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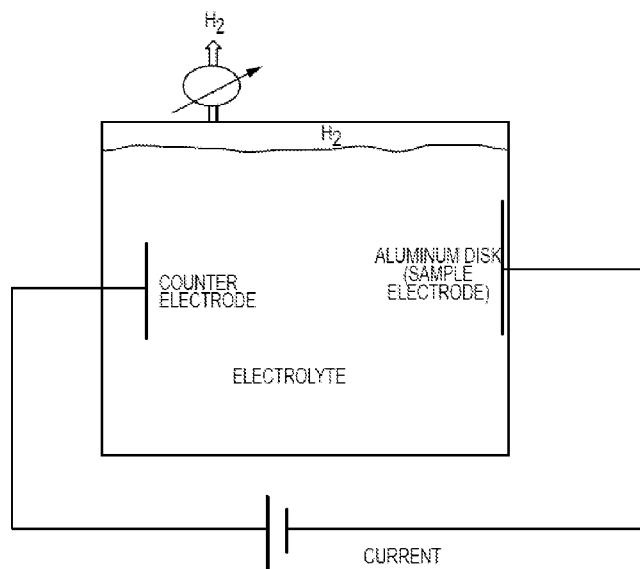


FIG. 1

(57) **Abstract:** An aluminum alloy composition is provided. The aluminum alloy composition includes an effective amount of a corrosion resistant additive, and an effective amount of phosphorous; wherein the corrosion resistant additive and phosphorous are present in amounts sufficient to provide an aluminum electrode alloy with improved corrosion resistance as compared to an aluminum electrode alloy without such corrosion resistant additive and phosphorous, when measured in accordance with an electrochemical cell test.



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KM, ML, MR, NE, SN, TD, TG).

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CORROSION RESISTANT ALUMINUM ALLOY

FIELD OF THE INVENTION

[0001] The present disclosure is directed towards corrosion resistant aluminum alloys.

BACKGROUND

[0002] Clean, sustainable energy is a global concern. Electrochemical cells are utilized as clean, sustainable energy. By commercially deploying these sustainable forms of energy, it is possible to lower the global dependence on fossil fuels.

SUMMARY OF THE INVENTION

[0003] Utilizing aluminum alloy compositions as an electrode (anode) in an electrochemical cell can be evaluated by quantifying and/or qualifying two phenomena: (1) the anodic reaction and (2) the corrosion reaction of the aluminum alloy composition. In the anodic reaction, aluminum reacts with hydroxyl ions which results in the release of electrons, the primary and desirable product of an electrochemical cell. Without being bound by any particular mechanism or theory, it is believed that in the corrosion reaction, the aluminum in the anode material is oxidized in the presence of water and, as the oxygen in the water reacts with the aluminum, aluminum oxide is formed, generating hydrogen gas as a byproduct of the corrosion reaction of the aluminum alloy composition. In the corrosion reaction, aluminum is consumed without contributing to the production of (creating) electrical energy in the electrochemical cell.

[0004] Without being bound by a particular mechanism or theory, it is believed that by reducing the amount of the corrosion reaction, more electrode material is available to participate in the anodic reaction, contributing to the longevity of the anode and production of electrical energy by the electrochemical cell.

[0005] The extent of the corrosion reaction, i.e. the amount of hydrogen generated for an aluminum alloy used as an anode, is a function of electrolyte temperatures and current densities in the electrochemical cell. As operating temperatures and applied current vary for the operation of the cell, so too does the aluminum alloy composition experience varying instances of high anodic reaction and high corrosion reaction windows within the operating parameters/ranges of the electrolytic cell.

i. Composition

[0006] The new aluminum alloys used to produce the new aluminum electrode alloys described herein may be any suitable aluminum alloy having low amounts of iron (e.g. from

0.001 wt. % Fe to 0.06 wt. % Fe) and an effective amount of a corrosion resistant additive plus phosphorous such that the aluminum electrode alloy has improved corrosion resistance as compared to an aluminum electrode alloy without such corrosion resistant additives and phosphorous. For the purposes of this patent application, a reference to an aluminum alloy composition is also a reference to an aluminum electrode alloy composition.

[0007] As used herein, “aluminum alloy” means an alloy having aluminum as the predominant alloying element. As used herein, the phrase “aluminum electrode alloy” means an aluminum electrode alloy configured for use as an anode or cathode in an electrochemical cell. In one embodiment, an aluminum alloy is one of a 1xxx, 2xxx, 3xxx, 4xxx, 5xxx, 6xxx, 7xxx, or 8xxx series aluminum alloys, as defined by the Aluminum Association document “International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys” (2015). In another embodiment, the aluminum alloy is a 1xxx series aluminum alloy. In yet another embodiment, the aluminum alloy is a 2xxx series aluminum alloy. In another embodiment, the aluminum alloy is a 3xxx series aluminum alloy. In yet another embodiment, the aluminum alloy is a 4xxx series aluminum alloy. In another embodiment, the aluminum alloy is a 5xxx series aluminum alloy. In yet another embodiment, the aluminum alloy is 6xxx series aluminum alloy. In another embodiment, the aluminum alloy is a 7xxx series aluminum alloy. In yet another embodiment, the aluminum alloy is an 8xxx series aluminum alloy. In another embodiment, the aluminum alloy is selected from the group consisting of a 1xxx series aluminum alloy and a 5xxx series aluminum alloy. In one embodiment, the aluminum electrode alloy may comprise a 5252 aluminum alloy. In another embodiment, the aluminum electrode alloy may comprise a 5005 aluminum alloy.

[0008] As noted above, the aluminum alloys may include phosphorous. The addition of phosphorous to the aluminum alloy may facilitate, for instance, lower corrosion, i.e. hydrogen generation. In one embodiment, the aluminum alloy includes at least 0.0001 wt. % (1 ppm) P. In another embodiment, the aluminum alloy includes at least 0.0002 wt. % (2 ppm) P. In yet another embodiment, the aluminum alloy includes at least 0.0003 wt. % (3 ppm) P. In another embodiment, the aluminum alloy includes at least 0.0004 wt. % (4 ppm) P. In yet another embodiment, the aluminum alloy includes at least 0.0005 wt. % (5 ppm) P. In another embodiment, the aluminum alloy includes at least 0.001 wt. % (10 ppm) P. In one embodiment, the aluminum alloy includes less than 0.10 wt. % (1000 ppm) P. In another embodiment, the aluminum alloy includes not greater than 0.0975 wt. % (975 ppm) P. In yet

