



(51) International Patent Classification:

C22C 21/00 (2006.01) E21B 33/12 (2006.01)
E21B 23/06 (2006.01)

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(21) International Application Number:

PCT/US2018/043267

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(22) International Filing Date:

23 July 2018 (23.07.2018)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

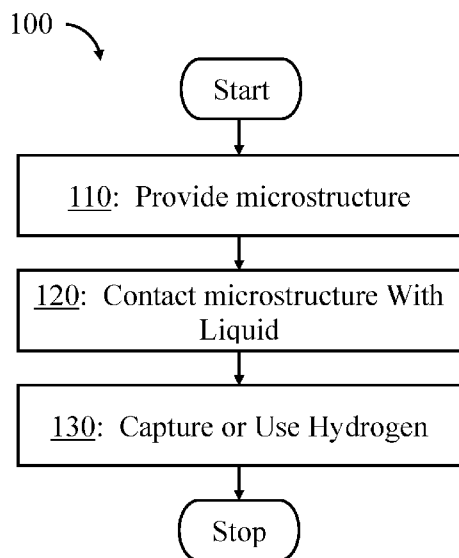
62/536,143 24 July 2017 (24.07.2017) US

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(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,

(54) Title: ALUMINUM BASED NANOGALVANIC COMPOSITIONS USEFUL FOR GENERATING HYDROGEN GAS AND LOW TEMPERATURE PROCESSING THEREOF



(57) Abstract: Alloys comprised of a refined microstructure, ultra-fine or nano scaled, that when reacted with water or any liquid containing water will spontaneously and rapidly produce hydrogen at ambient or elevated temperature are described. These metals, termed here as aluminum based nanogalvanic alloys will have applications that include but are not limited to energy generation on demand. The alloys may be composed of primarily aluminum and other metals e.g. tin bismuth, indium, gallium, lead, etc. and/or carbon, and mixtures and alloys thereof. The alloys may be processed by ball milling for the purpose of synthesizing powder feed stocks, in which each powder particle will have the above mentioned characteristics. These powders can be used in their inherent form or consolidated using commercially available techniques for the purpose of manufacturing useful functional components.

FIG. 13



MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

**ALUMINUM BASED NANOGALVANIC COMPOSITIONS
USEFUL FOR GENERATING HYDROGEN GAS
AND LOW TEMPERATURE PROCESSING THEREOF**

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CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This patent application claims the benefit of U.S. Provisional Patent Application no. 62/536,143 titled “Aluminum Based Nanogalvanic Alloys for Hydrogen Generation” and filed on July 24, 2017. The entire contents of said provisional patent application, including all attachments and documents referenced therein, are hereby
10 incorporated by reference herein.

Government Interest

[0002] The embodiments described herein may be manufactured, used, and/or
15 licensed by or for the United States Government without the payment of royalties thereon.

BACKGROUND

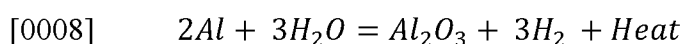
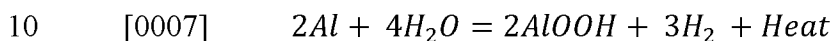
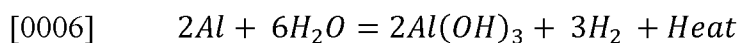
Technical Field

[0003] The embodiments herein generally relate to aluminum alloys and aluminum-
20 based microstructures that are useful for generating hydrogen gas.

[0004] Hydrogen has one of the highest energy density values per unit mass, 142 MJ/kg which is equivalent to 39.4 kWh of combustible energy. With such a large energy content, hydrogen can be used to generate power. Hydrogen gas can be used in cars, in houses, for portable power, and in many more military and civilian applications. Hydrogen

can be generated by any of the following processes: biomass gasification, biomass derived liquid forming, natural gas reforming, coal gasification, thermochemical water splitting, electrolysis, photobiological, and microbial biomass conversion (<https://energy.gov/eere/fuelcells/hydrogen-production>).

5 [0005] Another way to produce hydrogen is reacting certain chemical compounds, metals and alloys with certain solvents e.g. methanol, water etc. Aluminum reacts with water to produce hydrogen gas according to the following equations:



[0009] However it is often necessary for the solvent to be at high temperature and for
15 the water to be additionally alkaline (e.g. sodium hydroxide and potassium hydroxide) or acidic (e.g. hydrochloric acid and nitric acid) for the hydrogen producing reaction to take place. It is also often necessary to use a catalyst e.g. expensive platinum, gallium metal and/or externally applied power etc. Moreover many of the chemicals and the solvents are highly toxic e.g. methanol, sodium borohydride, lithium hydride, etc. and so also the reaction
20 byproduct.

[0010] It is well known that under certain conditions aluminum can react with water at room temperature to produce hydrogen and non-hazardous aluminum oxide/hydroxide or some combination thereof. This reaction releases heat equivalent to 4.3 kWh of energy per kg of aluminum. 1 kg of aluminum reacting water produces 111 g of hydrogen that is
25 equivalent to 4.4 kWh of combustible energy. Thus a total of 8.7 kWh of energy per kg of aluminum could be released from the aluminum-water reaction that could be utilized for a

multitude of applications. Water is readily available almost everywhere so in many cases it is not necessary to carry it, thereby removing the associated energy density penalty.

However if it needs to be carried, the total potential energy per kg of Al+ water will be 4.3 kWh. For certain applications, e.g. fuel cell applications, it is possible to reclaim 50% of the

5 water; and in that case the total potential energy available will be 5.8 kWh/kg. The energy density of gasoline and methanol, the two most common fuels, are 12.8 kWh and 5.5 kWh per kg., respectively. The gravimetric energy density of Al (with and/or without water) is similar to methanol, and 33%-66% of gasoline. In certain situations, it is more important to consider the volumetric energy density than the gravimetric. In this regard, aluminum has
10 the highest volumetric energy density among non-nuclear fuels – more than twice that of gasoline and more than five times that of methanol. If water is available, aluminum is a very desirable choice to generate power via hydrogen generation. If the total required volume of water is considered, the volumetric energy density of aluminum is 65% that of gasoline.

However, when the hydrogen is used in fuel cell technology, 50% of the water can be
15 reclaimed and utilized (i.e. removing half of the amount of water) then the energy density equals approximately that of gasoline. Currently methanol is the principal choice as the source of hydrogen for fuel cells. Hydrogen generated from aluminum can replace methanol. Thus, it is an object of the present invention to generate hydrogen gas using aluminum and water or a water containing liquid such as waste water, gray water, urine or any other liquid
20 that contains water.

