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METHOD FOR PREPARATION OF ALUMINUM-MERCURY ALLOYS

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This application is a continuation-in part of my copending application Ser. No. 328,195, filed Dec. 5, 1963, titled "Aluminum Alloy," now Patent No. 3,257,201, which application was a continuation-in-part of my then copending application Ser. No. 852,961, filed Nov. 16, 1959, and titled, "Aluminum Alloy," now abandoned.

This invention relates to an aluminum alloy formed of aluminum, mercury and magnesium, with or without zinc, and it relates more particularly to elements for use in electrolytic cells, such as anodes and the like formed of such aluminum alloys.

It is known in the art that aluminum, which is in contact with mercury or contains mercury, tends to oxidize in the open air very rapidly. Apparently, the mercury functions as a catalyst, greatly furthering the oxidation of aluminum, and, consequently, even extremely small quantities of mercury are sufficient to cause this undesirable effect.

It is, therefore, universally admitted that in industrial application any contamination of aluminum with mercury must be strictly avoided. Where aluminum alloys with mercury are prepared, containing a predominant percentage of aluminum, solid dispersions are obtained having a very poor stability and oxidizing very rapidly when exposed to air or an oxygen-containing medium. The oxidation occurs so rapidly that a veritable mushrooming effect of alumina can be observed. In electrolytic solutions such alloys are rapidly attacked and eventually destroyed by this highly undesirable oxidation. It is particularly disadvantageous in electrolytic cells where the anode tends to decompose very rapidly.

It is an object of the present invention ot provide an aluminum alloy having an improved resistance to corrosion.

It is another object of the present invention to provide an aluminum alloy which can be easily polished and is susceptible to furnish, when polished, a surface of exceptionally high gloss and brilliancy.

It is a further object of the present invention to provide an aluminum alloy which can be more easily worked than the known aluminum alloys.

It is another object of the present invention to provide an aluminum alloy which can be most advantageously used for the production of anodes, especially as used in electroytic cells, and it is a related object to produce a new and improved anode of said alloy.

It is still another object of the invention to provide an anode, particularly for use in electrolytic cells composed of an aluminum alloy of the present invention, having a far greater efficiency and a longer service life as well as having a more slightly and evenly decreasing yield than electrolytic cells using anodes composed of conventional alloys.

It is still a further object of the invention to provide an anode, particularly for use in electrolytic cells composed of an aluminum alloy of the present invention, which is particularly useful for the providing of objects with a protective layer by cathodic deposition, and wherein the anode has a far greater efficiency while being consumed far less rapidly and drastically than anodes composed of conventional alloys.

Further objects and advantages will become apparent upon reading the following description of the invention.

The objectives of this invention are achieved by the preferred practice of the invention by the formulation of an aluminum alloy containing mercury and magnesium as alloying elements with the magnesium present in an amount within the range of 0.5 to 15 percent by weight and preferably within the range of 3 to 8 percent by weight and with the mercury present in an amount within the range of 0.001 to 0.15 percent by weight and preferably in an amount within the range of 0.04 to 0.15 percent by weight, the remainder being aluminum plus small amounts of conventional impurities.

When zinc is present as an alloying element in the combination with mercury and magnesium, it is preferred to limit the amount of zinc to within the range of 0 to 4 percent by weight and preferably in an amount within the range of 0.25 to 2.0 percent by weight. Thus the aluminum alloy of this invention may be defined as having the following composition wherein the elements are given in percent by weight:

Element	Broad Range	Narrow Range
Magnesium	0.5–15	3–8
Mercury	0.001–0.15	0.04–0.15
Zinc	0–4	0.25–2.0
Aluminum	(1)	(1)

[1] Balance.

There are a number of ways in which the materials can be formulated in preparation of the aluminum alloy. By way of one example, the mercury can be alloyed first with zinc or with a zinc alloy having as low a melting point as possible. The alloy is then melted with the necessary amount of aluminum and magnesium to obtain the final composition.

According to a modification the alloy of mercury with zinc is prepared under a pressure exceeding 1 atmosphere, preferably in the presence of an inert gas such as argon. By following this procedure, the volatilization of mercury is reduced to a minimum. Under these conditions, the mercury is dissolved in the zinc to form master-alloy containing from 5 to 20 percent of mercury. The master-alloy is then alloyed with aluminum or an aluminum alloy in a quantity of, for example, 75 percent aluminum.

In order to make operations at low temperature possible, the mercury is preferably dissolved in the zinc/aluminum eutectic having an aluminum content of 5 percent by weight and which melts at a temperature of 380° C. This alloy is then diluted with the desired quantity of aluminum and magnesium to make up the desired composition.

