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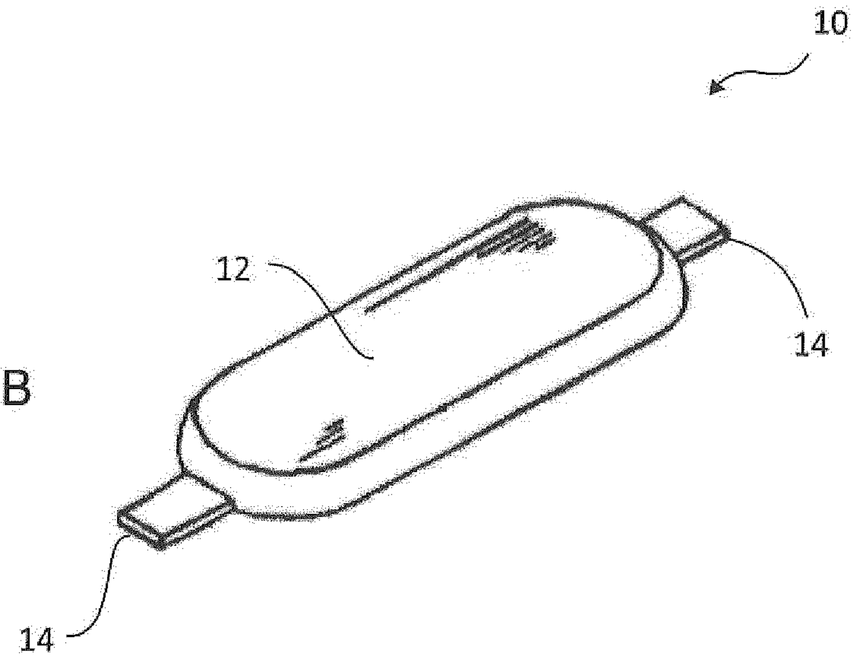
(54) ALLOY FOR USE IN A SACRIFICIAL ANODE AND A SACTIFICIAL ANODE

(57) The present invention relates to an aluminium-based alloy for use in a sacrificial anode and a sacrificial anode produced from the aluminium-based alloy.

The aluminium-based alloy comprises:
maximum 0.5% by weight of zinc,
maximum 0.04% by weight of indium,
maximum 0.1% by weight of gallium,
maximum 0.08% by weight of iron,
maximum 0.003% by weight of copper,
elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
balance aluminium.

The alloy has a high electrochemical efficiency and a low potential and provides good properties in respect of cathodic protection.

FIG. 1B



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Description

[0001] The present invention relates to an aluminium-based alloy for use in a sacrificial anode and a sacrificial anode produced from the aluminium-based alloy.

BACKGROUND ART

[0002] Cathodic protection using sacrificial anodes is a well-known technique within a number of areas including ships, vessels and offshore constructions, e.g. oil exploitation rigs.

[0003] The electrochemical process taking place is generally along the following scheme for a ferrous material:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

[0004] In most environments, the hydroxide ions and ferrous ions combine to form ferrous hydroxide, also known as rust:

$$F_e^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

[0005] It is desired to prevent or at least reduce the deterioration of the ferrous material, as this is the main structural material of the construction in question. Therefore, a sacrificial metal ranking lower in the electrochemical scheme, and therefore being more prone to the electrochemical reaction, is placed in electrical connection with the main construction and protects this main construction from deterioration. The most often used anode materials are aluminium or zinc or alloys comprising aluminium or zinc as the main component, but other materials may be used as alternatives to zinc and aluminium, such as magnesium as well as alloys containing magnesium.

[0006] Relevant areas of deployment are numerous; however, constructions in operation in seawater are in particular vulnerable to corrosion and will almost always be protected from such corrosion by means of cathodic protection using sacrificial anodes. Ships, vessels and offshore oil exploitation constructions are well-known examples of such.

[0007] The sacrificial anodes should be of a type suitable to the environment of operation, i.e. taking into consideration the chemical composition of the environment and also the temperature. Furthermore, the size of the anode(s) as well as their mutual positioning are relevant to consider in order to provide a satisfactory protection.

[0008] Many offshore oil exploitation constructions, pipelines or other equipment are from their very first installation provided with a cathodic protection system using sacrificial anodes, and most often the dimensioning of the anodes is designed for the design life time of the oil exploitation construction, meaning that no further exchange of the sacrificial anodes is foreseen. The oil exploitation constructions, pipelines or other equipment are however in many cases kept in operation well beyond the initial design life time, meaning that the cathodic protection obtained through the sacrificial anodes will disappear when the anodes are consumed after a certain time. For this situation, there is a need for arranging the anodes of the offshore oil exploitation construction, pipelines or other equipment with new functional anodes to ensure the cathodic protection for a further life extension of the oil exploitation construction, pipelines or other equipment. Even when erecting new structures such as the ones defined above, there is likewise the need for providing these new structures with cathodic protection.

