3

A)



B)



C)

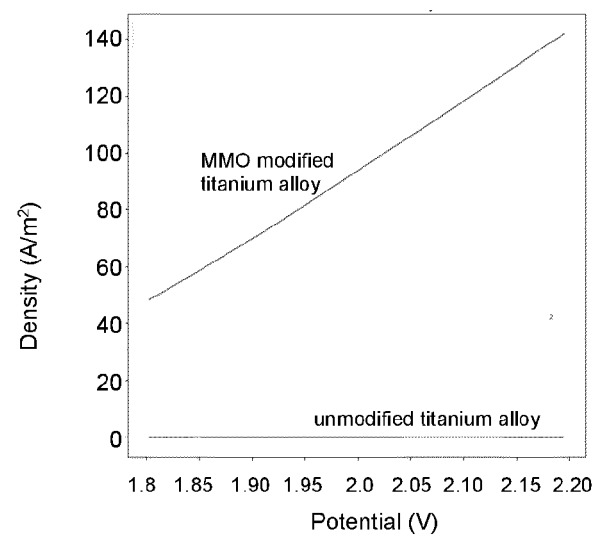


FIGURE 4

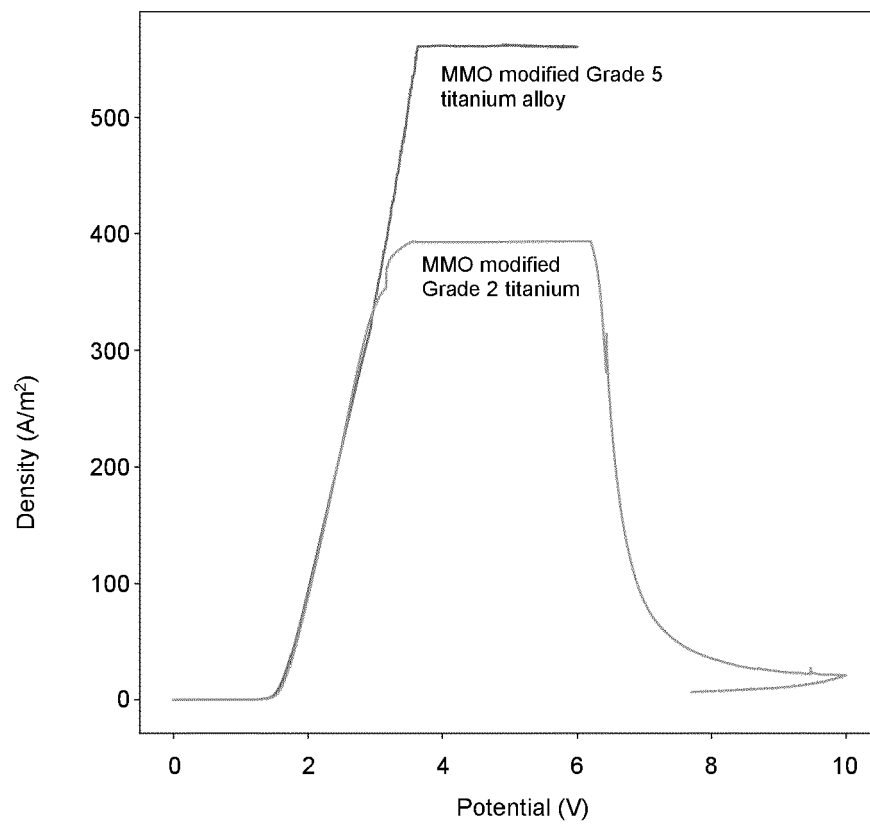
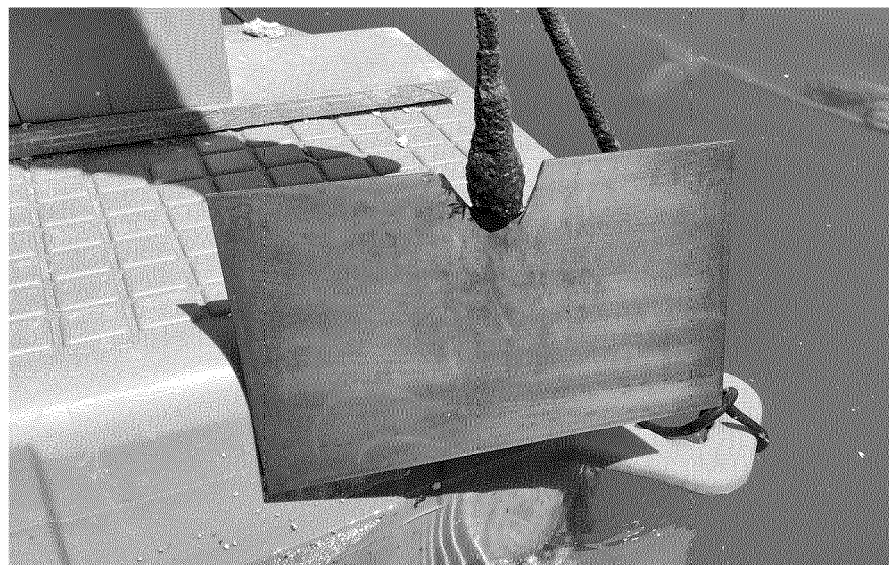


FIGURE 5





## EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims			
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CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	



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<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  .....  &amp; : member of the same patent family, corresponding document</p>			



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**CLAIMS INCURRING FEES**

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

**LACK OF UNITY OF INVENTION**

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

**see sheet B**

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☒ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

**10–12**

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



**LACK OF UNITY OF INVENTION  
SHEET B**

Application Number

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The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

**1. claims: 2, 3, 5 (completely); 1, 4, 7-11, 13 (partially)**

A method for preparing a titanium alloy having a mixed metal oxide (MMO) on its surface by thermal decomposition and a titanium alloy having a mixed metal oxide (MMO) on its surface.

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**2. claims: 6 (completely); 1, 4, 7-9, 11, 13 (partially)**

A method for preparing a titanium alloy having a mixed metal oxide (MMO) on its surface by electrodeposition and a titanium alloy having a mixed metal oxide (MMO) on its surface.

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**3. claims: 12 (completely); 10, 11 (partially)**

A method for protecting a titanium alloy having a MMO on its surface from bio-fouling.

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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