[0011] Aluminum reacts with water to produce hydrogen via the hydrolysis reaction. However in the case of aluminum powders, immediate oxidation (referred to in this case as passivation) occurs at room temperature when the particles come in contact with air or water

to form a continuous passivation layer on the free surface. This passivation layer inhibits further reaction with water preventing further hydrolysis. The ability to disrupt this oxidation/passivation mechanism is key to allowing efficient production of hydrogen via the reaction with water at room temperature without the use of the solvents, acidic and basic solutions, or other catalysts mentioned above.

[0012] U.S. Patent no. 9,011,572 describes aluminum nanoparticles that can be used for generating hydrogen. U.S. Patent no. 9,011,572 describes aluminum nanoparticles produced from decomposition for an alane precursor, AlH_3 or $(\text{AlH}_3)_n$, or alane complexes such as dimethylethyl alane in the presence of a catalyst. The nanoparticles require an organic passivation agent that forms an organic coating around the aluminum nanoparticles.

[0013] US Patent Pub. No.: US 2008/0056986 A1 describes a method of producing aluminum-gallium mixture pellets that is capable of oxidizing in water to form hydrogen and a passivation surface layer of the oxide component and a passivation preventing agent that is substantially inert to water in an effective amount to prevent passivation of the solid-state material during oxidation. Gallium is expensive and aluminum-gallium pellets are mechanically unstable and unsuitable for manufacturing bulk mechanically stable structures e.g. self-cannibalizing robots, and drones, utilizing conventional metallurgical and additive manufacturing processes. The present invention provides aluminum-based compositions that are capable of generating hydrogen without requiring the inclusion of gallium.

[0014] It is an object of the present invention to provide an aluminum-based composition that can generate hydrogen upon contact with water but does not require an alane precursor or an organic passivation agent. Desirably, such an aluminum-based composition would be less expensive and easier to make. It would also be desirable to

produce aluminum-based compositions that generate hydrogen but are not necessarily nanoparticle sized. Nanoparticles are considered to be difficult to handle and not as safe as larger particles, for example particles having an average size greater than 100 nm.

5

SUMMARY

[0015] In view of the foregoing, an embodiment of the present invention provides a method of forming an aluminum, an aluminum alloy or other aluminum-based composition that generates hydrogen gas upon contact with water or other aqueous compositions, the method comprising: providing aluminum, an aluminum alloy or another aluminum-based
10 composition; providing a second metal, second alloy or other second metal-based composition; milling the aluminum, aluminum alloy or other aluminum-based composition and second metal, alloy or other metal-based composition to produce a powder; producing a milled, powder composition that comprises grains or subgrains of aluminum with individual grains or subgrains of the dispersed second metal, second alloy or other second metal-based
15 composition having atomic to nano-scale or micro-scale dimensions.

[0016] In certain embodiments, the milling occurs at a temperature less than or equal to the ductile to brittle transition temperature of tin (Sn) 13.2 °C (286.2 K). In other embodiments, the milling occurs at a temperature 50°C below the ductile to brittle transition temperature for Tin (Sn). In certain other embodiments, the milling occurs at a temperature
20 100°C below the ductile to brittle transition temperature for tin (Sn). In other embodiments, the milling occurs at a temperature 150°C below the ductile to brittle transition temperature for tin (Sn). In yet other embodiments the milling occurs at a temperature 270°C below the ductile to brittle transition temperature for tin (Sn). In other embodiments, the milling occurs

at a temperature within 25°C of the ductile to brittle transition temperature for tin (Sn). In yet other embodiments, the milling occurs at a temperature within 50°C of the ductile to brittle transition temperature for tin (Sn), or within 100°C of the ductile to brittle transition temperature for tin (Sn) or is conducted over temperature range from about + 100°C to about 5 -270°C in which the aluminum (Al) undergoes embrittlement. certain embodiments, the milling occurs over temperature range from about + 100°C to about -270°C and in which the dispersed phase or solute comprises tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn) carbon (C), or mixtures thereof and further wherein the disperse phase or solute undergoes embrittlement. In some embodiments, the 10 milling occurs under or in a low temperature liquid or fluid that is at a temperature ≤ 24 °C or under or in a cryogenic liquid that is at a temperature ≤ -75 °C.

[0017] In some embodiments the milled, powder composition comprises at least 0.1 atomic percent tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), 15 indium (In), zinc (Zn) or carbon (C), or a mixture thereof. In other embodiments, the milled, powder composition comprises at least 1 atomic percent tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn) or carbon (C), or a mixture thereof. In yet other embodiments, the milled, powder composition comprises at least 2.5 atomic percent tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), 20 indium (In), zinc (Zn) or carbon (C), or a mixture thereof. In still yet other embodiments, the milled, powder composition comprises between about 0.1 atomic percent tin and about 49.99 atomic percent tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn) or carbon (C), or a mixture thereof.

[0018] In certain embodiments, the milled, powder composition comprises at least

0.1 atomic percent tin or bismuth or a mixture thereof. In certain other embodiments, the milled, powder composition comprises finely divided powder particles having diameters ranging from about 1 micron to about 10,000 microns. In other embodiments, the milled, powder composition comprises finely divided powder particles having diameters ranging
5 from about 1 micron to about 1000 microns. In yet other embodiments, the milled, powder composition comprises finely divided powder particles having diameters ranging from about 10 nanometers to about 1000 nanometers.

[0019] In certain embodiments, the method further comprises adding a surfactant to prevent the powder from bonding to the milling container during milling. In certain
10 embodiments, the present invention provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in less than or equal to 30 seconds. In certain embodiments, the present invention also provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is
15 greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in 5 minutes. In yet other embodiments, the present invention provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in 50 minutes. In still yet other embodiments, the present invention provides a dispersion of solutes in the
20 solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in 500 minutes. And in other embodiments, the present invention provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of

the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in 5000 minutes.

[0020] In some embodiments, the method further includes compacting the milled, powder composition into a densified structure. And in some embodiments, the method
5 includes compacting the milled, powder composition into a tablet, a rod, a pellet or a bulk part wherein the tablet, rod, pellet or bulk part generates hydrogen when the tablet, rod, pellet or bulk part contacts water or a water containing liquid.

[0021] The present invention also provides a galvanic metal microstructure that
10 comprises: an anodic matrix comprising aluminum, an aluminum alloy or another aluminum-based composition; and a cathodic disperse phase comprising a second metal, second alloy or other second metal-based composition is selected from the group consisting of: tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C), and mixtures and alloys thereof wherein said cathodic disperse phase forms
15 galvanic couples with the anodic matrix and produce hydrogen gas when said galvanic metal microstructure contacts with water, a water containing liquid or another electrolyte. In some embodiments, the cathodic disperse phase comprises a plurality of discrete particles having a length of less than 1 millimeter. In other embodiments, the cathodic disperse phase comprises a plurality of discrete particles having a length of less than 1000 nanometers. In yet other
20 embodiments, the cathodic disperse phase comprises a plurality of discrete particles having a length of less than 500 nanometers, or a length of less than 200 nanometers, or less than 100 nanometers or even less than 50 nanometers.