[0009] There are a number of ways of ensuring the cathodic protection of the construction. Normally the anodes are mounted directly on the construction with a mutual distance, ensuring the most efficient protection according to the design criteria as mentioned above. Another way of ensuring the correct function is by placing the anodes remotely from the construction to be protected and connecting each anode electrically to the designed connection position of the construction, pipelines or other equipment.

[0010] When arranging anodes to an offshore construction, pipelines or other equipment the remote positioning of the anodes is often the most effective way of doing this and therefore the preferred way of ensuring the continued cathodic protection.

[0011] It is known in the art to provide an anode construction for the purpose of arranging anodes to an offshore construction, pipelines or other equipment where the previously known construction comprises a framework with the anodes placed in mutually distanced positions to ensure the proper functioning of the cathodic protection. The anodes are connected to suitable connection points of the construction to be protected by means of suitable wiring. Such previously known anode construction is relatively bulky and therefore difficult to transport from the production site to the actual operational site.

[0012] The alloy compositions described herein are designed to have high operating efficiencies to make the alloy as cost-effective as possible, high current output to enable high and long-lasting performance for a given weight of anode (energy density), and optimized operating potential, which will vary depending on the application. An important added benefit is that in the alloys of this invention the content of zinc is very low. The most used commercial aluminium anode alloy is aluminium-5% zinc-0.02% indium. This alloy is specified in MIL-DTL-24779 and has proven to be very effective in worldwide climates to protect a variety of materials including iron, steel, and aluminium piers, ships, off-shore rigs, and bridges among other applications. It is approximately 90% efficient, which is lower than pure zinc, which is about 98% efficient, but much higher than magnesium, which is about 60% efficient.

[0013] Unfortunately, zinc is an aquatic toxin and contains residual cadmium from the mining process. Zinc is known to be toxic for marine plants and animals. Consequently, there is a raising demand for alloys in which the content of zinc is very low, but which still provide the same outstanding efficiency, current output and energy density. The alloy of this invention has the potential to replace the aluminium-zinc-indium alloy for use as described above. Moreover, zinc is also more expensive than aluminium. Thus, replacing the amount of zinc in an alloy with aluminium, reduces the cost of producing the alloy.

DISCLOSURE OF THE INVENTION

[0014] An object of the present invention is to provide an alloy for sacrificial anodes which is environmental friendly and can be produced in a cost-effective manner.

[0015] A further object is to provide a sacrificial anode based on aluminium and with a very low amount of zinc, which provides good properties in respect of cathodic protection of more noble metals.

[0016] Consequently, the present invention relates to an aluminium-based alloy for use in a sacrificial anode, which alloy comprises:

maximum 0.5 %byweight of zinc,
maximum 0.04% byweight of indium,
maximum 0.1% by weight of gallium,
maximum 0.08% byweight of iron,
maximum 0.003% by weight of copper,
elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
balance aluminium.

[0017] The term "balance" indicates that aluminium constitutes the amount of the alloy which is required to reach 100% by weight, e.g. if the combined amount of zinc, indium, gallium, iron, copper, and optional impurities constitutes 0.5% byweight, the amount of aluminium constitutes 99.5% by weight.

[0018] The term "maximum" indicates that the specified percentage is the maximum content of the metal in the alloy.

[0019] The alloy may also comprise elements in form of impurities in an amount of maximum 0.02% by weight of each element. The impurities may e.g. be constituted by magnesium, mangan, silicium, chrome, cadmium, tin, boron and other elements. The impurities may originate from the aluminium grade used.

[0020] It has surprisingly appeared that the high amount of aluminium combined with low amounts of zinc, indium, gallium, iron, and copper provides an alloy for a sacrificial anode with good properties and which is significantly lesser harmful to the environment that sacrificial anodes comprising high amounts of zinc.

[0021] In an embodiment, the aluminium-based alloy comprises:

between 0.01 - 0.5% by weight of zinc,
between 0.01 - 0.04% by weight of indium,
between 0.02 - 0.1% by weight of gallium,
between 0.01 - 0.08% by weight of iron,
between 0.0005 - 0.003% by weight of copper,
elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
balance aluminium.

