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ALUMINUM ALLOY FOR CATHODIC PROTECTION SYSTEM AND PRIMARY BATTERY

Michael J. Pryor and Douglas S. Keir, Hamden, and Philip R. Sperry, North Haven, Conn., assignors to Olin Mathieson Chemical Corporation

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ABSTRACT OF THE DISCLOSURE

An aluminum alloy advantageously utilized as sacrificial anode in cathodic protection and as anode in a primary battery, said alloy consisting essentially of between 0.001 and 0.1% boron, with the tin being retained in solid solution to the maximum degree, said maximum degree being 0.1% balance essentially aluminum.

This application is a continuation-in-part of United States patent application Ser. No. 60,166 filed Oct. 3, 1960, now U.S. Patent 3,180,728, Ser. No. 171,114 filed Feb. 5, 1962, now U.S. Patent 3,186,836 and Ser. No. 313,445 filed Oct. 3, 1963, now U.S. Patent 3,241,953.

Magnesium and magnesium alloys in the form of sheet are generally used as the anodes of electric cells or batteries adapted to utilize sea water or similar aqueous electrolytes. The cost of conventional sea water batteries utilizing magnesium and magnesium alloys has been found to be prohibitively high except for military applications. This prohibitively high cost is due in part to the high price of magnesium and also due to the difficulty in rolling the hexagonal metal down to light gage sheet of less than 0.020 inch thickness.

Further disadvantages of magnesium and magnesium alloys for this application include the fact that they generally corrode readily in saline mediums even when uncoupled. In addition, relatively low power efficiency on the order of about 60 percent is obtained. Further, they are accompanied by a marked hydrogen evolution problem and are characterized by a power output which falls with time and for which special design allowances must be made.

Zinc is disadvantageous, inter alia, as it provides insufficient power output to be useful anode material in this type of power cell.

The more widely used sacrificial anodes for protection of ferrous structures against corrosion are the zinc and magnesium anodes. Aluminum alloys have not been as widely adopted for this purpose as the zinc and magnesium anodes because they have previously produced only low protective currents equivalent to those generated by zinc anodes but at a much higher unit cost. Furthermore, aluminum alloys have frequently shown the characteristic of becoming highly polarized due to the accumulation of insoluble corrosion products so that ultimately little useful protective current is delivered. Moreover, aluminum alloys which have been used as sacrificial anodes generally display relatively low anodic efficiency. However, the magnesium depresses the potential of steel in sea water into the hydrogen evolution range and stripping of protective coatings from the steel can result, for example, paint coatings. Furthermore, magnesium itself produces copious quantities of hydrogen when it serves as an anode in sea water. This is of particular significance in connection with protection of sea water ballast tanks in ships for which purpose magnesium anodes have been found to be hazardous. Zinc is undesirable due to the low

galvanic currents delivered which necessitates the use of a plurality of anodes in order to provide acceptable current levels.

It is therefore an object of the present invention to provide an improved aluminum alloy having a wide variety of uses, for example, which is capable of being utilized as a sacrificial anode and in an improved electric cell or battery adapted to utilize sea water or other electrolytes.

It is a further object of the present invention to provide an improved battery as aforesaid which attains high average current density, and high power output for the amount of anode metal consumed.

It is a still further object of the present invention to provide an improved battery as aforesaid which is inexpensive and economical while still attaining excellent results.

It is a still further object of the present invention to provide an improved cathodic protection system and an improved method of cathodically protecting a ferrous metal structure in contact with a medium corrosive thereto.

Further objects and advantages of the present invention will appear hereinafter.

In accordance with the present invention it has now been found that the foregoing objects and advantages may be readily accomplished by providing an aluminum base alloy containing at least 90% aluminum, between 0.04 and 0.5% tin and from 0.001 to 0.1% boron, with the tin being retained in solid solution to the maximum degree.

The alloy of the present invention is particularly useful for fabrication into a metal anode. The anode may be advantageously utilized in a primary electric cell containing a metal anode, a cathode and an electrolyte in contact with said anode and cathode, for example, a dry cell, an air cell, a sea water battery, etc. Still further, the anode may be advantageously utilized in a cathodic protection system comprising a cathodic metal structure and the aluminous sacrificial anode of the present invention electrically connected thereto, with the metal structure and the anode being in contact with a medium corrosive to said metal structure.

The above identified co-pending applications Ser. No. 60,166 and Ser. No. 171,114 teach that a metal anode comprising an aluminum base alloy containing at least 0.04% tin with the tin retained in solid solution to the maximum degree, is highly useful and advantageous and in fact attains surprising advantages over previously known systems.