[0022] In certain embodiments, the cathodic disperse phase comprises tin (Sn). In certain other embodiments, the cathodic disperse phase consists primarily of tin (Sn) or an
25 alloy of tin. In some embodiments, galvanic metal microstructures of the present invention

are made by melt spinning, spray atomization, inert gas condensation, solution precipitation, physical vapor deposition, or electrodeposition.

[0023] The present invention also provides a method of generating hydrogen.

5 BRIEF DESCRIPTION OF THE DRAWINGS

[0024] The embodiments herein will be better understood from the following detailed description with reference to the drawings, in which:

[0025] FIG. 1 is a back-scattered electron (BSE) micrograph taken with a scanning electron microscope (SEM) of an aluminum-tin alloy of the present invention (the dark
10 phase is primarily aluminum and the lighter/bright phase is primarily tin)

[0026] FIG. 2 is another BSE micrograph illustrating the existence of stringers (elongated thin ribbons) of tin of varying size and dispersion in an aluminum-tin alloy of the present invention;

[0027] FIG. 3 is a schematic of a nanogalvanic microstructure for rapid hydrogen
15 generation in aluminum-tin alloy of the present invention;

[0028] FIG. 4 illustrates dispersion of small particles in the grains of a matrix in an aluminum-tin alloy of the present invention;

[0029] FIG 5 illustrates large particles residing at the grain boundary in an aluminum-tin alloy of the present invention;

20 [0030] FIG 6 illustrates existence of ribbon-shaped stringers in an aluminum-tin alloy of the present invention;

[0031] FIG. 7 is a graph illustrating the reaction rate (volume of hydrogen generated per gram of aluminum) for three embodiments of the present invention with water;

[0032] FIG. 8 is a graph illustrating the reaction rate for additional embodiments of the present invention;

[0033] FIG. 9 is a graph illustrating the reaction another two embodiments of the present invention;

5 [0034] FIG. 10 is a graph illustrating the reaction rate for additional embodiments of the present invention; and

[0035] FIG. 11 is a graph illustrating the reaction rate for additional embodiments of the present invention; and

10 [0036] FIG. 12 is a graph illustrating the reaction rate an embodiments of the present invention with urine instead of water.

[0037] FIG. 13 is a flowchart describing one embodiment for generating hydrogen.

[0038] FIG. 14 is a flowchart describing one embodiment for producing a nanogalvanic microstructure.

15

DETAILED DESCRIPTION

[0039] The embodiments herein and the various features and advantageous details thereof are explained more fully with reference to the non-limiting embodiments that are illustrated in the accompanying drawings and detailed in the following description.

20 Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments

herein.

[0040] As used herein, the term nano-scale means diameter of particles less than 1000 nm, preferably less than 100 nm and even less than 10 nm. Micro-scale means diameter of particles less than 1000 micrometers, preferably less than 100 micrometers and
5 even less than 10 micrometers. Atomic scale means particles having physical dimensions as small as the atomic diameter of the specified elements and as large as particles containing a few hundred individual atoms of those elements.

[0041] Embodiments described herein provide compositions useful for generating hydrogen gas when contacted with water or water containing liquids including but not
10 limited to gray water, urine, pond water and so forth. Aluminum based alloys can be made to generate hydrogen very rapidly by reaction with water at room temperature by forming galvanic cells. The galvanic effect continuously allows the exposure of new unoxidized metallic surface thus allowing for further hydrolysis at room temperature. The alloys may be composed of primarily aluminum and other metals including, but not limited to, tin (Sn),
15 magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), Gallium (Ga), Indium (In), Zinc (Zn), Carbon (C), or the like and mixtures thereof.

[0042] In certain desirable embodiments the present invention provides nanostructured aluminum-based alloys for spontaneous, facile and rapid generation of hydrogen at room or elevated temperatures without externally applied power, by reacting the
20 composition, for example in powder form, with water and/or liquids containing water. By coupling compositions of the present invention with fuel cells or a hydrogen internal combustion engine, the compositions will enable effortless generation of power to run electronic equipment, transportation vehicles, and powered mechanisms and so forth. This

will be useful for various products and services for defense and civilian applications.

Actuation and propulsion systems that require rapid pressurization may also be benefitted.

Thus, hydrogen generation from water or water based reactions with compositions of the present invention can replace or supplement hydrocarbon fuels.

- 5 [0043] A method of producing nanogalvanic structured aluminum based particulate material of the present invention is described herein and includes high energy ball milling of aluminum and other optional metals at room temperature, preferably at reduced temperatures and more preferably at cryogenic temperatures. Thus, in certain embodiments the method of the present invention includes ball milling of aluminum at temperatures below about 30°C,
- 10 more preferably below about 25°C, still more preferably below about 20°C, still more preferably below about 10°C, still more preferably below about 5°C, still more preferably below about 0°C, still more preferably below about -25°C, still more preferably below about -50°C, still more preferably below about -100°C, still more preferably below about -150°C, still more preferably below about -200°C and still more preferably below about -250°C.
- 15 Milling of aluminum and aluminum alloys at reduced temperatures is capable of producing nanogalvanic alloys that can produce hydrogen very rapidly by the hydrolysis reaction with water at room temperature without an externally coupled power supply. Thus, the method of making compositions of the present invention may include cooling the metal or metallic
- 20 powders from ambient temperature to cryogenic temperatures during processing of the powders. This can be achieved by cooling the milling device or milling device chamber with coolant fluids or coolant cryogens such as liquid nitrogen, liquid oxygen, liquid argon or even liquid helium.

[0044] The aluminum may be essentially pure aluminum (i.e. greater than 98 atomic percent of aluminum and preferably greater than 99 atomic percent of aluminum), an alloy of aluminum, preferably an alloy of aluminum containing greater than 90 atomic percent of aluminum, more preferably greater than 70 percent of aluminum and more still preferably greater than 50 atomic percent of aluminum, and scrap aluminum for example aluminum cans. Suggested examples of aluminum alloys include but are not limited to, Al5056 and aluminum alloys of 1000, 2000, 3000, 5000, 6000, and 7000 series. Preferably the aluminum alloy contains at least 99, 98, 95, 90, and at least 80 atomic percent aluminum. Scrap aluminum powders were used to produce scrap Al-Sn alloys that produced hydrogen when the scrap Al-Sn alloys reacted with water.