[0022] Although the amount of impurities present in the alloy may be larger than the amount of some of the individual elements: zinc, indium, gallium, iron, and copper, the lower presence of these metals, however, appears to improve the electrochemical properties of the alloy.

[0023] The aluminium in the aluminium-based alloy generally has a high purity, and in an embodiment the aluminium has a purity of at least 99,0% by weight.

[0024] In an embodiment of the aluminium-based alloy according to the invention, the aluminium has a purity of at least 99,5% by weight.

[0025] In the aluminium-based alloy according to the invention, the aluminium may have purities in the ranges 99.00 to 99.99% byweight, preferably in the ranges 99.50 to 99.99% by weight, such as purities in the ranges 99.90 to 99.99 % by weight.

[0026] The aluminium-based alloy according to the invention has an excellent electrochemical efficiency, and in an embodiment the aluminium-based alloy has an electrochemical efficiency above 1500 Ah/kg, preferably above 2000 Ah/kg, such as above 2500 Ah/kg, when tested according to the DNV GL standards, such as DNV RP B401.

[0027] Moreover, the aluminium-based alloy according to the invention has low potential (potential vs. Ag/AgCl), and in an embodiment the potential is even lower than -800mV, such as lower than -1000mV. Thus, the aluminium-based alloy according to the invention is able to provide a very good cathodic protection to more noble metals, e.g. steel.

[0028] The invention also relates to the use of an aluminium-based alloy in a sacrificial anode for protecting metallic constructions in a humid and marine environment, said aluminium-based alloy comprising:

maximum 0.5% by weight of zinc,
maximum 0.04% by weight of indium,
maximum 0.1% by weight of gallium,
maximum 0.08% by weight of iron,
maximum 0.003% by weight of copper,
elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
balance aluminium.

[0029] According to the use of the aluminium-based alloy according to the invention, the aluminium may have purities in the ranges 99.00 to 99.99% by weight, preferably purities in the ranges 99.50 to 99.99% byweight, such as a purity in the ranges 99.90 to 99.99% by weight.

[0030] The use according to the invention provides sacrificial anodes with an excellent electrochemical efficiency, and in an embodiment the anodes with the aluminium- based alloy has an electrochemical efficiency above 1500 Ah/kg, preferably above 2000 Ah/kg, such as above 2500 Ah/kg, when tested according to the DNV GL standards such as DNV RP B401.

[0031] Moreover, the use according to the invention also provides sacrificial anodes with low potential (potential vs. Ag/AgCl), and in an embodiment the potential is even lower than -800mV, such as lower than -1000mV. Thus, use of the aluminium-based alloy according to the invention provides sacrificial anodes with very good cathodic protection to more noble metals, e.g. steel.

[0032] The invention further relates to a sacrificial anode for protecting metallic constructions in a humid and marine environment, said sacrificial anode comprising an aluminium-based alloy comprising:

maximum 0.5% by weight of zinc,
maximum 0.04% by weight of indium,
maximum 0.1% by weight of gallium,
maximum 0.08% by weight of iron,
maximum 0.003% by weight of copper,
elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
balance aluminium.

[0033] The aluminium in the aluminium-based alloy may have purities in the ranges 99.00 to 99.99% byweight, preferably purities in the ranges 99.50 to 99.99% byweight, such as a purity in the ranges 99.90 to 99.99% by weight.

[0034] The sacrificial anode according to the invention has an excellent electrochemical efficiency, and in an embodiment the sacrificial anode with the aluminium-based alloy has an electrochemical efficiency above 1500 Ah/kg, preferably above 2000 Ah/kg, such as above 2500 Ah/kg, when tested according to the DNV GL standards, such as DNV RP B401.

[0035] The sacrificial anode has a low potential (potential vs. Ag/AgCl), and in an embodiment the potential is lower than -800mV, such as lower than -1000mV. Thus, use of the aluminium-based alloy provides sacrificial anodes with very good cathodic protection to more noble metals.

DETAILED DESCRIPTION OF THE INVENTION

[0036] The invention will now be described in further details with reference to the drawings in which:

Figure 1A shows a first embodiment of a sacrificial anode;

Figure 1B shows a second embodiment of a sacrificial anode; and

Figure 1C shows a third embodiment of a sacrificial anode.

[0037] The figures are only intended to illustrate the principles of the invention and may not be accurate in every detail. Moreover, parts which do not form part of the invention may be omitted. The same reference numbers are used for the same parts throughout.

[0038] Figure 1A shows an embodiment of a sacrificial anode 10. The sacrificial anode comprises the aluminium alloy 12 shaped as a bar and with connection pieces 14 at each end. The connection pieces 14 comprise holes by which the sacrificial anode 10 can be connected to the item which requires cathodic protection by means of bolts or screws.

