United States Patent [19]
Reding et al.

[11] **3,878,081**
[45] **Apr. 15, 1975**

[54] ALUMINUM SACRIFICIAL ANODE

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[22] Filed: **July 15, 1974**

[21] Appl. No.: **488,334**

[52] **U.S. Cl.** **204/197;** 72/364; 72/365; 72/377; 75/138; 204/148; 204/293
[51] **Int. Cl.** **C23f 13/00**
[58] **Field of Search** 75/138; 204/148, 197, 293; 148/32; 72/364, 365, 377

[56] **References Cited**

UNITED STATES PATENTS

3,379,636	4/1968	Reding et al.	75/138

Primary Examiner—R. Dean
Attorney, Agent, or Firm—Robert W. Selby

[57] ABSTRACT

An extruded aluminum base sacrificial anode consisting essentially of about 0.02 to about 2 weight per cent bismuth, about 0.005 to about 0.05 weight per cent gallium and about 0.005 to about 0.5 weight per cent indium and a method to produce such anode are disclosed.

23 Claims, No Drawings

ALUMINUM SACRIFICIAL ANODE

BACKGROUND OF THE INVENTION

This invention pertains to sacrificial anodes and more in particular to a method of forming an improved aluminum alloy sacrificial anode.

Theoretically, aluminum should be expected to perform satisfactorily as a sacrificial anode because the element aluminum fulfills the two primary requirements for sacrificial anodes, that is, a high theoretical oxidation potential (1.90 volts v. saturated KCl calomel reference) and a high theoretical electrical output per unit mass of metal consumed (2.98 amp.-hrs. per gram). In actual practice, however, unalloyed aluminum has not proven to be satisfactory for use as a sacrificial anode since it does not exhibit these favorable theoretical properties when used as a sacrificial galvanic anode. The presence of the normally passive oxide surface film on the aluminum apparently presents a barrier to the oxidation of the aluminum metal, thereby reducing the effective oxidation potential to about 0.7 volt (as measured in a closed circuit at either 250 or 1,000 milliamperes per square foot (ma/ft^2) in a synthetic seawater electrolyte). Unless otherwise specified, all voltages herein are with respect to a saturated potassium chloride (KCl)-calomel half cell as a reference.

The effective oxidation potential of the aluminum metal in fresh water is about 0.4 volt (as measured in a closed circuit at 10 milliamperes per square foot in water having a resistivity of about 5000 ohm.cm). The effective oxidation potential of aluminum in a saturated calcium sulfate ($CaSO_4$) electrolyte is about 0.4 volt (as measured in a closed circuit at a current density of 50 milliamperes per square foot). At such low operating voltages, no effective cathodic protection is given to, for example, ferrous based structures; therefore, the anode exhibits no useful electrical output.

It is known in the art to add certain elements such as bismuth, gallium, indium, lead, magnesium, tin and zirconium to aluminum in an attempt to provide an aluminum anode of commercial utility. Examples of such aluminum alloys are illustrated in, for example, U.S. Pat. Nos. 3,240,688; 3,337,332; 3,337,333; 3,368,952 and 3,379,636.

A method to produce an aluminum alloy suitable for use as an anode in various environments including water heating systems and underground environments is desired.

SUMMARY OF THE INVENTION

The novel method of the present invention comprises first providing an aluminum alloy consisting essentially of about 0.02 to about 2 weight per cent bismuth, about 0.005 to about 0.05 weight per cent gallium, about 0.005 to about 0.5 weight per cent indium and the balance of the alloy being essentially aluminum. The aluminum alloy is then hot worked sufficiently to provide a worked alloy suitable for use as a galvanic anode with an oxidation potential of about 1.0 to about 1.3 volts at a current density of 10 ma/ft^2 in a fresh water electrolyte with a resistivity of 5,000 ohm.cm or about 1.3 to 1.6 volts at a current density of about 50 ma/ft^2 in a saturated $CaSO_4$ electrolyte. The sacrificial anode of the present invention is useful in low resistivity aqueous liquids and is especially useful for the galvanic protection of ferrous members in, for example, water heaters or other aqueous environments having a resistivity of at least about 200 ohms centimeter.

The method of forming the aluminum alloy galvanic anode comprises first hot working a preferred alloy consisting essentially of about 0.03 to about 0.3 weight per cent bismuth, about 0.005 to about 0.04 weight per cent gallium, about 0.02 to about 0.3 weight per cent indium with the balance of the alloy being essentially aluminum. This alloy contains the normal impurities present in aluminum. The aluminum alloy is worked sufficiently to provide the desired oxidation potential. The hot working can be carried out by the known processes of drawing, forging, rolling and the like; however, it is preferred that the work be imparted into the alloy by means of extrusion. Preferably the hot working is carried out in a manner to provide a reduction in crossectional area from the starting aluminum billet to the final worked anode of at least about 9 to 1 and more preferably at least about 25 to 1. The temperature of the solid metal during hot working is at least about 200°C. and preferably from about 400° to about 600°C.