[0045] Nanogalvanic cells with aluminum as the anode can be coupled with another element acting as the cathode e.g. metals including, but not limited to, tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C),, or the like and mixtures thereof. The galvanic couple is made by the close and intimate contact of the two dissimilar metals which have different corrosion potentials (i.e. one acting as an anode and other as a cathode). The nanogalvanic effect disrupts the oxide layer rapidly exposing new metallic surfaces and thus enhances the hydrolysis reaction at room temperature which in turn rapidly accelerates hydrogen production.

[0046] Galvanic corrosion occurs when two dissimilar metals make contact with one another in the presence of an electrolyte thereby forming a galvanic couple. The more noble metal (more cathodic on the galvanic series) provides additional surface area for the reduction reaction to occur on. This accelerates the oxidation/corrosion of the less noble metal (more anodic on the galvanic series). The extent of corrosion is greatest at the interface of the two

metals, but may also occur at some distance away from the actual interface. In addition, the cell kinetics in this case are enhanced when the cathode is smaller in surface area relative to the anode.

[0047] Nanostructured nanogalvanic binary or higher order alloys consisting of aluminum (Al) metal comprising 50 to 99.9 atomic percent (at. %) as one of the constituents were processed by a non-equilibrium process. The other constituent(s) may be one or a combination of the following elements including, but not limited to: tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C) and mixtures thereof ranging from about 0.1 to about 50 atomic percent of the constituent(s).

[0048] Examples of milling apparatuses can be far ranging to include but not limited to: The SPEX Industries, Edison, N.J. series of mills or Zoz GmbH, Germany, series of mills. Relatively lower energy types include the Pulverisette planetary ball mills from Fritsch GmbH, Idar-Oberstein, Germany; the PM series of planetary ball mills from Retsch GmbH, Dusseldorf, Germany; or the attritor type mills from Union Process, Akron, Ohio, Jet Mill and Jar Mill from Glen Mills, Clifton, NJ. Relatively lower energy types of suggested milling apparatuses include the Pulverisette planetary ball mills from Fritsch GmbH, Idar-Oberstein, Germany; the PM series of planetary ball mills from Retsch GmbH, Dusseldorf, Germany; or the attritor type mills from Union Process, Akron, Ohio, Jet Mill and Jar Mill from Glen Mills, Clifton, NJ. To avoid cold welding and sticking to the vial and milling media, the milling process can be carried out at liquid nitrogen temperatures and/or with surfactants/additives. Suggested additives and surfactants include, but are not limited to, stearic acid, oleic acid, oleyl amine, valeric acid, octanoic acid, decanoic acid, undecanoic acid, palmitic acid, ethanol, hexane, dodecane and other long chain hydrocarbon compounds

and mixtures thereof. Surfactants and additives can be utilized with the metallic powders and milling media and vials during the milling process. Desirably, the surfactant is a solid or a liquid at room temperature particularly when the milling is performed at ambient or room temperature. Desirably, the milling balls and the mixing vials are comprised of hard wear-resistant materials including, but not limited to, metals, ceramics, oxides and combinations thereof.

[0049] The alloys described herein, due to their unique compositions and synthesis method have the fastest rate of hydrogen generation at room temperature without externally applied power or other catalysts reported in literature when reacted with water – as high as 1000 ml of hydrogen per gram of aluminum in as low as about 30 seconds. These non-hazardous alloys consisting of abundantly available and inexpensive constituents will result in facile production of hydrogen for power generation and various other military and civilian applications. Furthermore, the reaction is so pervasive that the hydrolysis reaction will occur in any fluid containing water and many compounds containing OH (hydroxyl) groups.

[0050] Aluminum oxidizes rapidly when it comes in contact with air or water and an oxide layer is formed on the surface of the particles. This oxide layer typically inhibits reaction with water. In order for the reaction to take place it is necessary to disrupt the oxide layer. Current state of the art materials with unstable oxides consist of alloys of aluminum with gallium produced by conventional melt casting. These alloys are very expensive – the price of gallium metal is about 100 times that of aluminum.. Small grains and/or small anodic or cathodic dispersions provide the efficient nanogalvanic effect that sweeps away the oxide layer rapidly exposing new metallic surfaces and thus enhances the hydrolysis reaction at room temperature reported here. This invention, however, achieves the enhanced reaction

kinetics through processing of nanostructured aluminum based galvanic alloys by high energy ball milling at cryogenic temperature.

[0051] The Al-alloy powders may be produced by ball milling pure aluminum with other metals including but not limited to, tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C), for 0.01 to 8 hours at cryogenic temperature such as at -100 °C and -196 °C. Pure aluminum may be substituted by or commercially available aluminum alloys e.g. AA5056, AA5083, etc. The individual powder particulate size can be in the range of 0.01 μm – 6 mm in diameter. Additionally, the powder could be consolidated to form compacts or functional parts for tuning the hydrogen generation rate and yield. For example, powders of the present invention could be consolidated to produce a tablet, a rod, a pellet or a bulk part. Additionally, powders of the present invention would be coated on to the surface of a component or part. Suggested processes include, but are not limited to, metal injection molding, cold and hot isostatic pressing, additive manufacturing techniques including laser and non-laser techniques, thermal and cold spray and additive friction stir welding, powder forging, hot pressing, pressure less sintering, shock consolidation and field assisted sintering.

[0052] The nanogalvanic structured Al-alloys when reacted with water at room temperature will produce ~1000 ml of hydrogen gas per gram of aluminum in as low as ~30 seconds after reaction starts and also as high as 100% the theoretical limit in ~3 min. However, there exist other applications where lower or higher reaction rates/hydrogen yields may be required or beneficial. Please see included data plots (FIGS. 7-12) to see general volumes and rates of hydrogen generation versus reaction time. Any aluminum base material (e.g. scrap aluminum, etc.) when alloyed with other specific metals e.g. tin (Sn), magnesium

(Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C), or the like by high energy ball milling at cryogenic temperature may produce hydrogen at room temperature when reacted with water without externally coupled power. The inherent ability to form corrosive galvanic couples with aluminum was considered in selecting the
5 aforementioned elements. The addition of carbon to the alloys during ball milling may enhance hydrogen generation rate, both as a surfactant as well as a galvanic couple. Furthermore, the data present here, is a starting point, that is the method has not been optimized but rather some adjustments of compositions and processing parameters have been done to maximize the rate and amount of hydrogen generation for a particular composition
10 and processing i.e. cryogenic milling. However, currently, only one synthesis technique has been pursued. Other alternative processing techniques, such as room temperature large scale ball milling utilizing surfactants and or melt-spinning or spray atomization can be used to produce nanogalvanic powders having the same patentable characteristics.

[0053] In order that the invention may be more readily understood, reference is made
15 to the following examples which are intended to illustrate the invention, but not limit the scope thereof.

