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"A PROCESS FOR THE PREPARATION OF A NEW ALUMINIUM BASED ALLOY ANODE FOR CATHODIC PROTECTION OF STRUCTURES SUBMERGED BOTH IN SALINE AND FRESH WATERS"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

This is an invention by Sri. Balkunje Anantha Shenoi, Dr. Krishnaswamy Balakrishnan, Sri Pattarakulam Luka Joseph, Sri Vasudeva Sastri Kapali, and Sri Venkataraman Balasubramanian, all of the Central Electrochemical Research Institute, Karaikudi-6 Tamilnadu, India and all Indian citizens and relates to improvement in or relating to the development of a process for the preparation of new aluminium based galvanic anode for cathodic protection of submerged structure.

Hitherto it has been proposed to use the usual alloys of aluminium like Al-Zn-Hg, Al-Zn-Sn, Al-Zn-Cd, Al-Zn-In, etc. as galvanic anodes for cathodic protection of submerged structures.

This is open to the objections that:

i) In some places especially where water is quite stagnant, presence of mercury in the anode material is quite objectionable from pollution point of view.

ii) In the case of cathodic protection of sturctures buried in sea-mud the above objection holds good. In addition this alloy could compete favourably with the Al-Zn-In alloy which is being used at present.

(iii) The 'In' present as third element can easily be replaced by other elements which are more easily available in India, thereby avoiding import of costly Indium.

(iv) Though Al-Zn-Sn alloy has good electrochemical properties required in a galvanic anode, yet this alloy needs very critical heat treatment sequence during the manufacture which can be

avoided by using other aluminium alloys wherein Sn has been replaced by a more suitable substute.

(v) Al-Zn-Hg alloy anode cannot be used in affecting cathodic protection to condenser tube which are non-ferrous in nature due to the presence of 'Hg' which will give rise to untimely failure of the condenser tubes.

The object of this invention is to obviate the disadvantages by using a newer alloy based on aluminium and containing zinc and magnesium which can be used as a galvanic anode in seawater, seamud and n brackish water under both stagnant and flowing conditions and in effecting cathodic protection to condenese tubes.

To these ends the invention broadly consists in developing new alloy compositions based on aluminium, zinc and magnesium which when used as galvanic anode would bring about efficient cathodic of structures submerged in sea or saline water, and structures burried in sea mud and other stagnant brackish waters and in heat exchangers.

The method of preparation of the anode comprises preparation of master alloy of magnesium and zinc or magnesium and aluminium whose compositions are adjusted such that when they are added to the molten base metal ternary alloys with requisite compositions are obtained; addition of calculated amount of any of the two master alloys to the main component, kept at a suitable range of temperature and the alloy obtained is poured into moulds of different sizes and shapes to get the required anode. Suitable

temperature range is between 700-740°C.

The proportions of the constitutents of the alloy may range fro
alloy may range from

(i) Aluminium (not less than .. 80% to 99% wt/wt

(ii)Zinc (not less than 99.8 .. 1% wt/wt to 20% wt/wt
to 99.9% purity)

(iii)Magnesium (purity 99.8 to..0.01% wt/wt to 15% wt/wt
99%)

Preferably, the compositions of various alloys to be formed o
of above general composition for particular or specific uses m
be:

Aluminium	... 99% to 88% wt/wt
Zinc	... 1% to 12% wt/wt
Magnesium	... 0.01% to 10% wt/wt

Following are the advantages of the invention:

1. The compositions of the alloys covered under t
specification do not contain any ecologically controvert
element like mercury and hence can be employed safely for
cathodic protection of structures submerged even in river wat

2. The alloys covered under this specifications can be use
wraught form itself and no heat treatment is necessary.

3. In addition to its use in river water the alloys covered
this specification can also be used for the cathodic prote
of structures submerged in sea water.

4. The alloys mentioned in this specification can be safely used in condenser boxes and heat exchangers where copper bearing alloys are present.

5. The alloys covered under this specification is competitive to any of the existing aluminium alloy sacrificial anodes.

6. The constituents of the alloys covered under this specification are readily available in the country.

Dated this 7th day of May 1985.

(N.R. SUBBARAM)
JOINT ADVISER (PATENTS)
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

164581

THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

"A PROCESS FOR THE PREPARATION OF A NEW ALUMINIUM BASED ALLOY ANODE FOR CATHODIC PROTECTION OF STRUCTURES SUBMERGED BOTH IN SALINE AND FRESH WATERS"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

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This is an invention by Balkunje Anantha Shenoi, Krishnaswamy Balakrishnan, Pattarakulam Luka Joseph, Vasudeva Sastri Kapali, and Venkataraman Balasubramanian, all of the Central Electrochemical Research Institute, Karaikudi-6 Tamilnadu, India and all Indian citizens and relates to a process for the preparation of new aluminium based galvanic anode for cathodic protection of structures submerged both in saline and fresh waters.