The described alloy is preferably prepared by melting aluminum with a purity of at least about 99.5 weight per cent aluminum and then adding a sufficient amount of the elements bismuth, gallium and indium to the molten aluminum to provide an alloy within the above defined composition ranges when the added elements are substantially uniformly dispersed within the aluminum. These elements can be readily dispersed in the aluminum by mixing equipment and methods commonly accepted in the art. Naturally the addition of aluminum, bismuth, gallium, and/or indium alloys in amounts sufficient to form an aluminum alloy within the herein described composition ranges is contemplated and included herein. To minimize the impurity level in the aluminum alloy anode or to produce an aluminum base alloy consisting of bismuth, gallium and indium within the afore-specified ranges, it is desirable that the metal melted have an aluminum purity of at least about 99.7 weight per cent and preferably at least about 99.85 weight per cent.

After the bismuth, gallium and indium are admixed with the molten aluminum to provide the desired alloy, the molten metal is poured or cast into a suitable form or mold of a predetermined shape. The molten alloy is solidified and removed from the mold. The as-cast shape, such as an ingot, is heated to or maintained at a temperature sufficient for hot working of the metal. Preferably the temperature is sufficient to afford extrusion into a shape adapted for use as a galvanic anode in, for example, water heaters. The described worked alloy can be employed as a sacrificial anode using methods known to those skilled in the art. For example, attaching the anode to a more electropositive metal structure, such as a steel member contained in a water heater, to afford an electrical contact between the anode and the steel causes preferential corrosion of the anode in corrosive environments.

As can be seen in the following examples and tables addition of bismuth, gallium and indium in the stipulated amounts to aluminum produces a hot worked sacrificial anode with a high useful voltage and a high current capacity (amp.-hr. per pound output) in corrosive environments.

EXAMPLES 1–8

Aluminum with a purity of 99.9 weight per cent was melted and heated to a temperature of 750°C. Sufficient amounts of bismuth, gallium, and indium were dissolved in the molten aluminum to provide alloys with the compositions shown in Table I after mixing these elements into the molten aluminum. The described alloys were cast into 2 ½ inch diameter by 6 inch long ingots. The solidified ingots were removed from the molds and heated to a temperature of 480°C. prior to being extruded into ½ inch diameter rod. The extruded rod was cut into about 7 inch long sections. The individual sections were tested in an electrolyte comprising a mixture of tap water and deionized water. The water had an electro-resistivity of 5,000 ohm-centimeters and a temperature of 70°C. Each of the sections was immersed in the aqueous electrolyte to a depth of 1 ½ inches and electrically attached to the stainless steel container, which acted as the cathode. The anode current density was approximately 10 ma/ft² during testing. The voltage potentials shown in Table I were measured with reference to a standard saturated potassium chloride-calomel half cell.

TABLE I

Ex	Bi	Analysis (wt.%) Ga	In	Al	Measured Potential (volts)	Current Capacity (amp.hrs/lb)
1	0.06	0.01	0.02	Bal.	1.02	535
2	0.07	0.01	0.09	″	1.06	440
3	0.07	0.02	0.08	″	1.15	480
4	0.07	0.04	0.02	″	1.03	480
5	0.22	0.05	0.04	″	1.8	<100
6	0.23	0.04	0.01	″	1.05	340
7	0.26	0.01	0.02	″	1.18	410
8	0.31	0.01	0.12	″	1.15	405

EXAMPLES 9–21

Specimens obtained substantially as described in Examples 1 through 8 were tested in a saturated $CaSO_4$ aqueous electrolyte. Each specimen was immersed in the aqueous electrolyte to a depth of 3 inches and electrically connected through an 18,200 ohm resistor to the positive side of a rectifier. Stainless steel rods were connected to the negative side of the rectifier and immersed in the electrolyte to act as cathodes. The anode current density during testing was approximately 50 ma/ft². The voltage potentials shown in Table II were measured with reference to a standard saturated KCl calomel half cell.