another embodiment, the aluminum alloy includes not greater than 0.095 wt. % (950 ppm) P. In another embodiment, the aluminum alloy includes not greater than 0.0925 wt. % (925 ppm) P. In yet another embodiment, the aluminum alloy includes not greater than 0.09 wt. % (900 ppm) P. In another embodiment, the aluminum alloy includes not greater than 0.0875 wt. % (875 ppm) P. In yet another embodiment, the aluminum alloy includes not greater than 0.085 wt. % (850 ppm) P. In another embodiment, the aluminum alloy includes not greater than 0.0825 wt. % (825 ppm) P. In yet another embodiment, the aluminum alloy includes not greater than 0.08 wt. % (800 ppm) P. In another embodiment, the aluminum alloy includes not greater than 0.06 wt. % (600 ppm) P. In yet another embodiment, the aluminum alloy includes not greater than 0.04 wt. % (400 ppm) P. In another embodiment, the aluminum alloy includes not greater than 0.02 wt. % (200 ppm) P. In yet another embodiment, the aluminum alloy includes not greater than 0.01 wt. % (100 ppm) P. In another embodiment, the aluminum alloy includes not greater than 0.005 wt. % (50 ppm) P. In one embodiment, the aluminum alloy includes 0.0001 to 0.10 wt. % (1 to 1000 ppm) P. In one embodiment, the aluminum alloy includes 0.0005 to 0.08 wt. % (5 to 800 ppm) P. In another embodiment, the aluminum alloy includes 0.0005 to 0.06 wt. % (5 to 600 ppm) P. In yet another embodiment, the aluminum alloy includes 0.0005 to 0.04 wt. % (5 to 400 ppm) P. In another embodiment, the aluminum alloy includes 0.0005 to 0.02 wt. % (5 to 200 ppm) P. In yet another embodiment, the aluminum alloy includes 0.0005 to 0.01 wt. % (5 to 100 ppm) P. In another embodiment, the aluminum alloy includes 0.0005 to 0.005 wt. % (5 to 50 ppm) P. In yet another embodiment, the aluminum alloy includes 0.001 to 0.08 wt. % (10 to 800 ppm) P.

[0009] As noted above, the aluminum alloys generally comprise an effective amount of a corrosion resistant additive. Examples of corrosion resistant additives are defined and described in commonly-owned International Patent Application No. PCT/US2017/066053, entitled, "Corrosion Resistant Aluminum Alloy," filed December 13, 2017, published as WO2018/112018. Various embodiments relating to corrosion resistant additives are described in section i.a., below.

[0010] As noted above, the aluminum alloys may include from 0.001 to 0.06 wt. % (10 to 600 ppm) Fe. Low iron content may facilitate, for instance, lower corrosion, i.e. hydrogen generation. In one embodiment, the aluminum alloy includes at least 0.001 wt. % Fe (10 ppm). In another embodiment, the aluminum alloy includes at least 0.0015 wt. % (15 ppm) Fe. In one embodiment, the aluminum alloy includes not greater than 0.06 wt. % (600 ppm) Fe. In another embodiment, the aluminum alloy includes not greater than 0.04 wt. %

(400 ppm) Fe. In yet another embodiment, the aluminum alloy includes not greater than 0.03 wt. % (300 ppm) Fe. In another embodiment, the aluminum alloy includes not greater than 0.025 wt. % (250 ppm) Fe. In yet another embodiment, the aluminum alloy includes not greater than 0.02 wt. % (200 ppm) Fe. In another embodiment, the aluminum alloy includes not greater than 0.01 wt. % (100 ppm) Fe. In yet another embodiment, the aluminum alloy includes not greater than 0.0075 wt. % (75 ppm). In another embodiment, the aluminum alloy includes not greater than 0.005 wt. % (50 ppm) Fe. Fe. In one embodiment, the aluminum alloy includes 0.001 to 0.04 wt. % (10 to 400 ppm) Fe. In another embodiment, the aluminum alloy includes 0.001 to 0.03 wt. % (10 to 300 ppm) Fe. In yet another embodiment, the aluminum alloy includes 0.001 to 0.025 wt. % (10 to 250 ppm) Fe. In another embodiment, the aluminum alloy includes 0.001 to 0.01 wt. % (10 to 100 ppm) Fe. In yet another embodiment, the aluminum alloy includes 0.001 to 0.0075 wt. % (10 to 75 ppm) Fe. In another embodiment, the aluminum alloy includes 0.001 to 0.005 wt. % (10 to 50 ppm) Fe. In yet another embodiment, the aluminum alloy includes 0.015 to 0.025 wt. % (150 to 250 ppm) Fe. Appropriate aluminum alloy base materials may be used to facilitate casting of the new aluminum alloy; such base materials generally will have similar iron and silicon contents. Thus, the aluminum alloys described herein generally contain silicon levels similar to the above-described levels of iron.

[0011] As noted above, the new aluminum alloys may be a 5xxx series alloy. In one embodiment, the aluminum alloy may include at least 0.01 wt. % Mg. In another embodiment, the aluminum alloy may include at least 0.1 wt. % Mg. In yet another embodiment, the aluminum alloy may include at least 0.5 wt. % Mg. In another embodiment, the aluminum alloy may include at least 1.0 wt. % Mg. In yet another embodiment, the aluminum alloy may include at least 1.5 wt. % Mg. In another embodiment, the aluminum alloy may include at least 2.0 wt. % Mg. In one embodiment, the aluminum alloy may include not greater than 5.0 wt. % Mg. In one embodiment, the aluminum alloy may include not greater than 4.0 wt. % Mg. In another embodiment, the aluminum alloy may include not greater than 3.0 wt. % Mg. In yet another embodiment, the aluminum alloy may include not greater than 2.0 wt. % Mg. In another embodiment, the aluminum alloy may include not greater than 1.5 wt. % Mg. In yet another embodiment, the aluminum alloy may include not greater than 1.0 wt. % Mg. In another embodiment, the aluminum alloy may include not greater than 0.5 wt. % Mg. In one embodiment, the aluminum alloy may include 0.01 to 5.0 wt. % Mg. In another embodiment, the aluminum alloy may include 0.1 to 5.0 wt. % Mg. In

yet another embodiment, the aluminum alloy may include 0.5 to 5.0 wt. % Mg. In another embodiment, the aluminum alloy may include 1.0 to 5.0 wt. % Mg. In yet another embodiment, the aluminum alloy may include 1.5 to 5.0 wt. % Mg. In another embodiment, the aluminum alloy may include 2.0 to 5.0 wt. % Mg. In yet another embodiment, the aluminum alloy may include 3.0 to 5.0 wt. % Mg. In another embodiment, the aluminum alloy may include 4.0 to 5.0 wt. % Mg. In another embodiment, the aluminum alloy may include 0.01 to 4.0 wt. % Mg. In yet another embodiment, the aluminum alloy may include 0.01 to 3.0 wt. % Mg. In another embodiment, the aluminum alloy may include 0.01 to 2.0 wt. % Mg. In another embodiment, the aluminum alloy may include 0.01 to 1.5 wt. % Mg. In another embodiment, the aluminum alloy may include 0.01 to 1.0 wt. % Mg. In one embodiment, the aluminum alloy has no Mg (i.e. includes Mg as an impurity only).

[0012] In some embodiments, the new aluminum alloy may be substantially free of impurities, meaning that the alloy contains no more than 0.10 wt. % of any one impurity, and that the total combined amount of the impurities in the aluminum alloy does not exceed 0.35 wt. %. In one embodiment, each one of the impurities, individually, does not exceed 0.05 wt. % in the aluminum alloy, and the total combined amount of the impurities does not exceed about 0.15 wt. %. In another embodiment, each one of the impurities, individually, does not exceed 0.03 wt. % in the aluminum alloy, and the total combined amount of the impurities does not exceed about 0.12 wt. %. In yet another embodiment, each one of the impurities, individually, does not exceed 0.01 wt. % in the aluminum alloy, and the total combined amount of the impurities does not exceed about 0.03 wt. %.

i.a. Corrosion Resistant Additives

[0013] As noted above, the aluminum alloys generally comprise an effective amount of a corrosion resistant additive. As used herein, an “effective amount” in this embodiment is a large enough quantity to provide an improved corrosion resistance in the aluminum alloy composition (e.g. measurable, observable, and/or quantifiable). As used herein, “corrosion resistant additive” refers to an addition of a component to the aluminum alloy in order to impart corrosion resistance (e.g. reduce corrosion when evaluated as an electrode in an electrochemical cell) as compared to the alloy’s corrosion without such additions.