[0039] Figure 1B shows another embodiment of a sacrificial anode 10 with sacrificial alloy 12 and connectors 14. The connectors 14 can be welded to the item that requires cathodic protection.

[0040] Figure 1C shows yet an embodiment of a sacrificial anode 10 with sacrificial alloy 12 and connectors 14. The connecters 14 are "S"-shaped and can be attached by welding to the structure which requires cathodic protection. The amount of the sacrificial alloy 12 shaped as a bar may be 100 kg or more.

Example

[0041] A sacrificial anode according to the invention was produced using the aluminium-based alloy with the approximate composition:

Zinc:	0.5% by weight
Indium:	0.02% by weight
Gallium:	0.05% byweight
Iron:	0.06% byweight
Copper:	0.002% byweight
Impurities:	0.03% by weight in total
Aluminium:	balance

[0042] The aluminium-based alloy was shaped into a cylindrical rod constituting a sacrificial anode, and the electrochemical efficiency and the potential were determined.

[0043] The sacrificial anode had an electrochemical efficiency above 2500 Ah/kg when tested according to the DNV GL standards, such as DNV RP B401.

[0044] The sacrificial anode had a potential (potential vs. Ag/AgCl) lower than -1050mV.

[0045] Thus, the sacrificial anode provided very good properties in respect of cathodic protection for metallic structures.

Claims

1. An aluminium-based alloy for use in a sacrificial anode, **characterized in that** it comprises

   maximum 0.5% by weight of zinc,
   maximum 0.04% by weight of indium,
   maximum 0.1% by weight of gallium,
   maximum 0.08% byweight of iron,
   maximum 0.003% by weight of copper,
   elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
   balance aluminium.

2. Aluminium-based alloy according to claim 1 comprising:

   between 0.01 - 0.5% by weight of zinc,
   between 0.01 - 0.04% by weight of indium,
   between 0.02 - 0.1% by weight of gallium,
   between 0.01 - 0.08% by weight of iron,
   between 0.0005 - 0.003% by weight of copper,
   elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
   balance aluminium.

3. Aluminium-based alloy according to claim 1 or 2, wherein the aluminium has a purity of at least 99,0% by weight.

4. Aluminium-based alloy according to claim 1 or 2, wherein the aluminium has a purity of at least 99,5% by weight.

5. Aluminium-based alloy according to claim 1 or 2, wherein the aluminium has a purity in the ranges 99.90 to 99.99% by weight.

6. Aluminium-based alloy according to anyone of the preceding claims, wherein the aluminium-based alloy has an electrochemical efficiency above 1500 Ah/kg, preferably above 2000 Ah/kg, such as above 2500 Ah/kg, when tested according to DNV GL standards, such as DNV RP B401.

7. Use of an aluminium-based alloy in a sacrificial anode for protecting metallic constructions in a humid and marine environment, said aluminium-based alloy comprising:

maximum 0.5% by weight of zinc,
maximum 0.04% by weight of indium,
maximum 0.1% by weight of gallium,
maximum 0.08% by weight of iron,
maximum 0.003% by weight of copper,
elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
balance aluminium.

8. Use according to claim 7, wherein the aluminium-based alloy has an electrochemical efficiency above 1500 Ah/kg, preferably above 2000 Ah/kg, such as above 2500 Ah/kg, when tested according to DNV GL standards, such as DNV RP B401.

9. A sacrificial anode for protecting metallic constructions in a humid and marine environment, said sacrificial anode comprises an aluminium-based alloy comprising

maximum 0.5%byweight of zinc,
maximum 0.04% by weight of indium, maximum 0.1% byweight of gallium,
maximum 0.08% byweight of iron,
maximum 0.003% by weight of copper,
elements in form of impurities in an amount of maximum 0.02% by weight of each element, and
balance aluminium.

10. Sacrificial anode according to claim 9, wherein the aluminium-based alloy has an electrochemical efficiency above 1500 Ah/kg, preferably above 2000 Ah/kg, such as above 2500 Ah/kg, when tested according to DNV GL standards, such as DNV RP B401.