In accordance with another modification, preferably employed in the preparation of a master alloy containing mercury, the aluminum-zinc, the magnesium-zinc or tellurium-zinc components are reduced to a molten state. The mercury to be introduced is housed in a syphon or tube that is sealed at one end and capped at the other end with a cap that is formulated of the alloy materials or of an alloy formulated of one or more of the metals embodied in the alloy system but which has a melting point corresponding to the melting point of the melt and preferably lower. The capped end of the tube is plunged into the melt whereby, when the cap is heated by the adjacent materials to the molten state, the mercury flows from the tube directly into the submerged portion of the melt.

In the preferred practice in the preparation of the alloy of this invention, the mercury is formed first into a master

alloy of zinc and mercury, which may be represented by the following compositions:

	Percent by wt.
Mercury	5 to 20
Zinc	Balance

or

Zinc	41.6
Magnesium	38.4
Mercury	20.0

or

Mercury	15.0
Aluminum	3.9
Zinc	81.1

or

Mercury	10
Tellurium	15
Zinc	75

The latter ones find use in the preparation of alloys containing little if any magnesium.

The necessary quantity of this alloy is then wrapped in several layers or otherwise enclosed with sheet of a metal of the desired alloy, such as aluminum, magnesium, zinc, copper and the entire package is then immersed into a bath of molten aluminum whereby the mercury is released while within the bath greatly to minimize the amount of mercury that might be lost by vaporization.

The new alloy can be used for various purposes but particular advantage is found in making use of the alloy as anodes for electroyltic cells and particularly for cathodic protection. When used in cathodic protection, due to the high value of potential of the alloys of this invention, the anodes promote the deposition of protective layers on the cathodes. The known anodes could not be used in a basic environment having a pH value above 10.8 and notably in the black liquor (aqueous solution of sodium carbonate, soda, and sodium sulphite). The anode consisting of the alloy of the invention can be safely used for these purposes. The same applies to the application to certain brines in which the dissolved salts can be precipitated by permutating their respective metals with magnesium, if an anode is used containing Mg as an adjuvant. The known anodes composed of an aluminum/zinc alloy cannot be used because of an excessive polarization even at currents as low as 20 milliamperes.

The anodes composed of the alloys of the invention have substantial negative potential generally comprised between −1.1 and −2.0 volts according to the environment in which they are used; the potentials are extremely stable over a long period of time. In addition they have an efficiency which is generally greater than 70 percent as compared with known electrodes having an efficiency substantially below 70 percent, the efficiency of conventional aluminum/zinc alloy electrodes not exceeding 50 percent.

The known aluminum/copper alloys for industrial use generally have a copper content of from 0.5 to 13 percent and particularly from 3 to 5 percent. The alloys of the invention preferably contain copper in the range from 0.5 to 15 percent and more preferably yet from 1 to 5 percent.

The excellent electro-chemical quality of the new alloys of the invention makes it possible to prepare anodes for use in electrolytic or galvanic or dry cells. The potential, the current density and the yield of such electrolytic cells or dry cell batteries is greatly improved. At the same time the alloys of the invention are highly resistant to corrosion and constitute an excellent anode for cathodic protection.

Most advantageously the aluminum alloys used for anodes in electrolytic cells, galvanic elements or dry cell batteries or cathodic protection contain both magnesium and zinc along with the mercury, the zinc content being equal or inferior to the magnesium content.

Apart from the electro-chemical applications the alloys of the invention can also be used as soft metals, particularly for the production of elements coming into slight mutual frictional contact such as, for example, journal bearings, bushings and the like.

Example I

An electrolytic cell is prepared having an anode composed of an aluminum alloy containing 8.5 percent of Mg and 0.125 percent of Hg, the rest being aluminum. The cathode is composed of manganese bioxide and carbon. The electrolyte consists of an aqueous solution containing, for each liter of water:

	G.
NH_4Cl	250
Ammonium chromate	2
Lauryldimethylbenzylammonium	0.2
Sodium benzoate	5

The pH value of this solution is brought to 9.2 by adding ammonia. The electromotive force of the cell is 1.85 volts.

Example II

An electric cell is prepared having a cathode consisting of a carbon cylinder of a diameter of 6 millimeters and a length of 65 millimeters. The depolarizer consists of:

	Percent
MnO_2	75
Acetylene black	20
Barium chromate	5

The following solution is used for wetting the depolarizer: an aqueous solution having a specific gravity of 28° Baumé of calcium chloride containing per liter 1 gram of barium chromate and 3 cubic centimeters of a 10% solution of the bromide of lauryldimethylbenzylammonium.

The same solution, but with the addition of a jellifying substance, is used as the electrolyte.

The anode consists of an aluminum alloy containing 0.066 percent by weight of mercury, 6 percent of magnesium, the rest being aluminum. The anode has an outer diameter of 33 millimeters and a length of 62 millimeters, corresponding to the conventional dimensions of a conventional dry cell torch battery.