[0014] In one embodiment, the corrosion resistant additive is Zn. In another embodiment, the corrosion resistant additive is Ga. In yet another embodiment, the corrosion resistant additive is Zn and Ga. In another embodiment, the corrosion resistant additive is selected from the group consisting of: Zn, Ga, and combinations thereof.

[0015] In some embodiments, the effective amount of corrosion resistant additive is at least 0.0005 wt. % (5 ppm); at least 0.001 wt. % (10 ppm); at least 0.0015 wt. % (15 ppm); at least 0.002 wt. % (20 ppm); at least 0.005 wt. % (50 ppm); at least 0.01 wt. % (100 ppm); at least 0.015 wt. % (150 ppm); at least 0.02 wt. % (200 ppm); at least 0.025 wt. % (250 ppm); at least 0.03 wt. % (300 ppm); at least 0.035 wt. % (350 ppm); at least 0.04 wt. % (400 ppm); at least 0.045 wt. % (450 ppm); at least 0.05 wt. % (500 ppm); at least 0.055 wt. % (550 ppm); at least 0.06 wt. % (600 ppm); at least 0.065 wt. % (650 ppm); at least 0.07 wt. % (700 ppm); at least 0.075 wt. % (750 ppm); at least 0.08 wt. % (800 ppm); at least 0.085 wt. % (850 ppm); at least 0.09 wt. % (900 ppm); at least 0.095 wt. % (950 ppm); or at least 0.10 wt. % (1000 ppm), where at least some (an effective amount of) Zn and Ga are present, when both Zn and Ga are utilized as the corrosion resistant additives.

[0016] In some embodiments, the effective amount of corrosion resistant additive is not greater than 0.0005 wt. % (5 ppm); not greater than 0.001 wt. % (10 ppm); not greater than 0.0015 wt. % (15 ppm); not greater than 0.002 wt. % (20 ppm); not greater than 0.005 wt. % (50 ppm); not greater than 0.01 wt. % (100 ppm); not greater than 0.015 wt. % (150 ppm); not greater than 0.02 wt. % (200 ppm); not greater than 0.025 wt. % (250 ppm); not greater than 0.03 wt. % (300 ppm); not greater than 0.035 wt. % (350 ppm); not greater than 0.04 wt. % (400 ppm); not greater than 0.045 wt. % (450 ppm); not greater than 0.05 wt. % (500 ppm); not greater than 0.055 wt. % (550 ppm); not greater than 0.06 wt. % (600 ppm); not greater than 0.065 wt. % (650 ppm); not greater than 0.07 wt. % (700 ppm); not greater than 0.075 wt. % (750 ppm); not greater than 0.08 wt. % (800 ppm); not greater than 0.085 wt. % (850 ppm); not greater than 0.09 wt. % (900 ppm); not greater than 0.095 wt. % (950 ppm); or not greater than 0.10 wt. % (1000 ppm), where not greater than some (an effective amount of) Zn and Ga are present, when both Zn and Ga are utilized as the corrosion resistant additives.

[0017] In one or more of the aforementioned embodiments, the amount of Zn as a corrosion resistant additive as an individual addition is not greater than 0.05 wt. % of the corrosion resistant alloy. In some embodiments, the effective amount of corrosion resistant additive of Zn is at least 0.002 wt. % (20 ppm); at least 0.005 wt. % (50 ppm); at least 0.01 wt. % (100 ppm); at least 0.015 wt. % (150 ppm); at least 0.02 wt. % (200 ppm); at least 0.025 wt. % (250 ppm); at least 0.03 wt. % (300 ppm); at least 0.035 wt. % (350 ppm); at least 0.04 wt. % (400 ppm); at least 0.045 wt. % (450 ppm); at least 0.05 wt. % (500 ppm). In some embodiments, the effective amount of corrosion resistant additive of Zn is not greater

than 0.002 wt. % (20 ppm); not greater than 0.005 wt. % (50 ppm); not greater than 0.01 wt. % (100 ppm); not greater than 0.015 wt. % (150 ppm); not greater than 0.02 wt. % (200 ppm); not greater than 0.025 wt. % (250 ppm); not greater than 0.03 wt. % (300 ppm); not greater than 0.035 wt. % (350 ppm); not greater than 0.04 wt. % (400 ppm); not greater than 0.045 wt. % (450 ppm); not greater than 0.05 wt. % (500 ppm). In some embodiments, an effective amount of the corrosion resistant additive of Zn is at least 0.002 wt. % (20 ppm) to not greater than 0.05 wt. % (500 ppm).

[0018] In one or more of the aforementioned embodiments, the amount of Ga as a corrosion resistant additive as an individual addition is not greater than 0.06 wt. % of the corrosion resistant alloy. In one or more of the aforementioned embodiments, the amount of Ga as a corrosion resistant additive as an individual addition is not greater than 0.0 wt. % of the corrosion resistant alloy. In some embodiments, the effective amount of corrosion resistant additive of Ga is at least 0.0005 wt. % (5 ppm); at least 0.001 wt. % (10 ppm); at least 0.0015 wt. % (15 ppm); at least 0.002 wt. % (20 ppm); at least 0.005 wt. % (50 ppm); at least 0.01 wt. % (100 ppm); at least 0.015 wt. % (150 ppm); at least 0.02 wt. % (200 ppm); at least 0.025 wt. % (250 ppm); at least 0.03 wt. % (300 ppm); at least 0.035 wt. % (350 ppm); at least 0.04 wt. % (400 ppm); at least 0.045 wt. % (450 ppm); at least 0.05 wt. % (500 ppm); at least 0.055 wt. % (550 ppm); or at least 0.06 wt. % (600 ppm). In some embodiments, the effective amount of corrosion resistant additive of Ga is not greater than 0.0005 wt. % (5 ppm); not greater than 0.001 wt. % (10 ppm); not greater than 0.0015 wt. % (15 ppm); not greater than 0.002 wt. % (20 ppm); not greater than 0.005 wt. % (50 ppm); not greater than 0.01 wt. % (100 ppm); not greater than 0.015 wt. % (150 ppm); not greater than 0.02 wt. % (200 ppm); not greater than 0.025 wt. % (250 ppm); not greater than 0.03 wt. % (300 ppm); not greater than 0.035 wt. % (350 ppm); not greater than 0.04 wt. % (400 ppm); not greater than 0.045 wt. % (450 ppm); not greater than 0.05 wt. % (500 ppm); not greater than 0.055 wt. % (550 ppm); not greater than 0.06 wt. % (600 ppm). In some embodiments, an effective amount of the corrosion resistant additive of Ga is at least 0.002 wt. % (20 ppm) to not greater than 0.05 wt. % (500 ppm).

[0019] In some embodiments, an effective amount of the corrosion resistant additive is at least 0.0005 wt. % (5 ppm) to not greater than 0.06 wt. % (600 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.001 wt. % (10 ppm) to not greater than 0.03 wt. % (300 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.0005 wt. % (5 ppm) to not greater than

0.01 wt. % (100 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.0005 wt. % (5 ppm) to not greater than 0.005 wt. % (50 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.002 wt. % (20 ppm) to not greater than 0.01 wt. % (100 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.002 wt. % (20 ppm) to not greater than 0.005 wt. % (50 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.002 wt. % (20 ppm) to not greater than 0.10 wt. % (1000 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.005 wt. % (50 ppm) to not greater than 0.10 wt. % (1000 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.005 wt. % (50 ppm) to not greater than 0.07 wt. % (700 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.005 wt. % (50 ppm) to not greater than 0.05 wt. % (500 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.005 wt. % (50 ppm) to not greater than 0.03 wt. % (300 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.005 wt. % (50 ppm) to not greater than 0.02 wt. % (200 ppm). In some embodiments, an effective amount of the corrosion resistant additive is at least 0.005 wt. % (50 ppm) to not greater than 0.01 wt. % (100 ppm). In some embodiments, an effective amount of corrosion resistant additive is at least 0.002 wt. % (20 ppm) to not greater than 0.05 wt. % (500 ppm) of each additive, where the total amount of corrosion resistant additive is not greater than 0.10 wt. % (1000 ppm).

[0020] In some embodiments, an effective amount of corrosion resistant additive is not greater than 0.10 wt. % (1000 ppm), where at least some corrosion resistant additive is present. In some embodiments, an effective amount of corrosion resistant additive is not greater than 0.05 wt. % (500 ppm), where at least some corrosion resistant additive is present. In some embodiments, an effective amount of corrosion resistant additive is not greater than 0.025 wt. % (250 ppm), where at least some corrosion resistant additive is present. In some embodiments, an effective amount of corrosion resistant additive is not greater than 0.01 wt. % (100 ppm), where at least some corrosion resistant additive is present. In some embodiments, an effective amount of corrosion resistant additive is not greater than 0.005 wt. % (50 ppm), where at least some corrosion resistant additive is present. In some embodiments, an effective amount of corrosion resistant additive is not greater than 0.002 wt. % (20 ppm), where at least some corrosion resistant additive is present.

[0021] In any of the foregoing embodiments, the corrosion resistant additive is Zn and Ga in equal amounts. In any of the foregoing embodiments, the corrosion resistant additive is Zn and Ga, with a greater amount of Zn than Ga. In any of the foregoing embodiments, the corrosion resistant additive is Zn and Ga, with a lesser amount of Zn than Ga.

ii. Processing

[0022] The new aluminum alloys described herein may be formed/processed by any suitable processing method. In one embodiment, and with reference now to FIG. 4, a method comprises casting the aluminum alloy (100) and then forming an aluminum electrode alloy (200) from the cast aluminum alloy. The composition of the aluminum alloy may be any composition described in Section i, above.

[0023] Regarding the casting step (100), the casting may be any suitable casting method. In one embodiment, the casting (100) may be continuous casting. In one embodiment, the continuous casting comprises continuous casting as described in U.S. Patent Nos. 7,823,623, 7,380,583, and 6,672,368. In another embodiment, the continuous casting comprises roll casting. In yet another embodiment, the continuous casting comprises belt casting. In another embodiment, the continuous casting comprises block casting. In one embodiment, the continuous casting may result in an as-cast product in the form of a strip. In one embodiment, the casting may be shape casting. In one embodiment, the shape casting comprises die casting. In one embodiment, the casting (100) may be semi-continuous casting. In one embodiment, the semi-continuous casting may be direct chill casting. In one embodiment, the direct chill casting may result in an as-cast product in the form of an ingot or billet. In one embodiment, the casting comprises additive manufacturing processes.

[0024] In one embodiment, the casting step (100) comprises solidifying a melt (150) of the aluminum alloy. The solidification rate of the solidifying step (150) may be any appropriate rate that facilitates achievement of a suitable amount of iron particles in the aluminum alloy. As used herein, “solidification rate” means the rate of cooling of a molten material (e.g. molten alloy, molten aluminum alloy), which is defined as the rate of temperature loss (in Kelvin/second) in the liquid metal immediately ahead of the solidification front. For example, solidification of a molten aluminum alloy during cooling occurs over a temperature range, which depends upon the alloying elements in that particular alloy material. As a non-limiting example, the solidification rate is sometimes deduced and/or quantified from the spacing of the secondary dendrite arms in the as-cast product. In one

embodiment, the solidification rate is selected based, at least in part, on the amount of iron in solid solution, e.g. as shown in FIG. 1.

[0025] The amount of iron in the aluminum alloy may be related to the amount of hydrogen generated when a current is applied to an aluminum electrode alloy in an electrochemical cell. The total amount of iron in the as-cast alloy is the sum of iron in solid solution and the iron contained in iron-bearing particles (“iron particles”). Iron in solid solution may contribute less to the hydrogen generation than iron particles. Thus, the presence of iron particles may be detrimental vis-à-vis hydrogen generation. In one embodiment, and referring back to FIG 4, as a result of the solidification rate of the casting process (100), the cast aluminum alloy may contain iron in solid solution and/or iron particles. In one embodiment, the total amount of iron in the as-cast alloys may be determined by chemical analysis such as a Quantometer (spark source optical emission spectrometry). In one embodiment, the volume fraction of iron particles (vol. % of iron) in the as-cast alloys may be quantified by SEM analysis. The quantification process is described in detail in Example 3.

[0026] In one embodiment, an as-cast aluminum alloy includes not greater than 0.03 vol. % of iron particles. In another embodiment, an as-cast aluminum alloy includes not greater than 0.02 vol. % of iron particles. In yet another embodiment, an as-cast aluminum alloy includes not greater than 0.01 vol. % of iron particles. In another embodiment, an as-cast aluminum alloy includes not greater than 0.005 vol. % of iron particles. In one embodiment, the iron particles are iron-bearing intermetallic particles. In another embodiment, the iron particles consist essentially of iron.

[0027] In one embodiment, the solidification rate is at or above a threshold solidification rate, and the threshold solidification rate is sufficiently high to achieve a volume fraction of iron particles in the as-cast product of not greater than 0.03 vol. %. In another embodiment the solidification rate is at or above a threshold solidification rate, and the threshold solidification rate is sufficiently high to achieve a volume fraction of iron particles in the as-cast product of not greater than 0.02 vol. %. In yet another embodiment the solidification rate is at or above a threshold solidification rate, and the threshold solidification rate is sufficiently high to achieve a volume fraction of iron particles in the as-cast product of not greater than 0.01 vol. %. In another embodiment the solidification rate is at or above a threshold solidification rate, and the threshold solidification rate is sufficiently high to

achieve a volume fraction of iron particles in the as-cast product of not greater than 0.005 vol. %.

[0028] In one embodiment, the casting process is conducted to achieve a solidification rate of at least 10 Kelvin/second (K/s). In another embodiment, the casting process is conducted to achieve a solidification rate of at least 50 K/s. In yet another embodiment, the casting process is conducted to achieve a solidification rate of at least 70 K/s. In another embodiment, the casting process is conducted to achieve a solidification rate of at least 100 K/s. In yet another embodiment, the casting process is conducted to achieve a solidification rate of at least 150 K/s. In one embodiment, the casting process is conducted to achieve a solidification rate of not greater than 200 K/s. In another embodiment, the casting process is conducted to achieve a solidification rate of not greater than 500 K/s. In yet another embodiment, the casting process is conducted to achieve a solidification rate of not greater than 3000 K/s. In one embodiment, the casting process is conducted to achieve a solidification rate of 10K/s to 200 K/s. In yet another embodiment, the casting process is conducted to achieve a solidification rate of 70 K/s to 200 K/s. In another embodiment, the casting process is conducted to achieve a solidification rate of 100 K/s to 200 K/s. In yet another embodiment, the casting process is conducted to achieve a solidification rate of 150 K/s to 200 K/s. In another embodiment, the casting process is conducted to achieve a solidification rate of 10 K/s to 150 K/s. In yet another embodiment, the casting process is conducted to achieve a solidification rate of 50 K/s to 150 K/s. In another embodiment, the casting process is conducted to achieve a solidification rate of 50 K/s to 100 K/s. In yet another embodiment, the casting process is conducted to achieve a solidification rate of 50 K/s to 75 K/s. In one embodiment, the casting process is conducted to achieve a solidification rate of 10 K/s to 3000 K/s. In one embodiment, the casting process is conducted to achieve a solidification rate is 50 K/s to 3000 K/s. In one embodiment, the casting process is conducted to achieve a solidification rate of 50 K/s to 500 K/s.

[0029] With continued reference to FIG. 4, in embodiments where continuous casting is used, after the casting (100), the as-cast product may have any suitable as-cast thickness (e.g. to achieve appropriate solidification rates (150)). Faster solidification rates may be achieved in thinner as-cast alloys. In one embodiment, the as-cast aluminum alloy comprises a thickness of at least 1 millimeter (mm). In another embodiment, the as-cast aluminum alloy comprises a thickness of at least 2 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of at least 3 mm. In another embodiment, the as-cast aluminum

alloy comprises a thickness of at least 5 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of at least 10 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of at least 12 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of at least 15 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of at least 20 mm. In one embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 25 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 20 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 15 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 12 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 10 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 8 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 5 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 3 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of not greater than 2 mm. In one embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 25 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 20 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 15 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 12 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 10 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 8 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 5 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 3 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of 1 to 2 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of 2 to 25 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of 3 to 25 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of 5 to 25 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of 10 to 25 mm. In another embodiment, the as-cast aluminum alloy comprises a thickness of 12 to 25 mm. In yet another embodiment, the as-cast aluminum alloy comprises a thickness of 15 to 25 mm. In another embodiment, the as-cast aluminum electrode alloy comprises a thickness of 20 to 25 mm.

[0030] With continued reference to FIG. 4, after casting (100), the cast aluminum alloy may be formed into an aluminum electrode alloy (200). In one embodiment, the forming may comprise working of the as-cast alloy. In one embodiment, due to the working, the formed aluminum electrode alloy may comprise a wrought microstructure. In one embodiment, the working may include rolling. In one embodiment, the rolling may include hot and/or cold rolling. In one embodiment, the rolled product is a sheet. In another embodiment, the rolled product is a foil. In yet another embodiment, the rolled product is a plate. In one embodiment, the working may include extruding. In another embodiment, the working may include forging. In one embodiment, the working may comprise free form forging, also known as open die forging. In one embodiment, the forming may include solution heat treatment.

[0031] Referring now to FIG. 5, after the forming step (200), the method may comprise producing the final product form (300). In one embodiment, the producing (300) may comprise machining. In another embodiment, the producing (300) may comprise cutting. In yet another embodiment, the producing (300) may comprise stamping. In another embodiment the producing (300) comprises producing disc. In yet another embodiment, the producing (300) comprises producing a block.

[0032] With continued reference to FIG. 5 an aluminum alloy may be selected (50) from one of the previously described aluminum alloy compositions. An appropriate aluminum alloy may be selected, e.g. to achieve a low volume fraction of iron particles. In one embodiment, a user may predetermine an aluminum alloy composition prior to the selecting step (50).

iii. Properties

[0033] Without being bound by any particular mechanism or theory, it is believed that using phosphorous in combination with effective amounts of corrosion resistant additives (e.g. Zn and/or Ga) in aluminum alloys will provide improved corrosion resistance (e.g. reduced corrosion), as compared to aluminum alloys that do not have phosphorous and effective amounts of corrosion resistant additives (e.g. Zn and/or Ga). In one embodiment, improved corrosion resistance of an electrode in an electrochemical cell may be realized during a wide range of electrochemical cell operating conditions (e.g. temperature and current efficiency). In particular, it is believed that using phosphorous in combination with effective amounts of corrosion resistant additives (e.g. Zn and/or Ga) will provide significant improvement to corrosion resistance at electrochemical cell operating conditions of high

corrosion (e.g. low current densities and/or low temperatures) over aluminum alloys without phosphorous and effective amounts of corrosion resistant additives (e.g. Zn and/or Ga).

[0034] The figures constitute a part of this specification and include illustrative embodiments of the present invention and illustrate various objects and features thereof. In addition, any measurements, specifications and the like shown in the figures are intended to be illustrative, and not restrictive. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for teaching one skilled in the art to variously employ the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] FIG. 1 is a schematic view of an example of an electrochemical cell that is configured for use in evaluating the corrosion of electrodes in an electrolyte in accordance with the present disclosure.

[0036] FIG. 2 is a graph showing the hydrogen generation for various Example 1 low iron alloys.

[0037] FIG. 3 is a graph showing the hydrogen generation for various Example 1 medium iron alloys.

[0038] FIG. 4 is a flow chart illustrating one embodiment of the processing steps for producing an aluminum electrode alloy.

[0039] FIG. 5 is a flow chart illustrating another embodiment of the processing steps for producing an aluminum electrode alloy.

DETAILED DESCRIPTION

[0040] The various embodiments to the present disclosure will be further explained with reference to the attached drawings, wherein like structures are referred to by like numerals throughout the several views. The drawings shown are not necessarily to scale, with emphasis instead generally being placed upon illustrating the principles of the present invention. Further, some features may be exaggerated to show details of particular components.

[0041] Among those benefits and improvements that have been disclosed, other objects and advantages of this invention will become apparent from the following description taken in conjunction with the accompanying figures. Detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely illustrative of the invention that may be embodied in various forms.

In addition, each of the examples given in connection with the various embodiments of the invention is intended to be illustrative, and not restrictive.

[0042] Throughout the specification and claims, the following terms take the meanings explicitly associated herein, unless the context clearly dictates otherwise. The phrases “in one embodiment” and “in some embodiments” as used herein do not necessarily refer to the same embodiment(s), though they may. Furthermore, the phrases “in another embodiment” and “in some other embodiments” as used herein do not necessarily refer to a different embodiment, although they may. Thus, as described below, various embodiments of the invention may be readily combined, without departing from the scope or spirit of the invention.

[0043] In addition, as used herein, the term "or" is an inclusive "or" operator, and is equivalent to the term "and/or," unless the context clearly dictates otherwise. The term "based on" is not exclusive and allows for being based on additional factors not described, unless the context clearly dictates otherwise. In addition, throughout the specification, the meaning of "a," "an," and "the" include plural references. The meaning of "in" includes "in" and "on".

[0044] The following examples are intended to illustrate the invention and should not be construed as limiting the invention in any way.

Examples:

Example 1 – Preparing Aluminum Electrode Alloy Samples

[0045] Aluminum electrode alloys, having the compositions shown in Table 1, were cast as ingots, rolled to the desired thickness, and machined into disks (samples) having the desired thickness and a diameter, with a sufficient cross-sectional surface area to provide a viable testing surface for immersion into an electrochemical cell, schematically depicted in FIG. 1. Two general categories of samples were tested: low-iron samples (e.g. <0.002 wt. % or <20 ppm iron, Control 1 and Alloys 1-3) and medium-iron samples (about 0.02 wt. % or 200 ppm iron, Control 2 and Alloys 4-5). All samples included about 2.5 wt. % Mg.