[0054] **EXAMPLES 1A-1K**: FORMATION OF ALUMINUM ALLOY POWDERS METAL USING HIGH-ENERGY MILLING AT CRYOGENIC TEMPERATURE (-75 °C to -270 °C)

20 [0055] Alloys consisting of an aluminum alloy AA5056 and tin (Sn) were prepared by loading the respective powders with the correct weight ratio into a clean hardened steel vial to produce the desired atomic percent alloy. AA5056 alloy at -140/+325 mesh was obtained from Valimet, Inc., 431 East Sperry Road, Stockton, CA 95206. The AA5056 alloy

is reported to contain Al (balance), 0.15%Cr, <0.01%Cu, 0.10%Fe, 5.22%Mg, 0.13% Mn, 0.04% Si, <0.01% Zn, others total <0.15%. Sn was obtained from Alfa Aesar and is reported to have 98.5% purity, -325 mesh (approximately 45 μ m). The AA5056:Sn mass ratio in Example 1A was maintained at 7.5:1. As such, it was

5 expected that the resultant alloy would have had a similar composition of AA5056-2.97.0 at. %Sn. Alternatively, alloys consisting of pure aluminum and tin with compositions Al-x at.% Sn (with x = 1, 2.97, 3.7, 4.5, 5.7, 7 and 20, Examples 1B to 1H, respectively) were prepared by loading the respective powders with the correct weight ratio into a clean hardened steel vial to produce the desired atomic percent

10 alloy. Al was obtained from Alfa Aesar and is reported to have 99.5% purity, -325 mesh (approximately 45 μ m). The Al:Sn mass ratio were varied from 19:1 to 1:1 depending on the composition of the powders. Also AA5056-Bi and Al-Bi powders were prepared by loading the respective powders with the correct weight ratio into a clean, hardened steel vial to produce the desired atomic percent alloy. Bi, -325 mesh

15 (approximately 45 μ m), was obtained from Alfa Aesar and is reported to have 99.5% purity. Both the AA5056:Bi and Al:Bi mass ratio here was maintained at 4:1. As such, it was expected that the resultant alloys would have had a similar composition of AA5056-3.1 at. %Bi and Al-3.1 at. %Bi. Additionally, AA5056- x at.% Sn- (3-x) at.% Bi (with x = 1.5, 1.8, and 2.25) alloys were also synthesized (Examples 1I to 1K,

20 respectively).

[0056] Thirty three (33) stainless steel (440C) ball-bearings, 17 of which having a diameter of ¼ inch and the other 16 having a diameter of 5/16 inch, were used as the milling media in a 8000D SPEX shaker mill. The 10-gram powder mass

of the constituent elements (e.g. AA5056, Al, Sn and Bi) comprising the particular alloys were milled with a 5:1 ball-to-powder mass (weight) ratio. Suggested ball-to-powder mass (weight) ratio ranged from 5:1 to less than or equal to about 1:1. Vials were sealed in a primarily Argon atmosphere (i.e., with O₂ < 1 ppm). This milling procedure resulted in a finely divided powder mass, consisting of particulates in the micron range i.e. diameters between 1 and 10000 microns. However, the interior structure of the particles consist of further structural refinement, specifically, grains or subgrains of Al with individual Sn grains or dispersed Sn particles having nanometer (e.g. less than 100 nanometers) or micron (e.g. less than 100 micrometers) dimensions throughout for alloys containing Sn.

[0057] During the high-energy milling process, the metal powder may be subjected to a low or cryogenic temperatures to embrittle the constituents. In general all metals become more brittle with decrease in temperature, because their active slip systems (relating to dislocation and other thermally activated processes governing their mechanical behavior become statistically less active). The type of embrittlement is clearly demonstrated by the well-known ductile-to-brittle transition (DTBT) of ferritic steels. Low temperature processing is defined by processing that occurs at temperature ranging from just below room temperature (24 °C) down to -270 °C. Low temperature ball milling here is utilized in this example to keep the powders (AA5056, Al, Sn, and Bi) cold, such that they remain as brittle as possible and thereby preventing or, more precisely, reducing and minimizing the powder from adhering to the milling media and walls of the vial. An additional benefit of low temperature milling is that certain metals or metal powders will undergo a temperature induced crystallographic transformation, also known as an allotropic transformation, from a ductile to a brittle state. For example, pure tin transforms from the silvery, ductile metallic

allotrope of β -form white tin to the brittle, nonmetallic, α -form grey tin with a diamond cubic structure at a temperature that is equal to or less than 13.2 °C (286.2 K). Specifically, this brittle transformation induces advantageous milling kinetics, resulting in a favorable dispersion of Sn in Al that would otherwise not be possible and or as optimized for producing a dispersed galvanic couple (a microstructural building box required for successful hydrogen production) having reduced length scales.

[0058] In this example, cryogenic temperature is typically defined as temperature below about -150 °C. Liquid nitrogen, for instance, having a temperature as low as -196 °C (77K), may be supplied to provide such cooling. Liquid nitrogen milling was made possible by placing the sealed vial in a thick nylon sleeve modified to allow placement into the high energy mill as well as to allow the in-flow and out-flow of liquid nitrogen. The vial was allowed to cool to liquid nitrogen temperature before starting the mill. Mechanical alloying at liquid nitrogen temperatures in the SPEX shaker mill for approximately 4 hours was performed. After the ball milling procedure was completed, the alloyed AA5056-Sn (or Al-Sn) powder was removed from the steel vial in an Ar glove box and stored. This milling procedure resulted in a finely divided powder mass, consisting of particulates in the micron range i.e. diameters between 1 and 10,000 microns. While 4 hours of cryogenic milling was used in this example, it doesn't define the time range over which hydrogen producing powders can be synthesized. This is the same with, the milling energy, ball-to-powder ratio and/or other generic aspects of the milling process including composition.

[0059] **EXAMPLE 2: FORMATION OF ALUMINUM ALLOY (AA5056)-Sn and Al-Sn POWDER METAL USING HIGH-ENERGY MILLING AT LOW TEMPERATURE (≤ 24 °C)**

[0060] In this example, alloys consisting of an aluminum alloy AA5056 and tin (Sn) as well as Al and Sn were prepared by loading the respective powders with the correct weight ratio into a clean hardened steel milling jar to produce the desired atomic percent alloy. 500 g powder mass of AA5056 and tin and 200 g powder mass of Al and Sn along with 1.25 g and 0.5 g of stearic acid were milled with a 10:1 ball-to-powder mass (weight) ratio (i.e. with 5000 g and 2000 g of stainless steel (440C) ball-bearings respectively) were used as the milling media in CM08 and CM02 Zoz mill respectively. The AA5056:Sn and Al:Sn mass ratio in Example 2 were maintained at 7.5:1. As such, it was expected that the resultant alloys would have had similar composition of AA 5056-2.97 at. %Sn and Al-2.97 at. %Sn.

[0061] In this example, low temperature here is defined as a temperature ranging from just below the room temperature (< 24 °C). Chilled ethylene glycol may be supplied to provide the cooling down to -20 °C. Low temperature milling was made possible by circulating ethylene glycol through the built-in cooling jacket around the milling jars (8 L and 2 L capacity for CM08 and CM02 Zoz Mill respectively). The ethylene glycol was continuously cooled and circulated using a water chiller. The milling was performed at 400 RPM for up to 11 hours.

[0062] Stainless steel milling jars were sealed in (primarily) an Argon atmosphere (i.e., with $O_2 < 1$ ppm). After the ball milling procedure was completed, the alloyed powder was transferred from the steel jar into an argon glove box and the powder was stored there. This milling procedure resulted in a finely divided powder mass, consisting of particulates in

the micron range i.e. diameters between 1 and 10,000 microns. However, the interior structure of the particles consist of further structural refinement, specifically, grains or subgrains of Al with individual Sn grains or dispersed Sn particles having nanometer or micron dimensions throughout.

5 [0063] **EXAMPLE 3: FORMATION OF ALUMINUM ALLOY (AA5056)-Sn and Al-Sn POWDER METAL USING HIGH-ENERGY MILLING AT ROOM TEMPERATURE (~ 24 °C)**

[0064] In this example, AA5056-Sn and Al-Sn powders were prepared by the inventors by loading the respective powders with the correct weight ratio into a clean
10 hardened steel vial to produce the desired atomic percent alloy. The Al:Sn mass ratio in Example 3 was maintained at 7.5:1. Additionally 0.15-0.5 wt% of stearic acid was added. As such, it was expected that the resultant alloy would have had a similar composition of Al-2.97 at. %Sn.

[0065] Thirty three (33) stainless steel (440C) ball-bearings, 17 of which having a
15 diameter of ¼ inch and the other 16 having a diameter of 5/16 inch, were used as the milling media in a 8000D SPEX shaker mill. The 10-gram powder mass of Al and Sn was milled with a 5:1 ball-to-powder mass (weight) ratio. Vials were sealed in a primarily Argon atmosphere (i.e., with O₂ < 1 ppm). Mechanical alloying was then performed in a SPEX 8000 shaker mill for up to 6 hours. After the ball milling procedure was completed, the
20 alloyed Al-Sn powder was removed from the steel vial in an argon glove box and stored. Mechanical milling resulted in powders with a particle range of 1-10,000 µm.

[0066] **Results:** Compositions produced in some of the examples above were characterized using scanning electron microscopy. While not wishing to be bound by the

theories provided below, the significance of the structure of some compositions of the present invention is discussed with relation to the hydrogen generation.

[0067] FIG. 1 shows enlarged scanning electron micrograph of one exemplary microstructure of a nanogalvanic metal as it pertains to the invention, specifically Example 2.

5 The dark phase in FIGS. 1 and 2 is primarily Al and the lighter/bright phase is primarily Sn. The Sn exist primarily as discrete particles and or stringers (elongated thin ribbons of Sn) of varying size and dispersion. A galvanic couple is made by the close and intimate contact of the two, in this case Al and Sn, dissimilar metals which have different corrosion potentials (i.e. one acting as an anode and other as a cathode). In this case Al is the anode and Sn the cathode.

10 [0068] Galvanic corrosion occurs when two dissimilar metals make contact with one another in the presence of an electrolyte thereby forming a galvanic couple. The more noble metal (more cathodic on the Galvanic Series) provides additional surface area for the reduction reaction to occur on. This accelerates the oxidation/corrosion of the less noble metal (more anodic on the Galvanic Series). The extent of corrosion is greatest at the interface of the two
15 metals, but may also occur at some distance away from the actual interface. In addition, the cell kinetics are enhanced when the cathode is smaller in surface area relative to the anode.

[0069] FIG. 2 is a lower magnification scanning electron micrograph giving a more macroscopic view of the nanogalvanic microstructure than seen in FIG. 1. The nanogalvanic microstructure of the present invention can be defined as a crystallite material in which its
20 microstructure is nano-sized (i.e., on the order of 1, 10 or 100 nm). Some aspects of the microstructure may also be in the ultra-fine length scale (being defined as a length scale between 100 and 1000 nm). Still, some aspects of the microstructure can be even larger i.e. length scales of greater than 1000nm. The microstructure consists of phases, i.e. the matrix

phase and the dispersed phase have at least some of the length scales mentioned above. These phases i.e. matrix phase and the dispersed phase, are composed of solvent and solute species. Here the solvent is primarily Al and the solute species primarily is Sn. However, other elements can be acting as both, e.g. magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga),
5 indium (In), zinc (Zn), carbon (C),, or the like. The matrix phase in this case mainly contains the solvent Al. However the matrix phase may consist of a solid solution of aluminum in combination with other dissolved solvents and solutes. A solid solution is a solid-state solution of one or more solutes in a solvent or solvents. Such a multi-component system is considered a solution rather than a compound when the crystal structure of the solvent remains unchanged
10 by addition of the solutes or the solvents in the form of a randomly dispersed atoms i.e. a random solid solution resulting in the chemical components remaining in a single homogeneous phase. Conversely the dispersed phase is primarily made up of solutes that are dispersed in the matrix solvent. Small agglomerations of solute atoms in the solvent are referred to as nuclei or clusters containing one to a few hundred atoms typically being 2-100
15 nm in diameter. As more and more atoms agglomerate they are termed as particles once the diameters of the agglomerates become greater than 100 nm. These particles can range from 100 nm to 1 mm. Stringers are hereby defined as ribbon-shaped particles primarily composed of solutes that are larger than previously described particles having length from 10 nm up to 10 mm. The ribbons may have finite dimensions in all the three dimensions and may be termed
20 as sheets also.

[0070] The matrix can consist of a polycrystalline grain structure in which the grains can be nanocrystalline (i.e., on the order of 1, 10 or 100 nm) or ultra-fine (being defined as a length scale between 100 and 1000 nm) or can be even larger i.e. length scales of greater than

1000nm. Please note that the cellular structure of grains are separated by grain boundary.

Also the larger ribbons could contain polycrystalline grain structure in which the grains can

be nanocrystalline (i.e., on the order of 1, 10 or 100 nm) or ultra-fine (being defined as a

length scale between 100 and 1000 nm) or can be even larger i.e. length scales of greater than

5 1000nm.