The electromotive force of the cell is 2.10 volts. The cell has a constant yield of 250 milliamperes during 24 hours, i.e. 6 ah., until the voltage has been reduced to substantially half the initial voltage, i.e. 1.1 volts. Thereafter the discharge is continued for 12 hours whereafter the voltage is 0.9 volt and the total capacity 9 ah.

In comparison a cell comprising a conventional zinc anode is tested in the same manner. The discharge is continued for 16 hours, and the obtained capacity is thus 4 ah., the initial voltage being 1.5 volts and the final voltage being 0.75 volt.

Thus, the alloy of the invention is greatly superior in that the discharge up to 50 percent of normal capacity furnishes 6 ampere hours compared with only 4 ah. when using a conventional composition. In addition, the alloy of the invention is capable of furnishing a further appreciable amount of electricity in the order of 9 ampere hours after the voltage has dropped to 50 percent of the initial voltage which is not possible with conventional compositions.

Instead of forming the anode in the previous example of the composition set forth therein, the anode can be formed of an aluminum alloy containing 0.06 percent by weight of mercury, 6.0 percent by weight of magnesium, 1.5 percent by weight of zinc, with the remainder aluminum plus impurities.

It will be understood that this invention is susceptible to further modification and, accordingly, it is desired to

comprehend such modifications within this invention as may fall within the scope of the appended claims.

For instance, it is possible to introduce directly mercury, either in molten aluminum or in a molten master-alloy containing all the components, but no mercury, of the desired alloy, by means of the sealed tube described thereabove.

I claim:

1. In the method of producing an aluminum alloy containing mercury as an alloying element, the steps of reducing the aluminum containing componet to a molten state, wrapping a product of the group consisting of mercury and mercury alloys in a sheet of metal to form a substantially enclosed package, submerging the package below the surface of the molten aluminum containing component whereby the product is heated while the wrapping of metal is melted away to release the heated product while submerged in the bath of molten component for alloying with said component without excessive loss of mercury vapors.

2. A method according to claim 1, in which the mercury alloy is an alloy containing mercury and zinc.

3. A method according to claim 2, in which the mercury alloy is an alloy containing mercury, zinc and magnesium.

4. A method according to claim 2, in which the mercury alloy is an alloy containing mercury, zinc and aluminum.

5. A method according to claim 2, in which the mercury alloy is an alloy containing mercury, zinc and tellurium.

6. A method according to claim 1, in which the metal of the sheet is aluminum.

7. A method according to claim 1, in which the metal of the sheet is magnesium.

8. A method according to claim 1, in which the metal of the sheet is zinc.

9. A method according to claim 1, in which the metal of the sheet is copper.

10. A method according to claim 2, in which the master-alloy is an alloy containing 5 to 20% by weight of mercury.

11. In the method according to claim 1, a process to produce the mercury alloy by the steps of reducing to a molten state a component comprising the elements other than mercury of the alloy, introducing the mercury into an elongate tube which is tightly sealed at one end and sealed at the other end with a cap of a meltable metallic material adapted to form a part of the alloy, plunging

the tube downwardly into the bath of molten component whereby the temperature of the mercury within the tube is raised and the cap is melted away to release the heated mercury into a submerged portion of the molten bath of component whereby mercury vapors are condensed and retained for alloying purposes with the component.

12. The method as claimed in claim 11 in which the cap is formed of a metallic material having a melting joint below the temperature of the molten bath of component.

13. The method as claimed in claim 11, in which the mercury is introduced in an amount to supply the amount of mercury for the master alloy with zinc.

14. The method as claimed in claim 11, in which the mercury is introduced in an amount to supply the amount of mercury for the master alloy with zinc and magnesium.

15. The method as claimed in claim 11, in which the mercury is introduced in an amount to supply the amount of mercury for the master alloy with zinc and aluminum.

16. The method as claimed in claim 11, in which the mercury is introduced in an amount to supply the amount of mercury for the master alloy with zinc and tellurium.

17. In the method of producing an aluminum alloy containing mercury as an alloying element, the steps of reducing the aluminum containing component to a molten state, introducing the mercury into an elongate tube which is tightly sealed at one end and sealed at the other end with a cap of a meltable metallic material adapted to form a part of the alloy, plunging the tube downwardly into the bath of molten aluminum whereby the temperature of the mercury within the tube is raised and the cap is melted away to release the heated mercury into a submerged portion of the molten bath of aluminum whereby mercury vapors are condensed and retained for alloying purposes with the aluminum, the mercury being introduced in an amount to supply the amount of mercury calculated for direct alloying with the aluminum containing component.

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