TABLE II

Ex.	Bi	Analysis (wt.%) Ga	In	Al	Potential (volts)	Current Capacity (amp.hrs./lb)
9	0.06	0.01	0.02	Bal.	0.6	—
10	0.06	0.01	0.04	″	1.5	900
11	0.07	0.01	0.09	″	1.5	916
12	0.07	0.02	0.08	″	1.5	700
13	0.07	0.02	0.12	″	1.5	885
14	0.07	0.04	0.02	″	1.5	625
15	0.10	0.01	0.02	″	1.55	860
16	0.15	0.02	0.08	″	1.55	825
17	0.22	0.05	0.04	″	1.55	455
18	0.23	0.04	0.01	″	1.55	767
19	0.26	0.01	0.02	″	1.50	826
20	0.45	0.01	0.02	″	1.44	617
21	0.51	0.01	0.07	″	1.37	662

EXAMPLES 22–26

Aluminum with a purity of 99.9 weight per cent was melted and heated to a temperature of 750°C. Sufficient amounts of bismuth, gallium, and indium were dissolved in the molten aluminum to provide the alloy compositions shown in Table III after mixing these elements into the molten aluminum. The described alloys were cast into 2 ½-inch in diameter by 6 inch long ingot and ⅝ inch in diameter by 6 inch long specimens. The solidified 2 ½ by 6 inch ingots were removed from the molds, heated to a temperature of 480°C. and extruded into ½ inch diameter rod. The extruded rod was cut into about 7 inch long specimens. The individual extruded and as-cast specimens were tested in saturated $CaSO_4$ aqueous electrolyte.

The extruded rods were immersed in the electrolyte to a depth of 3 inches and the as-cast specimens were immersed to a depth of 2.5 inches. All extruded and as-cast test samples were electrically connected through a 18,200 ohm resistor to the positive side of a rectifier. Stainless steel rods were connected to the negative side of the rectifier and immersed in the electrolyte to act as cathodes. The anode current density was approximately 50 ma/ft². The voltage potential as shown in Table III was measured with reference to a standard saturated KCl calomel half cell. It is readily apparent that extrusion of the indicated alloys significantly improved the anode characteristics of the alloys.

EXAMPLES 27–58

Aluminum base alloys with a composition as shown in Table IV were prepared substantially as described in Examples 22–26. The anode current density was about 36 ma/ft². The data contained in Table IV represents the anode characteristics after about 30 days in the corrosive environment. It is apparent that the anode voltage potential and current capacity of the extruded anodes are more uniform than and improved over the as-cast material.

TABLE III

Example	Bi	Analysis (wt.%) Ga	In	Al	As-Cast Potential (volts)	Extruded Potential (volts)	Current Capacity (amp.hrs/lb)
22	0.1	0.01	0.01	Bal.	0.4	1.4	800
23	0.1	0.04	0.01	″	0.5	1.5	790
24	0.15	0.01	0.10	″	0.5	1.4	870
25	0.2	0.01	0.01	″	0.4	1.5	775
26	0.2	0.04	0.01	″	0.7	1.5	750

TABLE IV

	Analysis (wt.%)			As-cast		Extruded	
Examples	Bi	Ga	In	Pot. (volts)	Current Capacity (amp. hr/lb)	Pot. (volts)	Current Capacity (amp. hr/lb)
27	0.040	0.031	<0.01	0.62	880	1.48	787
28	0.075	0.016	0.01	–	–	1.35	861
29	0.12	0.010	0.011	0.45	1181	1.45	800
30	0.12	0.023	0.015	1.34	794	1.50	647
31	0.12	0.011	0.12	1.51	430	1.57	693
32	0.13	0.011	0.020	0.50	1202	1.55	804
33	0.14	0.005	0.012	1.31	995	1.52	769
34	0.15	0.011	<0.01	0.5	981	1.55	691
35	0.17	0.009	0.032	0.51	1195	1.50	831
36	0.17	0.010	<0.01	0.4	905	1.55	736
37	0.17	0.010	0.086	0.55	1191	1.45	871
38	0.17	0.018	0.010	0.40	959	1.56	778
39	0.18	0.012	0.032	1.36	923	1.55	765
40	0.20	0.009	<0.01	0.50	1195	1.51	794
41	0.20	0.024	<0.01	0.46	946	1.47	720
42	0.21	0.012	0.056	1.44	703	1.58	695
43	0.21	0.043	<0.01	0.43	1175	1.54	652
44	0.22	0.014	<0.01	0.43	1181	1.56	637
45	0.23	0.019	0.010	0.39	956	1.58	702
46	0.23	0.040	0.01	0.50	1191	1.54	767
47	0.25	0.019	0.012	1.33	880	1.57	737
48	0.26	0.008	0.011	0.46	1168	1.51	776
49	0.27	0.013	<0.01	0.41	1219	1.50	654
50	0.29	0.022	0.053	1.34	742	1.59	696
51	0.31	0.012	<0.01	1.2	860	1.54	602
52	0.32	0.011	<0.01	0.7	927	1.53	747
53	0.46	0.032	<0.01	0.48	1020	1.49	599
54	0.52	0.012	<0.01	0.4	961	1.56	522
55	0.52	0.040	<0.01	1.0	735	1.55	502
56	0.55	0.039	<0.01	0.95	694	1.53	572
57	0.58	0.020	0.012	1.3	758	1.55	507
58	0.59	0.015	<0.01	1.2	822	1.55	510