[0071] Please note that the smaller the size of the grains and the size of the dispersed
phased, the higher is the galvanic reactivity. The cell kinetics are enhanced when the cathode
is smaller in surface area relative to the anode. In general greater the difference of corrosion
potential between the matrix and the dispersed phase higher is the galvanic reactivity.

10 [0072] The white portion of FIG. 3 represents the matrix. It forms the medium of the
metallic material. It may be Al or an Al-based alloy, for instance. While not truly circular
(and actually, of a more random polyhedral shape/cellular structure polygonal shape), grains
are assumed to have an average diameter. The grains of the matrix having diameters of no
more than about 500 nm, typically ranging from about 10-200nm. Grain boundaries occur at
15 the interface of separate adjacent grains.

[0073] A plurality of dispersed metallic particles formed of solute metal(s) in the
solvent metal matrix. The dispersed solute particle reside within grains and along the grain
boundaries. They typically have average diameters in the range 20- 500 nm. However they
could be smaller as well as larger than the given range. In addition at least some of the dispersed
20 particles may further contain additional element(s) such as aspects of the matrix and or other
advantageously included elemental species such as oxygen (O), nitrogen (N), carbon (C),
sulfur (S), silicon (Si), bismuth (Bi), carbon (C), gallium (Ga), indium (In), lead (Pb) or other
element(s) (i.e. from the remainder of the periodic table). Additionally, in some instances, due

to processing or otherwise, the particles may comprise solute metal and some small amount of a solvent metal or alloy (such as Al).

[0074] Particles may be characterized as being small or large based on their size or be ribbon-shaped stringers. Small particles may have diameters typically 2- 100 nm. They reside with the grains and/or on the grain boundaries, as further depicted in FIGs. 4 and 5. Large particles reside between the grains of the matrix as further depicted in FIG. 5. The chemistry of these particles will contain the solute metal(s). These larger particles have diameters typically greater than 100 nm and up to 1 mm. The frequency of the appearance of small and large particle will depend on the concentration of the solute metal(s) and the degree of processing. Ribbon-shaped stringers solute particles as depicted in FIG. 6 may have dimension from 10 nm up to 10 mm in all dimension and may have the similar compositions as the aforementioned small and large solute particles.

[0075] Some of the examples of the present invention were tested by contacting with water and urine to generate hydrogen gas. Results of the tests are provided in FIGS. 7-12. FIG. 13 provides a flowchart describing a method **100** for generating hydrogen wherein step **110** includes providing a microstructure, step **120** includes contacting the microstructure the microstructure with a liquid, for example water, urine or other water containing liquids and step **130** includes capturing and/or using hydrogen gas that is generated when liquid contacts the composition. And, FIG. 14 provides a flowchart describing a method **200** for producing a nanogalvanic microstructure wherein step wherein step **210** includes providing a matrix phase material, step **220** includes providing a dispersed phase material and step **230** includes milling the combined phases to produce a material that spontaneously generates hydrogen when the material contacts water, urine or another water containing liquid.

[0076] The processing techniques that may be used to produce compositions of the present invention may include but are not limited to, milling/machining (including ball milling and especially high energy ball milling), melt spinning, spray atomization, inert gas condensation, solution precipitation, physical vapor deposition, and electrodeposition. Melt spinning forms thin ribbons of material.

[0077] Patent documents and other publications mentioned in the specification are indicative of the levels of those skilled in the art to which the invention pertains. These documents and publications are incorporated herein by reference to the same extent as if each individual document or publication was specifically and individually incorporated herein by reference.

[0078] The foregoing description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others may, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein may be practiced with modification within the spirit and scope of the appended claims.

CLAIMS

What is claimed is:

1. A method of forming an aluminum, an aluminum alloy or other aluminum-based composition that generates hydrogen gas upon contact with water or other aqueous compositions, the method comprising:

providing aluminum, an aluminum alloy or another aluminum-based composition;

providing a second metal, second alloy or other second metal-based composition;

milling the aluminum, aluminum alloy or other aluminum-based composition and second metal, alloy or other metal-based composition to produce a powder;

producing a milled, powder composition that comprises grains or subgrains of aluminum with individual grains or subgrains of the dispersed second metal, second alloy or other second metal-based composition having atomic to nano-scale or micro-scale dimensions.

2. The method of claim 1, wherein the milling occurs at a temperature less than or equal to the ductile to brittle transition temperature of tin (Sn) 13.2 °C (286.2 K).

3. The method of claim 1, wherein the milling occurs at a temperature 50°C below the ductile to brittle transition temperature for tin (Sn).

4. The method of claim 1, wherein the milling occurs at a temperature 100°C below the ductile to brittle transition temperature for tin (Sn).

5. The method of claim 1, wherein the milling occurs at a temperature 150°C below the ductile to brittle transition temperature for tin (Sn).
6. The method of claim 1, wherein the milling occurs at a temperature 270°C the ductile to brittle transition temperature for tin (Sn).
7. The method of claim 1, wherein the milling occurs at a temperature within 25°C of the ductile to brittle transition temperature for tin (Sn).
8. The method of claim 1, wherein the milling occurs at a temperature within 50°C of the ductile to brittle transition temperature for tin (Sn).
9. The method of claim 1, wherein the milling occurs at a temperature within 100°C of the ductile to brittle transition temperature for tin (Sn).
10. The method of claim 1, wherein the milling is conducted over temperature range from about + 100°C to about -270°C in which the aluminum (Al) undergoes embrittlement.
11. The method of claim 1, wherein the milling occurs over temperature range from about + 100°C to about -270°C and in which the dispersed phase or solute comprises tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn) carbon (C), or mixtures thereof and further wherein the disperse phase or solute undergoes embrittlement.

12. The method of claim 1, wherein the milling occurs under or in a low temperature liquid or fluid that is at a temperature ≤ 24 °C.
13. The method of claim 1, wherein the milling occurs under or in a cryogenic liquid that is at a temperature ≤ -75 °C.
14. The method of claim 1, wherein the milled, powder composition comprises at least 0.1 atomic percent tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn) or carbon (C), or a mixture thereof.
15. The method of claim 1, wherein the milled, powder composition comprises at least 1 atomic percent tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn) or carbon (C), or a mixture thereof.
16. The method of claim 1, wherein the milled, powder composition comprises at least 2.5 atomic percent tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn) or carbon (C), or a mixture thereof.
17. The method of claim 1, wherein the milled, powder composition comprises between about 0.1 atomic percent tin and about 49.99 atomic percent tin (Sn), magnesium (Mg),

silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn) or carbon (C), or a mixture thereof.

18. The method of claim 1, wherein the milled, powder composition comprises at least 0.1 atomic percent tin or bismuth or a mixture thereof.

19. The method of claim 1, wherein the milling occurs under a cover gas comprising neon, hydrogen, helium, argon or a mixture thereof.