Table 1 - Composition of Ex. 1 Alloys (in ppm)

Composition in wt. %							
Sample Description	Sample Name	Si	Fe	Ga	Zn	P	Mg
Low Fe Control	Control 1	0.004 (40 ppm)	0.002 (20 ppm)	--	--	--	2.61
Low Fe + P	Alloy 1	0.005 (50 ppm)	0.002 (20 ppm)	--	--	0.0009 (9 ppm)	2.61

Low Fe + Zn, Ga	Alloy 2	0.0014 (14 ppm)	0.0013 (13 ppm)	0.0033 (33 ppm)	0.0042 (42 ppm)	--	2.55
Low Fe + Zn, Ga, P	Alloy 3	0.0019 (19 ppm)	0.0022 (22 ppm)	0.0037 (37 ppm)	0.0045 (45 ppm)	0.0009 (9 ppm)	2.55
200 ppm Fe control	Control 2	0.021 (210 ppm)	0.022 (220 ppm)	--	--	--	2.52
200 ppm Fe + P	Alloy 4	0.019 (190 ppm)	0.018 (180 ppm)	--	--	0.0019 (19 ppm)	2.52
200 ppm Fe + P, Zn, Ga	Alloy 5	0.022 (220 ppm)	0.020 (200 ppm)	0.0034 (34 ppm)	0.0037 (37 ppm)	0.0023 (23 ppm)	2.52

[0046] After casting, the disks of Controls 1-2 and Alloys 1-5 were tested for corrosion in an electrochemical cell, as described below.

Example 2 – Testing the Aluminum Electrode Alloy Product Samples

[0047] Controls 1-2 and Alloys 1-5 were tested for hydrogen generation via an electrochemical cell system (schematically depicted in FIG. 1). The electrochemical cell consisted of a counter electrode and an aluminum electrode (anode) alloy (the control or sample) submerged in an aqueous electrolyte. The electrochemical cell was equipped with a mass-flow meter for measuring hydrogen gas evolved from the aluminum electrode alloy product. Current was applied to the electrochemical cell and hydrogen was measured to quantify corrosion.

[0048] All samples were tested according to the following procedure. A predefined temperature-and-current step control program was applied to the cell so that the hydrogen evolution was measured over a set range of operating temperatures, i.e. between room temperature and 100 °C and over a set of current densities, ranging from 0 to 300 mA/cm².

[0049] The samples were run under identical conditions including electrolyte temperature, applied current, and test duration. Results were generated by accumulating the overall amount of hydrogen measured by the mass flow meter. Without being bound by a particular mechanism theory, it is believed that the overall amount of hydrogen generated by the system corresponds to the corrosion reaction (undesired side reaction). Thus, the less hydrogen produced, the more corrosion resistant the aluminum anode alloy is that is being evaluated.

[0050] Referring now to in FIG. 2, which shows data for the low-iron samples, Control 1 generated 1153 cm³ of hydrogen. Alloy 1 generated 1628 cm³ of hydrogen. Both Alloys 2 and 3 generated significantly less hydrogen at 370 cm³ and 313 cm³. There was a significant

improvement in hydrogen generation over the control when Zn and Ga are added to the low-iron alloy (Alloy 2). There was even further improvement, and the lowest hydrogen generated of all samples, with the addition of Zn, Ga and P to the low-iron alloy (Alloy 3). There was no improvement, and in fact, hydrogen generation increased with the addition of only phosphorous to the low-iron alloy (Alloy 1).

[0051] Referring now to in FIG. 3, which shows data for the medium-iron samples, Control 2 generated 2728 cm³. Alloys 4 and 5 both generated less hydrogen than the control at 2673 cm³ and 2621 cm³, respectively. Adding phosphorous (Alloy 4) to the medium-iron alloy resulted in some improvement over the control, while the addition of Zn, Ga and P (Alloy 5) resulted in the largest improvement over the control.

[0052] While a number of embodiments of the present invention have been described, it is understood that these embodiments are illustrative only, and not restrictive, and that many modifications may become apparent to those of ordinary skill in the art. Further still, the various steps may be carried out in any desired order (and any desired steps may be added and/or any desired steps may be eliminated).

CLAIMS

What is claimed is:

1. An aluminum electrode alloy comprising:
 - not greater than 600 ppm iron;
 - an effective amount of a corrosion resistant additive; and
 - an effective amount of phosphorous;wherein the corrosion resistant additive and phosphorous are present in an amount to provide an aluminum electrode alloy with improved corrosion resistance as compared to an aluminum electrode alloy without such corrosion resistant additive, when measured in accordance with an electrochemical cell test.
2. The aluminum electrode alloy composition of claim 1, wherein the effective amount of phosphorous comprises less than 1000 ppm phosphorous.
3. The aluminum electrode alloy composition of claim 2, wherein the effective amount of phosphorous comprises at least 1 ppm phosphorous.
4. The aluminum electrode alloy composition of any of the preceding claims, wherein the effective amount of phosphorous comprises not greater than 800 ppm phosphorous, or not greater than 600 ppm phosphorous, or not greater than 400 ppm phosphorous, or not greater than 200 ppm phosphorous, or not greater than 100 ppm phosphorous, or not greater than 50 ppm phosphorous.
5. The aluminum electrode alloy composition of any of the preceding claims, wherein the effective amount of phosphorous comprises at least 2 ppm phosphorous, or at least 3 ppm phosphorous, or at least 4 ppm phosphorous, or at least 5 ppm phosphorous, or at least 10 ppm phosphorous.
6. The aluminum electrode alloy composition of any of the preceding claims, wherein the aluminum electrode alloy comprises at least 10 ppm iron, or at least 15 ppm iron.
7. The aluminum electrode alloy composition of any of the preceding claims, wherein the aluminum electrode alloy comprises not greater than 400 ppm iron, or not greater than 300 ppm iron, or not greater than 250 ppm iron, or not greater than 100 ppm iron.
8. The aluminum electrode alloy composition of claim 1, wherein the aluminum electrode alloy comprises from 150 to 250 ppm iron.

9. The aluminum electrode alloy composition of any of the preceding claims, wherein the corrosion resistant additive is selected from the group consisting of Zn, Ga, and combinations thereof.
10. The aluminum electrode alloy composition of any of the preceding claims, wherein the corrosion resistant additive is Zn.
11. The aluminum electrode alloy composition of any of the preceding claims, wherein the corrosion resistant additive is Ga.
12. The aluminum electrode alloy composition of any of the preceding claims, wherein the corrosion resistant additive is Zn and Ga.
13. The aluminum electrode alloy composition of any of the preceding claims, wherein the corrosion resistant additive comprises from 20 ppm to 1000 ppm of corrosion resistant additive.
14. The aluminum electrode alloy composition of any of the preceding claims, wherein the corrosion resistant additive comprises from 20 ppm to 500 ppm Zn.
15. The aluminum electrode alloy composition of any of the preceding claims, wherein the corrosion resistant additive comprises from 20 ppm to 500 ppm Ga.

1/5

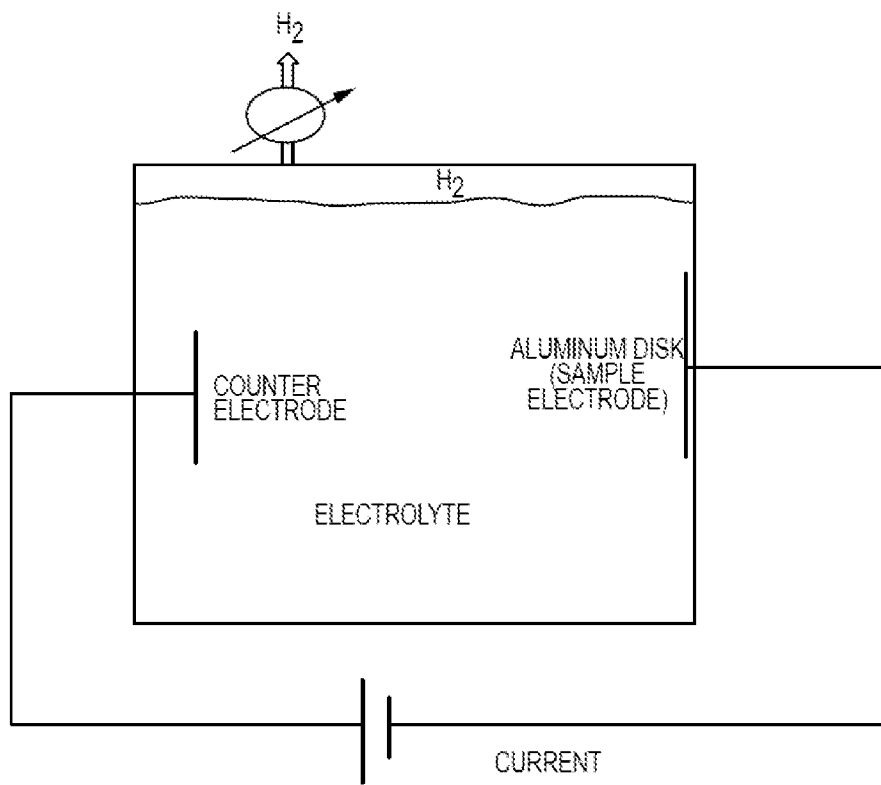


FIG. 1

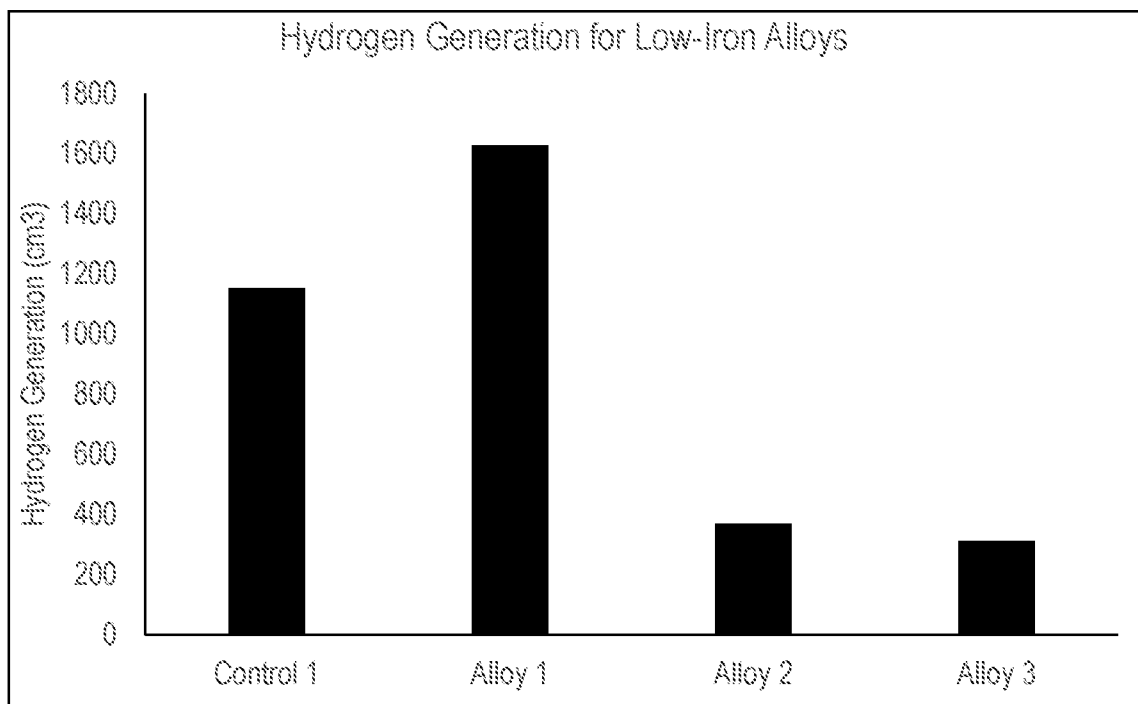


FIG. 2

3/5

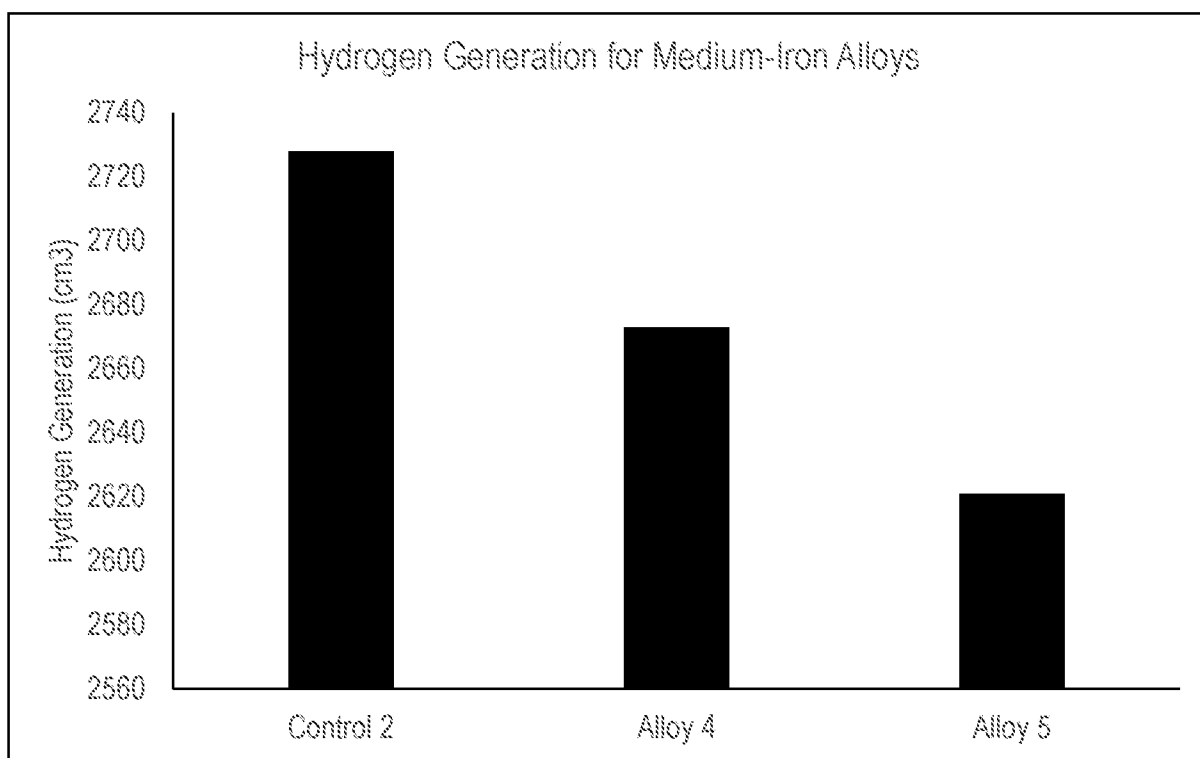


FIG. 3

4/5

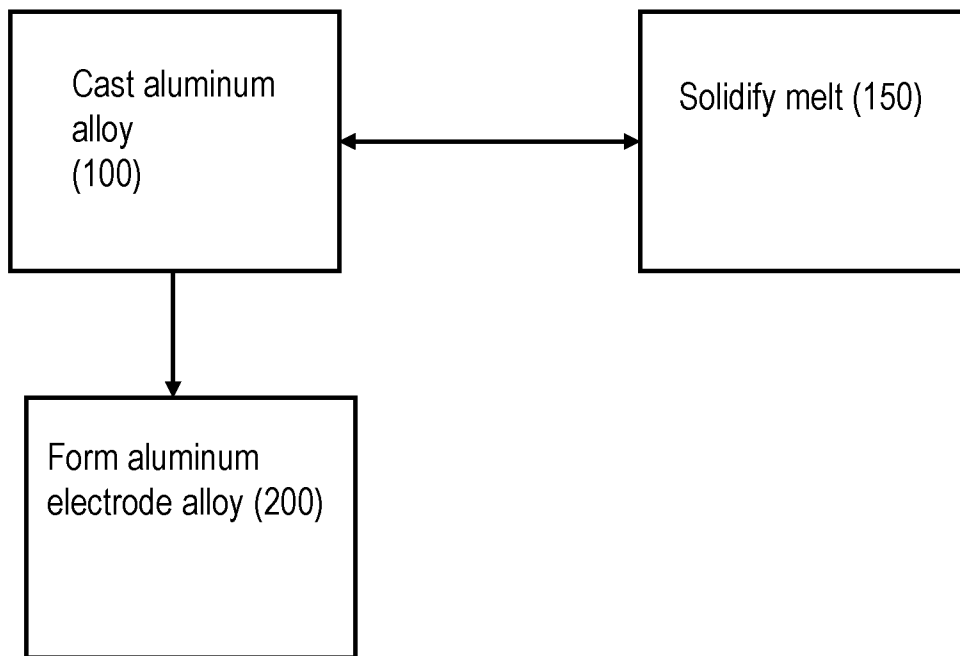


FIG. 4

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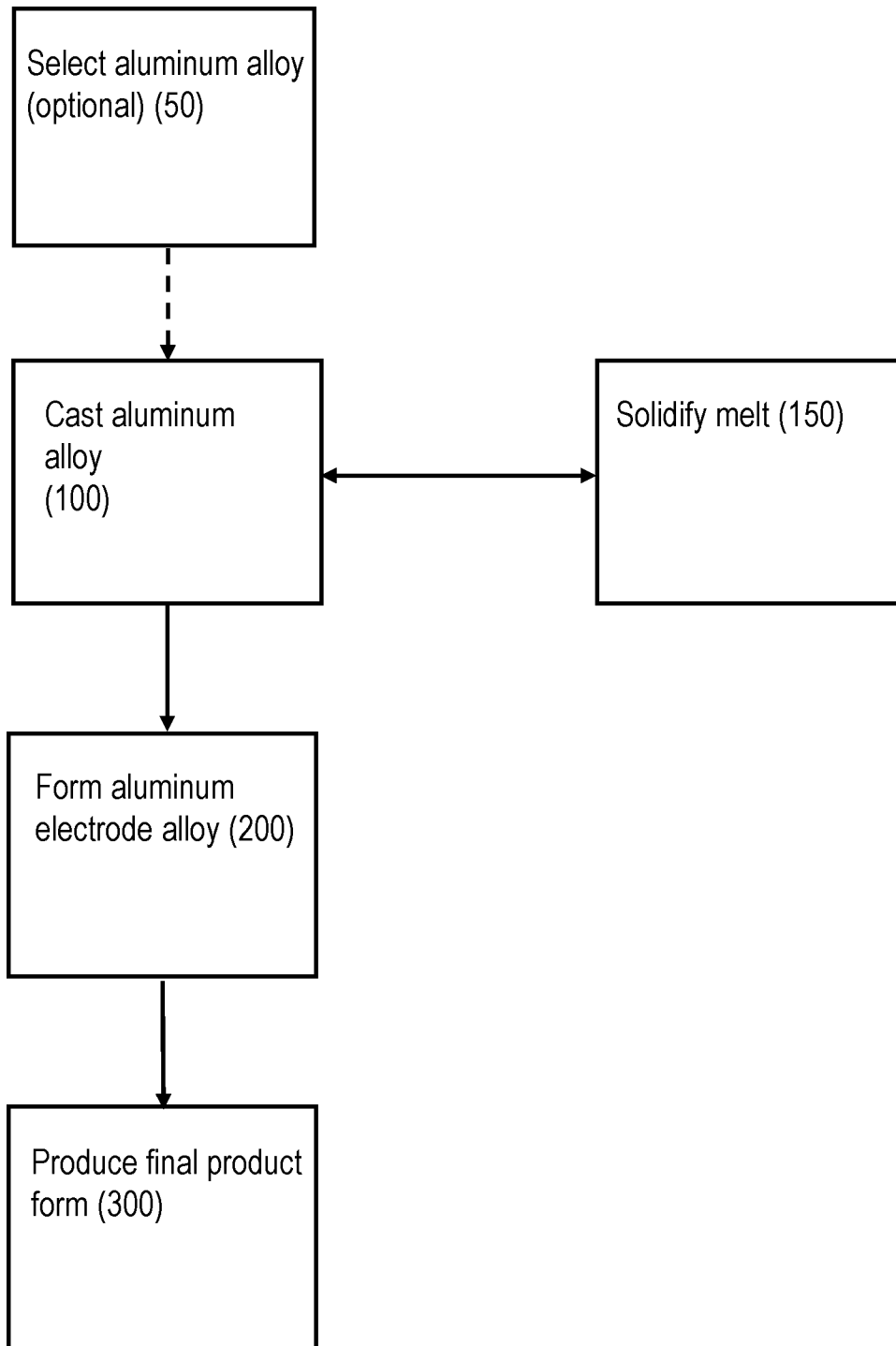


FIG. 5

A. CLASSIFICATION OF SUBJECT MATTER**C22C 21/10(2006.01)i, C25C 7/02(2006.01)i, H01B 1/02(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 21/10; C22C 21/00; C22C 21/02; C22C 21/06; C22F 1/04; C23C 22/07; C23C 28/00; G11B 5/73; H01G 9/04; C25C 7/02; H01B 1/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: corrosion, resistant, aluminium alloy, phosphorous, iron, zinc, gallium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2017-0327930 A1 (UACJ CORPORATION et al.) 16 November 2017 paragraphs [0039]-[0062] and claims 1-2	1-15
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A	JP 04-213810 A (SHOWA ALUM CORP.) 04 August 1992 paragraph [0008] and claim 1	1-15

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 December 2019 (26.12.2019)

Date of mailing of the international search report

26 December 2019 (26.12.2019)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

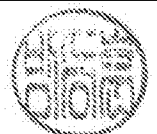
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2019/049661

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