FIG. 1A

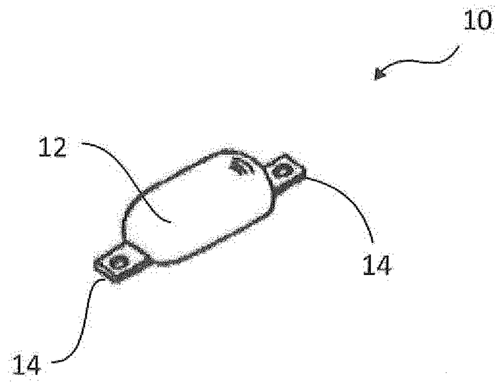


FIG. 1B

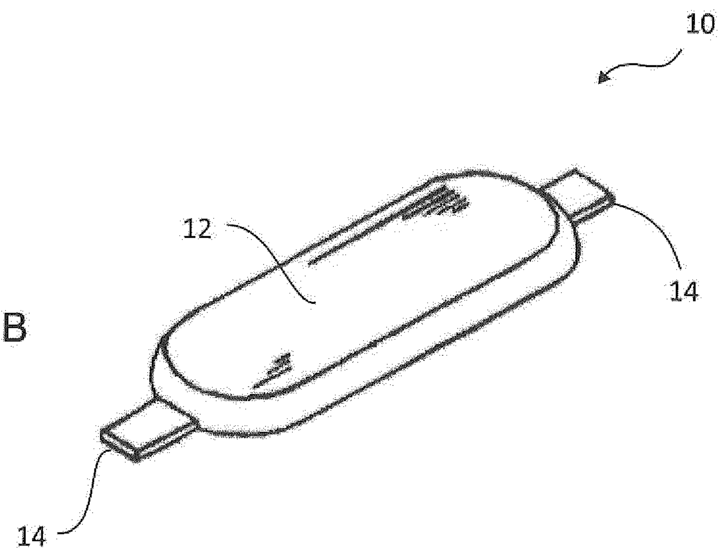
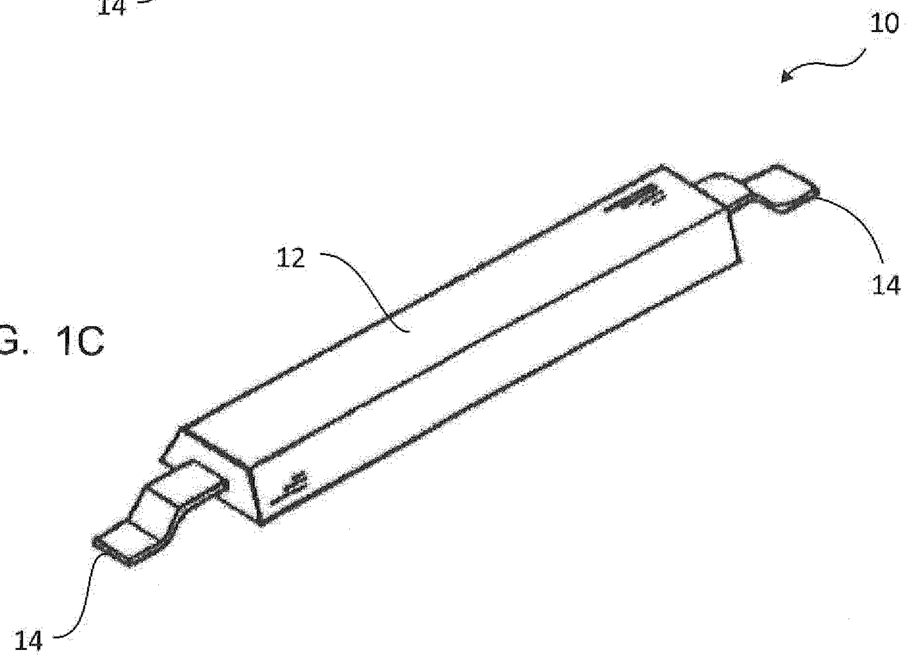


FIG. 1C



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EUROPEAN SEARCH REPORT

Application Number
EP 19 21 5052

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2013/084208 A1 (MISRA ABHIJEET [US] ET AL) 4 April 2013 (2013-04-04) * sample s33; page 3; example 3 * * page 2, paragraph [0015] * * claim 9 * * sample ss3; page 4; table 1 * -----	1-10	INV. C22C21/10 C23F13/14
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A	ANSHUMAN SHARMA ET AL: "and thermodynamic modelling of alloying effects on activity of sacrificial aluminium anodes", CORROSION SCIENCE, OXFORD, GB, vol. 53, no. 5, 20 January 2011 (2011-01-20), pages 1724-1731, XP028156793, ISSN: 0010-938X, DOI: 10.1016/J.CORSCI.2011.01.046 [retrieved on 2011-01-28] * the whole document * -----	1-10	TECHNICAL FIELDS SEARCHED (IPC) C22C C23F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	17 April 2020	Martinez Miró, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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