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ALUMINUM BASE ALLOYS CONTAINING THALLIUM

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This invention relates to sacrificial galvanic anodes and more particularly is concerned with a novel aluminum based alloy exhibiting high oxidation potential and a useful high electrical output per unit mass of metal; i.e. a high electrochemical equivalent which is suitable for use in such galvanic anodes.

Theoretically, aluminum should be expected to perform satisfactorily as a galvanic anode because the element aluminum fulfills the two primary requirements for anodes; (1) a high theoretical oxidation potential (1.80 volts versus calomel reference) and (2) a high theoretical electrical output per unit mass of metal consumed (2.98 amp-hours per gram). In actual practice, however, aluminum has not proved to be satisfactory for use in such applications 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 closed circuit at either 250 or 1000 milliamperes/square foot in a synthetic seawater electrolyte with a standard saturated KCl calomel cell as reference). At such low operating voltages, no cathodic protection is given, therefore the anode exhibits no useful electrical output. By comparison, the actual working potential of magnesium is about 1.5 volt and of zinc is about 1 volt.

It is known in the art to add certain elements such as barium, mercury, zinc, magnesium, tin, gallium or indium to aluminum in an attempt to provide an aluminum anode of commercial utility. Such additions have not been successful in that no marked increase in oxidation potential along with feasible efficiency has been realized with elements such as gallium, barium, zinc, or magnesium. Additionally, with aluminum alloys containing mercury or tin although an increased potential results, other problems are encountered. To illustrate, the relatively low boiling point of mercury, about 356.9° C., makes the addition of mercury to aluminum very difficult at atmospheric pressure. Of greater consequence, however, is the fact that aluminum based mercury containing alloys can exhibit a marked sensitivity to air oxidation. Such oxidation shows up as detrimental metal losses thereby lowering the total amount of useful current that can be obtained from an anode, i.e. lowered anode efficiency. Aluminum based tin containing alloy anodes exhibit a poor oxidation pattern in that a spongy layer of metal is formed on the anode. Massive pieces of this spongy metal fall or separate from the main anode body. These are lost as no useful current can be realized from such isolated pieces; in turn, this substantially lowers the actual efficiency of the anode.

It is a principal object of the present invention to provide an aluminum based galvanic anode which exhibits both high operating oxidation potential and a useful ampere-hour output.

It is another object of the present invention to provide a novel aluminum alloy particularly suitable for use as a sacrificial galvanic anode.

These and other objects and advantages readily will become apparent from the detailed description of the invention presented hereinafter.

The present invention comprises a novel aluminum based alloy composition containing a small amount of

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thallium and in combination therewith a small amount of gallium, zinc, barium, mercury, tin or magnesium.

More particularly, the present composition consists essentially of aluminum and from about 0.005 to about 1 weight percent thallium having in combination therewith a member selected from the following group; from about 0.01 to about 1 weight percent gallium, from about 0.3 to about 5 weight percent zinc, from about 0.1 to about 5 weight percent barium, from about 0.001 to about 0.5 weight percent mercury, from about 0.01 to about 10 weight percent tin or from about 1 to about 25 weight percent magnesium.

Preferably the alloys will consist essentially of aluminum and alloyed therewith from about 0.01 to about 0.5 weight percent thallium and a third member as follows in the concentrations set forth; gallium from about 0.03 to about 0.1 weight percent, zinc from about 0.5 to about 5 weight percent, barium from about 0.2 to about 1 weight percent, mercury from about 0.002 to about 0.02 weight percent, tin from about 0.03 to about 0.5 weight percent or magnesium from about 3 to about 15 weight percent. All weight percents are based on the total composition weight.

Unexpectedly, the present novel compositions when employed as sacrificial galvanic anodes exhibit a satisfactory corrosion pattern, a high operating oxidation potential and a high electrical output per unit mass of metal consumed.

Galvanic anodes can be prepared from the novel compositions by use of alloying and casting or fabricating techniques ordinarily employed in the aluminum art. No special metal handling or fabricating operations are required.

Aluminum for use in preparing the present novel alloy compositions should preferably be commercial high purity metal (99.99% Al) but can be comercial grade (99.9%) metal having normal production introduced impurities associated therewith. The alloying elements also can be of high purity or of commercial grade.

The resulting alloy product is not detrimentally degraded by storage in normal atmospheres through air oxidation.

The following example will serve to further illustrate the present invention but is not meant to limit it thereto.

Example.—A number of anodes of the present invention were prepared by melting commercial 99.9% or 99.99% purity aluminum ingot in a graphite crucible positioned within an electric furnace. Requisite amounts of thallium and a second predetermined alloying ingredient were introduced into the molten aluminum and the resulting mixture stirred to effect dispersion of the alloying ingredients throughout the melt. The resulting alloy was cast in a graphite mold into cylindrical specimens about 5½ inches long and about 5⁄16 inch in diameter. The cooling and solidification rate of the castings were controlled such that these simulated the cooling rate experienced in production of commercial, field-sized cast anodes.

The performance of the alloys was evaluated by positioning each cast cylindrical specimen (as anode) in a schedule 40 steel can 3 inches in diameter and 6 inches tall (as cathode). Synthetic seawater was used as an electrolyte with about 4 inches of each specimen being immersed. The cells were complete with respect to electrical circuitry, a rectifier being employed to maintain a constant current through a group of cells connected in series.

The results of a number of runs comparing the performance of the novel ternary aluminum alloy anodes of the composition of the present invention with the commercial aluminum used as a base metal for these alloys and binary alloys without thallium as well as magnesium and zinc anodes as controls are summarized in Table 1.

TABLE 1

Run No.	Alloying Ingredients		Test Conditions		Results		Comments
	Elements	Percent	Current Density, ma./ft.[2]	Total Current, amp.-hrs.	Oxidation Potential,[3] volts	Electrical Output, amp.-hr./gm.	
1	None (99.9% Al)	Control	1,000	6.7	0.71	(4)	
2 [1]	Sn Tl	0.026 0.04	1,000	4.4	1.35	1.98	Anode containing Sn-Tl exhibits 74% higher amp.-hr./gm consumed output than corresponding anode with Sn alone.
2a[1]	Sn (control)	0.025	1,000	4.4	1.37	1.14	
3 [1]	Sn Tl	0.05 0.045	1,000	4.4	1.47	2.08	Anode containing Sn-Tl exhibits 68% higher amp.-hr./gm. consumed output than anode with Sn alone. Also potential of Sn-Tl alloy is higher.
3a [1]	Sn (control)	0.09	1,000	4.4	1.38	1.24	
4 [1]	Hg Tl	0.0044 0.12	1,000	9.64	1.42	1.77	Anode containing Hg-Tl exhibits 740% higher amp.-hr./gm. consumed output than anode with Hg alone.
4a [1]	Hg (control)	0.009	1,000	2.1	1.58	0.21	
5 [1]	Ga Tl	0.046 0.37	1,000	11.14	1.21	1.72	Addition of Tl increases potential from that which is "borderline" regarding utility to an operable useful voltage while still providing good workable output.
5a [1]	Ga (control)	0.072	250	1.09	0.80	2.53	
6 [2]	Zn Tl	2.1 0.2	250	1.21	1.11	1.82	
6a [2]	Zn (control)	4.0	250	0.98	0.93	2.47	
7 [2]	Ba Tl	0.85 0.31	250	1.21	0.98	2.83	
7a [2]	Ba (control)	0.58	250	0.95	0.81	2.98	
8 [2]	Mg Tl	15.0 0.58	250	1.21	1.11	1.97	Addition of Tl increases potential from "borderline" to useful value as well as increases output.
8a [2]	Mg (control)	20.0	250	0.98	0.90	1.90	
9	Magnesium Anode (comparative control)				1.50	1.33	
10	Zinc Anode (comparative control)				1.05	0.82	

[1] Aluminum was 99.9% purity.
[2] Aluminum was 99.99% purity.
[3] Measurement made at completion of test.
At this low oxidation potential, no useful electrical output realized. The aluminum cannot function as an anode. Voltages as high as about 0.9 are still "borderline" with respect to realizing useful electrical output.

These results clearly show the superiority of the present novel thallium containing alloys with respect to oxidation potential and/or high electrochemical equivalent as compared to alloys containing no thallium. It is to be further noted that the oxidation potential and useful electrical output of the present novel compositions all are in the ranges desired and required for successful function as sacrificial anodes.