The process of this invention leads to a new type of ternary aluminium alloy galvanic anode without the involvement of mercury at any stage. These galvanic anodes can be used for the cathodic protection of submerged structures like oil drilling platforms, ships, sheet-piles of dockyards, Ports, etc. These anodes can be safely used in saline as well as river waters for the cathodic protection purposes. To achieve cathodic protection to structures submerged in sea or river waters, all that is to be done is to weld the cores of these anodes on to the underwater surface of the structure, where the alloy anodes dissolve and produce direct current which inturn protects the structure.

Hitherto it has been proposed to use the usual alloys of aluminium like Al-Zn-Hg, Al-Zn-Sn, Al-Zn-Cd, Al-Zn-In, etc. as galvanic anodes for cathodic protection of submerged structures. In our earlier Application No.146925 we have prepared a process for the preparation of alloy of magnesium containing mesh metal for use as galvanic anode.

The draw backs connected with hitherto known processes are:

i) In some places especially where water is quite stagnant, or where water is used for drinking purposes, e.g. river water, the presence of mercury in the anode material is quite objectionable from pollution point of view.

ii) In the case of cathodic protection of sturctures buried in sea-mud the above objection holds good.

(iii) Indium present in the hitherto known alloys is not manufactured in India and has to be only imported.

(iv) Although Al-Zn-Sn alloy has good electrochemical properties required in a galvanic anode, yet this alloy needs very critical heat treatment sequence during the manufacture.

(v) Al-Zn-Hg alloy anode cannot be used in effecting cathodic protection to condenser tube which are non-ferrous in nature due to the presence of 'Hg' which will give rise to untimely failure of the condenser tubes.

vi) The alloy described in our Patent No.146925 is a magnesium based alloy and not aluminium based as the alumina content is only 5-10%. This alloy also contains a mesh metal.

The main object of this invention is to obviate the above said disadvantages by providing a process for the preparation of an anode for cathodic protection from a new alloy based on aluminium and containing zinc and magnesium which can be used as an galvanic anode in seawater, seamud and in brackish water under both stagnant and flowing conditions and in effecting cathodic protection to condenser tubes.

This invention broadly consists in providing a process for the preparation of an anode for cathodic protection from an alloy composition based on aluminium and containing zinc and magnesium. The role of zinc and Mg in the alloy is to obviate self corrosion and to improve anodic polarisation characteristics and anode current efficiency. The use of Hg has also been completely elminated. The anode of the present invention would bring about efficient cathodic protection of structures submerged in sea or saline water and structures buried in seamud and other stagnant brackish or sea waters and in heat exchangers and condenser boxes.

Accordingly, the present invention provides a process for the preparation of a new aluminium based alloy anode for cathodic protection of submerged structures in saline and fresh water from ternary alloy of aluminium, zinc, magnesium which comprises adding 1 to 20% by wt. of zinc of purity of 99.9% to a molten master alloy of aluminium and magnesium prepared by adding 0.1 to 10% by wt. of magnesium of purity not less than 99.8% to 80-98% by wt. of aluminium of purity 99.5% at a temperature in the range of 720°C to 750°C such that in the resulting composition the amount of zinc, aluminium and magnesium has following ranges:

Aluminium	80% - 98% wt/wt
Zinc	1% - 20% wt/wt
Magnesium	0.1% - 10% wt/wt

heating the molten mixture at a temperature in the range of 700-740°C with constant stirring and casting the resultant molten mixture into the desired shape and size of the anode.

The anode resulting from the process of the present invention are based on ternary alloy compositions based on aluminium and are free from mercury and hence they are quite useful as effective sacrificial anodes in a range of waters namely from river water to seawater.

The preferred composition of the alloys for the preparation of anode is:

Aluminium	... 80% to 98% wt/wt
Zinc	... 1% to 20% wt/wt
Magnesium	... 0.01% to 10% wt/wt

Purity of the components may range as follows:

Aluminium	not less than 99.5%
Zinc	not less than 99.9%
Magnesium	not less than 99.8

The anode efficiency may be

a. in 3% NaCl	70 to 95%
b. in brackish water	80 to 85%
c. in river water	upto 90%

The open circuit potential	- 1.05V to -1.1V wrt SCE and
the close circuit potential	- 1.03V to -1.07V wrt SCE at 1 to 3 mA/sq.cm.anode current density

It is to be noted that no heat treatment is necessary after casting of the anode.