It has now been found that in accordance with the present invention still further improvements may be obtained by providing in addition to the aluminum and tin in the alloy a specified quantity of boron. For example, the alloy of the present invention attains a significant improvement in anodic efficiency. Anodic efficiency is a conventional term and means the ratio of the weight of consumed anode which goes directly into producing electric current from Faraday's Law to the actual total weight of the anode consumed, usually expressed as a percent. Higher efficiency means less anode wastage due to local corrosion and, hence, a lower cost of cathodic protection, longer life for the anode material, less corrosion by-products, such as insoluble hydrated oxides and gaseous hydrogen and more uniform galvanic current over the useful life of the anode.

An additional advantage of the alloys of the present invention is that they can be readily fabricated by casting by either hot or cold rolling, and can be readily rolled to small gages and readily formed into shapes, e.g., by drawing, stamping or extruding, desirable for power cell an-

odes in distinction to magnesium where its hexagonal crystal lattice severely restricts its fabricating.

The improved aluminum alloy in the present invention contains tin in an amount from 0.04 to 0.5%, at least 90% aluminum and from 0.001 to 0.1% boron, with the tin being retained in solid solution to the maximum degree, i.e., about 0.1% with the excess tin or a suitable third ingredient being provided as taught in co-pending application Ser. No. 60,166 to improve uniformity of corrosion and to improve anodic efficiencies. A particularly surprising aspect of the present invention is the consistently higher anodic efficiency in combination with good current delivery attained by the aluminum-tin-boron alloy of the present invention with the tin being retained in solid solution to the maximum degree. This improvement attained by the present alloy is considerable and surprising and in fact quite important where the alloy is used as an anode.

The preferred manner of preparing this alloy is to heat the aluminum tin sample at elevated temperatures, e.g., around 540 to 640° C., with 620° C. being preferred, for a sufficient period of time to dissolve the maximum amount of tin and to redistribute excess tin or other alloying additions in a uniform dispersion which produces maximum uniformity of attack and power efficiency. Generally, the heating period within the preferred temperature range may vary between 15 minutes and 24 hours. After the heating period, the sample is cooled rapidly, for example, by immersion in a large volume of water at ambient temperatures or in the case of thin sheet, by cooling in air. For simplicity, this treatment may be termed "homogenization treatment." Homogenization within the above temperature range yields maximum tin in solid solution. Outside of this range the amount of tin in solid solution falls off markedly, thus yielding poorer electrochemical characteristics.

The preferred amounts of tin are from 0.08 to 0.35 percent. In some instances high purity aluminum may be preferred, for example, in the primary cells; however, the present invention is not limited to the use of a high purity aluminum and in fact it is generally preferred to use lower purity aluminum, for example, containing up to 0.10% silicon and up to 0.10% iron. It should be naturally understood that the alloy of the present invention may contain in addition to the aluminum, tin, and boron and incidental impurities, other metallic components which may be added to achieve particularly desirable results.

In fact, a particularly surprising aspect of the alloys of the present invention is that the boron addition neutralizes certain minor impurities of the transition metal type, i.e., titanium, vanadium, manganese, zirconium and others, tying them up as boride compounds. The transition metal impurities generally range from traces to 0.25 percent. Thus, boron is a particularly worthwhile alloying addition since it enables the use of somewhat less pure raw materials by offsetting unintentional pickup of impurities during melting and casting as well as offsetting naturally occurring impurities in reduction pot aluminum.

Generally, insoluble elements may be added to the alloy, i.e., elements which have less than 0.03% maximum solid solubility in aluminum. The total amount of these insoluble elements should be no greater than 0.5%. These insoluble elements generally have no significant effect on current output as they do not reduce the solid solubility of tin in aluminum, but they act as a second phase particulate cathodes and large amounts ultimately reduce anodic efficiency by promoting local corrosion of the anode.

Boron may be considered as an insoluble element since it has less than 0.03% maximum solid solubility in aluminum.

Soluble elements may also be added to the alloy. The soluble elements may be considered either lattice expanders or lattice contractors, i.e., ternary addition elements which either expand or contract the aluminum lattice.

Generally, lattice expanders stabilize tin in retained solid solution and permit high galvanic currents to be drawn from the alloy. Lattice expanders may be used in an amount from about 0.001 to 8%, with typical lattice expanders and amounts thereof which may be used including: magnesium from about 0.001 to 7.0% which is particularly preferred; gallium from about 0.005 to 1.0%; zirconium from about 0.001 to 0.3%; bismuth from about 0.001 to 0.5%; indium from about 0.001 to 0.5%; and mixtures thereof. The transition metals listed above, e.g., titanium, might be necessary for grain refining or other effects in combination with lattice expanders which improve the galvanic characteristics.

The primary cell of the present invention may employ any cathode and any electrolyte. Preferably, the primary cell utilizes a consumable unpolarized cathode and a liquid electrolyte. Normally, any consumable or non-consumable and comparatively unpolarized or depolarized cathode may be conveniently employed and optimally is a readily reducible and insoluble metal salt or oxide, for example, a silver salt or oxide or a copper salt or oxide, a catalyzed porous electrode, such as porous metal or carbon wherein oxygen from without is continually consumed.

In the primary cell of the present invention it is preferred to utilize solid, fused silver chloride as a cathode. Alternatively, any silver salt may be utilized as the cathode material, provided the salt is at least as soluble as silver chloride, but sufficiently insoluble to avoid disintegration of the cathode during operation of the cell. Among such other cathodic materials which may be employed are silver oxide, silver chromate, silver sulfate, silver phosphate, silver acetate and silver carbamate. Cells may be formed with cathodes of silver salts more insoluble than silver chloride such as silver bromide and silver iodide, but the voltage is considerably lower since the cathodic material is much more insoluble than the silver chloride. Exemplificative copper compounds include preferably copper oxides.

The electrolytes which may be employed are broadly any liquid or fused or paste electrolyte and preferably the liquid-aqueous type electrolytes. The electrolyte which should preferably be employed should, in addition to being liquid at operating temperatures, be one which does not polarize the anode or the cathode and one free from inhibitive action on the anode. Likewise, non-consumable cathodes, such as graphite, can be used.

The primary cell of the present invention is especially adapted to utilizing sea water as the electrolyte; however, it is apparent that the cells and batteries of the present invention will operate advantageously in electrolytes other than sea water, for example, any aqueous solution of sodium chloride may be conveniently employed, such as a 3.5% aqueous solution of sodium chloride. Similarly, other alkali metal chlorides or alkaline earth metal chlorides will be satisfactory. Other suitable electrolytes, weak or strong, dilute or concentrated may be conveniently employed. Water also yields an operative cell although a considerable time may be required before the cell reaches its full capacity. Exemplificative of the non-aqueous type electrolytes include fused sodium chloride or potassium chloride, including low melting alkali halide eutectics.

Naturally, the primary cell of the present invention may be prepared by any of the conventional means well known in the art. In the preparation of the primary cell of the present invention, for example, the anode and cathode material may be separated or spaced apart by any conventional means, for example, thin films of a chemically stable material such as nylon may be adhered to the anode material. If the particular cell or battery under consideration is intended to operate at a high current density, the electrodes should be more closely spaced. In a cell or battery not intended to operate at high current densities, close spacing is not required. In some cases

rubber strips or tabs at the edges of the electrode sheets may be employed.

The cathode material may be prepared by any of the conventional means, for example, cast sheets of substantial thickness may be employed or rolled silver chloride may be produced by suspending a body of silver, such as silver screen, in a dilute chloride solution for a time sufficient to form a silver chloride coating of the desired thickness. Other means for preparing the cathodic material are well known in the art. It is preferred to set up a plurality of the primary cells spaced from one another so that individual cells are established between the plates of succeeding electrodes when immersed in an electrolyte.

It is one of the findings of the present invention that an improved cathodic protection system may be provided comprising a cathodic metal structure and at least one aluminous sacrificial anode electrically connected thereto, both the metal structure and the anode being in contact with a medium corrosive to said metal structure, said anode comprising the above aluminum alloy of the present invention.

The anodes of the present invention can be used in cathodic protection systems for underground structures, such as pipe lines, foundations, and the like. They may be used in fresh water or in saline aqueous media. They are particularly well suited for use in sea water, and provide cathodic protection systems for protection of iron, such as ships' hulls, ballast tanks, and commercial fishing devices, such as lobster pots, which for the first time are free from the shortcomings of previously used systems.

In carrying out the present invention, the sacrificial anode of the type previously described, is attached to a metal structure to be protected, such as, for example, a ferrous metal structure, by means of a suitable electrical conductor, and then immersed or imbedded in the surrounding corrosive medium, in accordance with the customary practice. The alloy anode may be of any desired shape or size, such as, for example, a cylindrical piece, or a trapezoidal shaped member.

The present invention and improvements resulting therefrom will be more readily apparent from a consideration of the following illustrative examples.

inches (5 mm. x 5 mm.) in cross section and 3 inches (75 mm.) length. They were chemically cleaned and a 10 sq. cm. area was exposed in a "Galvanic Cell Test" substantially as described in an article in the journal of the Electrochemical Society, volume 105, No. 11, starting at p. 629. All determinations were carried out in 0.1 N sodium chloride solution at $25 \pm 0.1^\circ$ C. The galvanic currents were measured continuously by shorting the cell through a 1 ohm resistance and continuously recording the drop in potential. A second set of similar test specimens was subjected to a modified test arrangement, "Impressed Current Test," for which 1 liter of 1.0 N NaCl solution was used and a constant current density of 10 ma./cm.² was maintained on the specimen, as the anode, for 24 hours, employing a 10 cm.² steel cathode. This current density was at least 10 times greater than that in the "Galvanic Cell Test" and it approximates conditions obtained in a larger scale galvanic test where the cathode area is many times larger than the anode area and where low efficiencies may be obtained if there is a tendency to form spongy corrosion product.

Electrochemical tests of the above two types produce a fairly large scatter. Therefore, individual test results are shown. The number of coulombs flowing in 48 hours in the "Galvanic Cell Test" is a measure of the ability of the anode to maintain a protecting current and depends upon the maximum tin being in solid solution or substantially the maximum tin in solid solution with the remainder very finely dispersed. The overall percent efficiency is the anodic efficiency. The weight of sponge in the "Impressed Current Test" refers to the amount of lightly adhering corrosion product containing entrained metallic particles which contributes to low efficiency.

The results are shown in the following table. Alloys A and F, without any boron, have low anodic efficiency in both tests. Alloy A, with deliberately added heavy metal, titanium, has low efficiency and forms more spongy corrosion product. Alloys B, C and D show that when boron is present, the efficiency markedly improves and sponge formation is reduced. Alloy E shows similar improvement for the alloy without deliberate addition of titanium compared with Alloy F.

TABLE I

Alloy No.	Alloy Composition and Method of Casting	Galvanic Cell Test		Impressed Current Test, 10 ma./sq. cm.	
		Coulombs Flowing in 48 hrs.	Overall Percent Efficiency	Total Wt. of Sponge ma./cm. ²	Overall Percent Efficiency
A.....	Al-0.12 Sn-0.15 Bi-0.01 Ti (DC Cast)....	909, 981, 955	33, 35, 35	58.8, 56.8, 53.8 4.3, 2.7	33, 34, 34 64, 68
B.....	Al-0.12 Sn-0.15 Bi-0.004 Ti-0.001 B (DC Cast)	890, 897, 920	53, 56, 54		
C.....	Al-0.12 Sn-0.15 Bi-0.002 Ti-0.022 B (DC Cast)	989, 1,108, 996	50, 54, 52	-----	78, 78, 78
D.....	Al-0.12 Sn-0.15 Bi-0.008 Ti-0.027 B (DC Cast)	1,106, 1,178, 1,176	58, 59, 59	-----	83, 83, 83
E.....	Al-0.12 Sn-0.15 Bi-0.01 B (TM Cast)....	1,070, 1,036, 962	68, 58, 60	----- 27.4, 43.6	84, 84, 84 44, 35
F.....	Al-0.12 Sn-0.15 Bi (TM Cast).....	952, 1,329	36, 38		

EXAMPLES

Various aluminum base alloys were cast by conventional direct chill (DC) casting and tilt mold (TM) methods. In the casting commercial purity aluminum was utilized containing the following impurities: iron 0.05% and silicon 0.03%. As alloying additions, pure tin and bismuth were added, with the alloys containing after casting 0.12% tin and 0.15% bismuth. In addition, some of the alloys contained titanium and boron, with master alloys of aluminum containing titanium and boron being utilized.

All of the alloys were given a homogenization treatment by heating to 620° C. for 16 hours and water quenching to room temperature.

All of the homogenized ingots were then given various tests to determine their galvanic characteristics.

Specimens were prepared from sections of the ingots by machining. Specifically, the specimens used for determining galvanic properties were milled to 0.197 x 0.197

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A cathodic protection system comprising a cathodic metal structure and at least one aluminous sacrificial anode electrically connected thereto, both the metal structure and the anode being in contact with a medium corrosive to said metal structure, said anode being an aluminum base alloy consisting essentially of between 0.04 and 0.5% tin, and between 0.001 and 0.1% boron, with the tin being retained in solid solution to the maximum degree, said maximum degree being 0.1% balance essentially aluminum.