What is claimed is:

1. An extruded sacrificial aluminum anode consisting essentially of about 0.02 to about 2 weight per cent bismuth, about 0.005 to about 0.05 weight per cent gallium, about 0.005 to about 0.5 weight per cent indium and the balance being essentially aluminum.

2. The extruded anode of claim **1** with an oxidation potential of about 1.0 to about 1.3 volts at a current density of about 10 ma/ft^2 in an aqueous electrolyte with a resistivity of about 5,000 ohm.cm.

3. The extruded anode of claim **1** with an oxidation potential of about 1.3 to about 1.6 volts at a current density of about 50 ma/ft^2 in a saturated calcium sulfate aqueous electrolyte.

4. The extruded anode of claim **1** consisting essentially of about 0.03 to about 0.3 weight per cent bismuth, about 0.005 to about 0.04 weight per cent gallium and about 0.02 to about 0.3 weight per cent indium.

5. The extruded anode of claim **4** with an oxidation potential of about 1.0 to about 1.3 volts at a current density of about 10 ma/ft^2 in an aqueous electrolyte with a resistivity of about 5000 ohm.cm.

6. The extruded anode of claim **4** with an oxidation potential of about 1.3 to about 1.6 volts at a current density of about 50 ma/ft^2 in a saturated calcium sulfate aqueous electrolyte.

7. A method to form a sacrificial anode comprising providing an alloy consisting essentially of about 0.02 to about 2 weight per cent bismuth, about 0.005 to about 0.05 weight per cent gallium, about 0.005 to about 0.5 weight per cent indium and the balance being essentially aluminum; and working the alloy sufficiently to provide a reduction ratio of the cross-sectional areas of the starting alloy to the extruded anode of at least about 9:1.

8. The method of claim 7 wherein the reduction ratio is at least about 25 to 1.

9. The method of claim **7** including working the alloy sufficiently to provide a sacrificial anode with an oxidation potential of about 1.0 to about 1.3 volts at a current density of about 10 ma/ft^2 in an aqueous electrolyte with a resistivity of about 5,000 ohm.cm.

10. The method of claim **7** including working the alloy sufficiently to provide a sacrificial anode with an oxidation potential of about 1.3 to about 1.6 volts at a current density of about 50 ma/ft^2 in a saturated calcium sulfate aqueous electrolyte.

11. The method of claim **9** wherein the working is carried out by extrusion.

12. The method of claim **10** wherein the working is carried out by extrusion.

13. The method of claim **7** wherein the working is carried out by extrusion.

14. The method of claim **13** including heating the alloy to provide an extrusion temperature of from about 400°C. to about 600°C.

15. The method of claim **13** wherein the reduction ratio is at least 25 to 1.

16. The method of claim **7** including heating the alloy to provide a working temperature of at least about 200°C.

17. The method of claim **7** wherein the alloy provided consists essentially of about 0.03 to about 0.3 weight per cent bismuth, about 0.005 to about 0.04 weight per cent gallium and about 0.02 to about 0.3 weight per cent indium.

18. The method of claim **17** wherein the reduction ratio is at least about 25 to 1.

19. The method of claim **17** wherein the working is carried out by extrusion.

20. The method of claim **19** including heating the alloy to provide an extrusion temperature of from about 400°C. to about 600°C.

21. The method of claim **20** wherein the reduction ratio is at least about 25 to 1.

22. An aluminum alloy consisting essentially of about 0.02 to about 2 weight per cent bismuth, about 0.005 to about 0.05 weight per cent gallium, about 0.005 to about 0.5 weight per cent indium and the balance being essentially aluminum.

23. The alloy of claim **22** consisting essentially of about 0.03 to about 0.3 weight per cent bismuth, about 0.005 to about 0.04 weight per cent gallium and about 0.02 to about 0.3 weight per cent indium.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,878,081 Dated April 15, 1975

Inventor(s) John T. Reding; Robert L. Riley, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 66, change "and" to --but--;

Column 4, line 50, after "the" second occurrence, insert --saturated $CaSO_4$--;

Column 4, Table III, the word "Extruded" should be centered above columns 7 & 8.

Signed and Sealed this

twenty-ninth Day of *July 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks