United States Patent Office

3,337,333
Patented Aug. 22, 1967

3,337,333
ALUMINUM ALLOYS AND GALVANIC ANODES MADE THEREFROM

John T. Reding, Freeport, and John J. Newport III, and James R. Minderhout, Lake Jackson, Tex., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware
No Drawing. Filed July 23, 1964, Ser. No. 384,795
4 Claims. (Cl. 75—138)

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 to 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 to ferrous based structures, for example; 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 gallium or bismuth 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.

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 high 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 small amounts of gallium, bismuth and lead.

More particularly, the present composition comprises aluminum and from about 0.003 to about 0.2 weight percent gallium, from about 0.02 to about 2 weight percent bismuth and from about 0.02 to about 2 weight percent lead.

Preferably the alloy comprises aluminum having alloyed therewith from about 0.005 to about 0.03 weight percent gallium, from about 0.03 to about 0.5 weight

percent bismuth and from about 0.03 to about 0.5 weight percent lead. All weight percents are based on the total composition weight.

The alloy is further characterized in that the bismuth/lead weight ratio preferably ranges from about 0.5 to about 2.

Unexpectedly, the present novel composition when employed as sacrificial galvanic anodes exhibits 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 of a grade having a purity of about 99.93% aluminum. Conveniently, commercial grade (99.9%) metal having normal production introduced impurities associated therewith can be blended with high purity (99.99% Al) to provide the aluminum matrix. The alloying elements also can be of high purity or of commercial grade. With aluminum of lower purity than specified, detrimental reduction in electropotential may be realized.

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 in a graphite crucible positioned within an electric furnace, a mixture of commercial 99.9% and 99.99% purity aluminum ingots to provide an aluminum matrix of about 99.97% purity or 99.99% purity aluminum ingots alone. Requisite amounts of gallium, bismuth and lead 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 ⅝ 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 sea water 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 aluminum alloy anodes of the composition of the present invention with the aluminum used as a base metal for these alloys and various binary and ternary alloys as controls are summarized in Table 1. The results present data showing both the oxidation potential and electrical output per unit mass of metal (efficiency) for the anodes tested.

TABLE 1

Run No.	Aluminum, Percent Purity	Alloying Ingredient (percent by weight)			Potential (volts)	Efficiency (percent)
		Ga	Bi	Pb		
1	99.99	0.013	0.14	0.14	1.45	80
2	99.99	0.01	0.17	0.17	1.50	63
3	[1] 99.99	0.01	0.07	0.12	1.44	86
4	99.99	0.005	0.03	0.025	1.45	79
5	99.99	0.005	0.50	0.39	1.48	78
6	99.99	0.005	1.0	0.40	1.52	79
7	99.99	0.005	0.2	1.0	1.47	84
8	99.99	0.031	0.12	0.14	1.54	57
9	99.97	<0.01	0.11	0.11	1.34	84
10	99.99	0.068	0.15	0.073	1.48	74
CONTROLS						
11	99.99	------	------	------	0.71	------
12	99.99	0.022	------	------	0.76	------
13	99.99	------	0.04	------	0.77	------
14	99.99	------	------	0.09	0.72	------
15	99.99	------	------	1.4	0.73	------
16	99.99	0.10	0.09	------	1.14	------
17	99.99	0.14	------	0.21	0.90	------
18	99.99	------	0.13	0.14	0.71	------

[1] 450 parts per million iron added as impurity.

These results clearly show the superiority of the present novel alloys with respect to oxidation potential and high electrochemical equivalent as compared to aluminum itself and the control alloys. 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.

These alloys 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 0.003 to about 0.2 weight percent gallium,
from about 0.02 to about 2 weight percent bismuth,
from about 0.02 to about 2 weight percent lead, and
balance aluminum.

2. An aluminum alloy having a high oxidation potential and a high electrical equivalent, said alloy consisting essentially of;
from about 0.005 to about 0.03 weight percent gallium,
from about 0.03 to about 0.5 weight percent bismuth,
from about 0.03 to about 0.5 weight percent lead, and
balance aluminum.

3. An aluminum based sacrificial galvanic anode having a high useful oxidation potential and a high electrical equivalent which comprises;
a cast anode structure, said structure consisting essentially of;
from about 0.003 to about 0.2 weight percent gallium,
from about 0.02 to about 2 weight percent bismuth,
from about 0.02 to about 2 weight percent lead, and
balance aluminum.

4. An aluminum based sacrificial galvanic anode having a high useful oxidation potential and a high electrical equivalent which comprises;
a cast anode structure, said structure consisting essentially of;
from about 0.005 to about 0.03 weight percent gallium,
from about 0.03 to about 0.5 weight percent bismuth,
from about 0.03 to about 0.5 weight percent lead, and
balance aluminum.

References Cited

UNITED STATES PATENTS

1,997,165 4/1935 Brown ---------- 75—138
2,565,544 8/1951 Brown ---------- 204—148

DAVID L. RECK, *Primary Examiner.*

R. O. DEAN, *Assistant Examiner.*