2. The method of cathodically protecting a ferrous metal structure in contact with a medium corrosive there- to which comprises: connecting to said metal structure an aluminous sacrificial anode and immersing said anode in said corrosive medium, wherein said anode is an alumi- num base alloy consisting essentially of between 0.04 and 0.5 percent tin and between 0.001 and 0.1 percent boron, with the tin being retained in solid solution to the maximum degree, said maximum degree being 0.1%, bal- ance essentially aluminum.

3. An aluminum base alloy consisting essentially of between 0.04 and 0.5% tin, between 0.001 and 0.1% boron, with the tin being retained in solid solution to the maximum degree, said maximum degree being 0.1%, bal- ance essentially aluminum.

4. An aluminum base alloy consisting essentially of be- tween 0.04 and 0.5% tin, between 0.001 and 0.1% boron, a material selected from the group consisting of between 0.001 and 8.0% of a lattice expander which has greater than 0.03% maximum solid solubility in aluminum, up to 0.25% of a transition metal, up to 0.10% silicon, up to 0.10% iron and mixtures thereof, with the tin being retained in solid solution to the maximum degree, said maximum degree being 0.1%, balance essentially alumi- num.

5. An alloy according to claim 4 wherein said lattice expander is selected from the group consisting of mag- nesium in an amount from 0.001 to 7.0%, gallium in an amount from 0.005 to 1.0%, zirconium in an amount from 0.001 to 0.3%, bismuth in an amount from 0.001 to 0.5%, indium in an amount from 0.001 to 0.5% and mixtures thereof.

6. In a primary electric cell containing a metal anode, a cathode, and an electrolyte in contact with said anode and said cathode, the improvement wherein said metal anode is of an aluminum base alloy consisting essentially of between 0.04 and 0.5% tin, between 0.001 and 0.1% boron, with the tin being retained in solid solution to the maximum degree, said maximum degree being 0.1%, bal- ance essentially aluminum.

7. A primary electric cell according to claim 6 wherein said cathode is a consumable, unpolarized cathode and wherein said electrolyte is liquid.

8. A primary cell according to claim 7 wherein said cathode is selected from the group consisting of a silver salt, a silver oxide, a copper salt and a copper oxide, and wherein said electrolyte is an aqueous electrolyte.

9. In a primary electric cell containing a metal anode, a cathode, and an electrolyte in contact with said anode and said cathode, the improvement wherein said metal anode is of an aluminum base alloy consisting essentially

of between 0.04 and 0.5% tin, between 0.001 and 0.1% boron, a material selected from the group consisting of between 0.001 and 8.0% of a lattice expander which has greater than 0.03% maximum solid solubility in alumi- num, up to 0.25% of a transition metal, up to 0.10% silicon, up to 0.10% iron, and mixtures thereof, with the tin being retained in solid solution to the maximum degree, said maximum degree being 0.1%, balance essentially aluminum.

10. A primary cell according to claim 9 wherein said lattice expander is selected from the group consisting of magnesium in an amount from 0.001 to 7.0%, gallium in an amount from 0.005 to 1.0%, zirconium in an amount from 0.001 to 0.3%, bismuth in an amount from 0.001 to 0.5%, indium in an amount from 0.001 to 0.5% and mixtures thereof.

11. A cathodic protection system comprising a cathodic metal structure and at least one aluminous sacrificial anode electrically connected thereto, both the metal structure and the anode being in contact with a medium cor- rosive to said metal structure, said anode being an alumi- num base alloy consisting essentially of between 0.04 and 0.5% tin, between 0.001 and 0.1% boron, a mate- rial selected from the group consisting of between 0.001 and 8.0% of a lattice expander which has greater than 0.03% maximum solid solubility in aluminum, up to 0.25% of a transition metal, up to 0.10% silicon, up to 0.10% iron, and mixtures thereof, with the tin being retained in solid solution to the maximum degree, said maximum degree being 0.1%, balance essentially alumi- num.

12. A cathodic protection system according to claim 11 wherein said lattice expander is selected from the group consisting of magnesium in an amount from 0.001 to 7.0 percent, gallium in an amount from 0.005 to 1.0 percent, zirconium in an amount from 0.001 to 0.3 per- cent, bismuth in an amount from 0.001 to 0.5 percent, indium in an amount from 0.001 to 0.5 percent and mix- tures thereof.

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HOWARD S. WILLIAMS, *Primary Examiner.*

50 JOHN R. MACK, *Examiner.*

T. TUNG, *Assistant Examiner.*