Addition of calculated amount of the master alloy to the main component, kept in molten condition at a suitable range of temperature and the ternary alloy obtained is poured into moulds of different sizes and shapes to get the required anode. Suitable temperature range is 700°C to 740°C.

Aluminium-Magnesium master alloy containing 90% wt. aluminium and 10% wt. magnesium is prepared in the following way.

99.8% pure aluminium is weighed and allowed to melt in a crucible. The temperature of the molten aluminium is maintained around 750°C. Calculated quantity of magnesium metal (99.8% pure) is weighed to prepare 90% Al- 10% Mg master alloy. The weighed magnesium metal is attached to a laddle with inverted cup and plunged into the molten aluminium without allowing the magnesium metal to float on the molten surface till all the magnesium metal get dissolved in molten aluminium. Dusting of fine powder of sulphur over the molten metal was done to avoid burning of magnesium metal. The alloy melt thus obtained is stirred well and cast to the required shape and size.

The Al-Mg master alloy thus obtained is used for the preparation of Al-Zn-Mg alloy anode.

The following example is given by way of illustration which should not be considered as to limit the scope of this invention.

Preparation of Al-Mg-master alloy

Quantity of master alloy to be prepared: 25 Kg/charge

22.5 Kgs of aluminium of purity not less than 99.5% is melted in a graphite crucible in a pit furnace fired by coke. The

temperature of the molten aluminium is maintained around 750°C. 2.5Kgs of magnesium of purity 99.8% is introduced into the molten aluminium, with the help of a laddle having an inverted cup. Sufficient care is taken not to allow the added magnesium metal to float on the surface of the molten aluminium and to see that the added magnesium is dissolved completely. Sulphur powder is dusted over molten alloy to avoid burning of magnesium during the addition of magnesium metal. The molten alloy is stirred well and cast into different shapes in graphite or iron moulds. Depending on the requirement the number of charges can be increased.

Preparation of Al-Mg-Zn ternary alloy

Quantity of the ternary alloy to be prepared: 25 Kgs/charge

The optimum preferred composition of the ternary alloy	Aluminium 88% to 98% wt/wt Zinc 12% to 1% wt/wt Magnesium 0.01 to 10% wt/wt
A typical example of the composition	Aluminium 88% wt/wt Zinc 11% wt/wt Magnesium 1% wt/wt

19.5 Kgs. of Aluminium of purity not less than 99.5% is kept under molten condition as before and maintained at above 720°C to 740°C. 2.5 Kgs of master alloy of Al/Mg and 2.75 Kgs of Zn of purity 99.9% are added to the molten aluminium at about 720-740°C and the resulting liquid alloy is stirred well. It is then cast into different shapes and sizes in graphite or iron moulds, as anodes, with steel strips or rods as cores. Depending on the requirement the number of charges can be increased.

Following are the advantages of the invention:

1. The anode prepared by the process of this invention do not contain any ecologically controvertial element like mercury and hence can be employed safely for the cathodic protection of structures submerged even in river water.

2. The anode prepared by the process of this invention can be used in wraught form itself and no heat treatment is necessary.

3. In addition to its use in river water the anode prepared by the process of this invention can also be used for the cathodic protection of structures submerged in sea water.

4. The anode prepared by the process of this invention can be safely used in condenser boxes and heat exchangers.

unless

WE CLAIM

164581

1. A process for the preparation of a new aluminium based allo anode for cathodic protection of submerged structures in salin and fresh water from ternary alloy of aluminium, zinc, magnesiu which comprises adding 1 to 20% by wt. of zinc of purity of 99.9 to a molten master alloy of aluminium and magnesium prepared b adding 0.1 to 10% by wt. of magnesium of purity not less tha 99.8% to 80-98% by wt. aluminium of purity 99.5%, at temperature in the range of 720°C to 750°C such that in th resulting composition the amount of zinc, aluminium and magnesiu has following ranges:

Aluminium	80% - 98% wt/wt
Zinc	1% - 20% wt/wt
Magnesium	0.1% - 10% wt/wt

heating the molten mixture at a temperature in the range of 700-740°C with constant stirring and casting the resultant molte mixture into desired shape and size of the anode.

2. A process as claimed in claim 1 wherein the molten mixture i cast into required shape and size at 730-750°C.

3. A process for the preparation of a new aluminium alloy anod for cathodic protection of submerged structures both in saline and fresh waters substantially as herein described with reference to the examples.

Dated this 16th day of July 1986

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