Large anodes, D-shaped in cross section, having dimensions of about 3½ inches diameter and 12 inches long can be prepared from the preseent novel compositions. Upon being subjected to actual field tests in flowing seawater these all can be expected to perform in the same satisfactory manner as sacrificial galvanic anodes.

In a manner similar to that described for the foregoing example, alloys comprising from about 0.005 to about 1 weight percent thallium and one of the following (a) about 0.01 to about 1 weight percent gallium (b) about 0.3 to about 5 weight percent zinc, (c) about 0.1 to about 5 weight percent barium, (d) about 0.001 to about 0.5 weight percent mercury, (e) about 0.01 to about 10 weight percent tin or (f) about 1 to about 25 weight percent magnesium, balance aluminum, all exhibit a high oxidation potential and electrical output and are suitable for use as sacrificial anodes for applications such as galvanic pigments in paint films, galvanic anode materials for primary batteries, sacrificial galvanic coatings for sheet steel and other metals cathodic to aluminum and sacrificial anodes for cathodic protection. Additionally these compositions find utility as an active ingredient in flares, for use in chemical reductions and in the preparation of aluminum alkyls.

Various modifications can be made in the present invention without departing from the spirit or scope thereof for it is understood that we limit ourselves only as defined in the appended claims.

We claim:

1. An aluminum alloy having a high oxidation potential and a high electrical equivalent, said alloy consisting essentially of:

from about 0.005 to about 1 weight percent thallium,
a member selected from the group consisting of
(a) gallium (about 0.01 to about 1 weight percent),
(b) zinc (about 0.3 to about 5 weight percent),
(c) barium (about 0.1 to about 5 weight percent),
(d) mercury (about 0.001 to about 0.5 weight percent),
(e) tin (about 0.01 to about 10 weight percent), and
(f) magnesium (about 1 to about 25 weight percent)

and
balance aluminum.

2. An aluminum alloy having a high oxidation potential and a high electrochemical equivalent, said alloy consisting essentially of:

from about 0.01 to about 0.5 weight percent thallium,
a member selected from the group consisting of
(a) gallium (about 0.03 to about 0.1 weight percent),
(b) zinc (about 0.5 to about 5 weight percent),
(c) barium (about 0.2 to about 1 weight percent),
(d) mercury (about 0.002 to about 0.02 weight percent),
(e) tin (about 0.03 to about 0.5 weight percent), and
(f) magnesium (about 3 to about 15 weight percent)

and,
balance aluminum.

3. An aluminum alloy having a high oxidation potential and a high electrochemical equivalent, said alloy consisting essentially of

about 0.04 to about 0.6 weight percent thallium,
a member selected from the group consisting of
(a) gallium (about 0.05 weight percent),
(b) zinc (about 2 weight percent),
(c) barium (about 0.85 weight percent),
(d) mercury (about 0.004 weight percent),
(e) tin (about 0.05 weight percent), and
(f) magnesium (about 15 weight percent),

and,
balance aluminum.

4. An aluminum based galvanic sacrificial galvanic anode having a high useful oxidation potential and a high electrochemical equivalent which comprises:

a cast anode structure, said structure consisting essentially of
from about 0.005 to about 1 weight percent thallium,
a member selected from the group consisting of
(a) gallium (about 0.01 to about 1 weight

percent),
(b) zinc (about 0.3 to about 5 weight percent),
(c) barium (about 0.1 to about 5 weight percent),
(d) mercury (about 0.001 to about 0.5 weight percent),
(e) tin (about 0.01 to about 10 weight percent), and
(f) magnesium (about 1 to about 25 weight percent)

and,
balance aluminum.

5. An aluminum alloy having a high oxidation potential and a high electrochemical equivalent, said alloy consisting essentially of from about 0.005 to about 1 weight percent thallium, from about 0.001 to about 0.5 weight percent mercury, and balance aluminum.

6. An aluminum alloy having a high oxidation potential and a high electrochemical equivalent, said alloy consisting essentially of from about 0.005 to about 1 weight percent thallium, from about 0.01 to about 1 weight percent gallium, and balance aluminum.

7. An aluminum alloy having a high oxidation potential and a high electrical equivalent, said alloy consisting essentially of from about 0.005 to about 1 weight percent thallium, from about 0.1 to about 25 weight percent magnesium, and balance aluminum.

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