20. The method of claim 1, wherein the high-energy milling occurs in or open or closed off to the atmosphere.

21. The method of claim 1, further comprising transferring the milled, powder composition to a container that is essentially free of oxygen.

22. The method of claim 1, further comprising transferring the milled, powder composition to a container that is essentially open to the atmosphere.

23. The method of claim 1, wherein the milled, powder composition comprises finely divided powder particles having diameters ranging from about 1 micron to about 10,000 microns.

24. The method of claim 1, wherein the milled, powder composition comprises finely divided powder particles having diameters ranging from about 1 micron to about 1000 microns.
25. The method of claim 1, wherein the milled, powder composition comprises finely divided powder particles having diameters ranging from about 10 nanometers to about 1000 nanometers.
26. The method of claim 1, wherein the second metal, second alloy or other second metal-based composition is selected from the group consisting of: tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), and carbon (C), and any mixtures and any alloys thereof.
27. The method of claim 1, further comprising adding a surfactant to prevent the powder from bonding to the milling container during milling.
28. The method of claim 1 which provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in less than or equal to 30 seconds.

29. The method of claim 1 which provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in 5 minutes.

30. The method of claim 1 which provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in 50 minutes.

31. The method of claim 1 which provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in 500 minutes.

32. The method of claim 1 which provides a dispersion of solutes in the solvent or matrix resulting in a reaction rate wherein the hydrogen production is greater than 74 % of the theoretical yield for aluminum at 25 °C (298 K) and 1 atm. in 5000 minutes.

33. The method of claim 1 further including compacting the milled, powder composition into a densified structure.

34. The method of claim 1 further including compacting the milled, powder composition into a tablet, a rod, a pellet or a bulk part wherein the tablet, rod, pellet or bulk structural part generates hydrogen when the tablet, rod, pellet or bulk structural part contacts water or a water containing liquid.

35. A galvanic metal microstructure comprising:
- an anodic matrix comprising aluminum, an aluminum alloy or another aluminum-based composition; and
 - a cathodic disperse phase comprising a second metal, second alloy or other second metal-based composition is selected from the group consisting of: tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C), and mixtures and alloys thereof
- wherein said cathodic disperse phase forms galvanic couples with the anodic matrix and produce hydrogen gas when said galvanic metal microstructure contacts with water, a water containing liquid or another electrolyte.
36. The galvanic metal microstructure of claim 35 where in the cathodic disperse phase comprises a plurality of discreet particles having a length of less than 1 millimeter.
37. The galvanic metal microstructure of claim 35 where in the cathodic disperse phase comprises a plurality of discreet particles having a length of less than 1000 nanometers.
38. The galvanic metal microstructure of claim 35 where in the cathodic disperse phase comprises a plurality of discreet particles having a length of less than 500 nanometers.
39. The galvanic metal microstructure of claim 35 where in the cathodic disperse phase comprises a plurality of discreet particles having a length of less than 200 nanometers.

40. The galvanic metal microstructure of claim 35 where in the cathodic disperse phase comprises a plurality of discrete particles having a length of less than 100 nanometers.
41. The galvanic metal microstructure of claim 35 where in the cathodic disperse phase comprises a plurality of discrete particles having a length of less than 50 nanometers.
42. The galvanic metal microstructure of claim 35 where in the cathodic disperse phase comprises tin (Sn).
43. The galvanic metal microstructure of claim 35 where in the cathodic disperse phase consists primarily of tin (Sn) or an alloy of tin.
44. The galvanic metal microstructure of claim 35 made by melt spinning, spray atomization, inert gas condensation, solution precipitation, physical vapor deposition, or electrodeposition.
45. A method of generating hydrogen, comprising:
providing a galvanic metal microstructure according to Claim 35;
causing a reaction by contacting the galvanic metal microstructure with a liquid comprising at least one hydroxyl group; and
capturing or using spontaneously generated hydrogen.

46. A nanogalvanic microstructure, comprising:
- a matrix phase comprising aluminum, and
 - a dispersed phase comprising at least one element selected from the group consisting of tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), and carbon (C), and mixtures and alloys thereof, wherein the microstructure comprises grains or subgrains of the matrix phase and individual grains or subgrains of the dispersed phase having at least one nano- or micro-dimension.
47. The nanogalvanic microstructure of claim 46 comprising stringers of the dispersed phase.
48. A method for producing a nanogalvanic microstructure, comprising:
- providing at least one matrix phase material comprising aluminum;
 - providing at least one dispersed phase material selected from the group consisting of tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), and carbon (C), and mixtures and alloys thereof;
 - producing a powder composition that comprises grains or subgrains of aluminum with individual grains or subgrains of the dispersed second metal, second alloy or other second metal-based composition having nano- or micro- dimensions by milling the at least one matrix phase material with the at least one dispersed phase material.

Figure 1

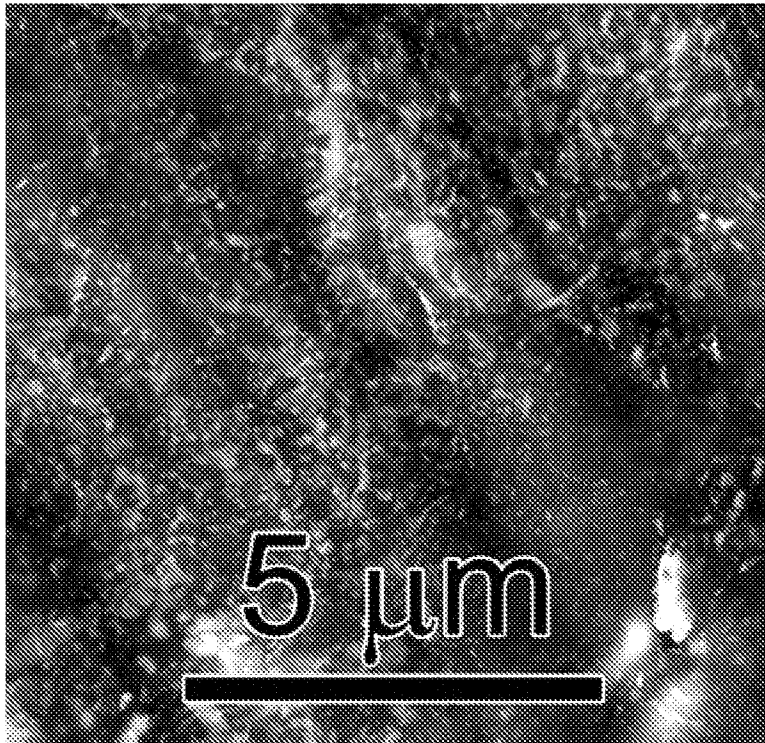


Figure 2

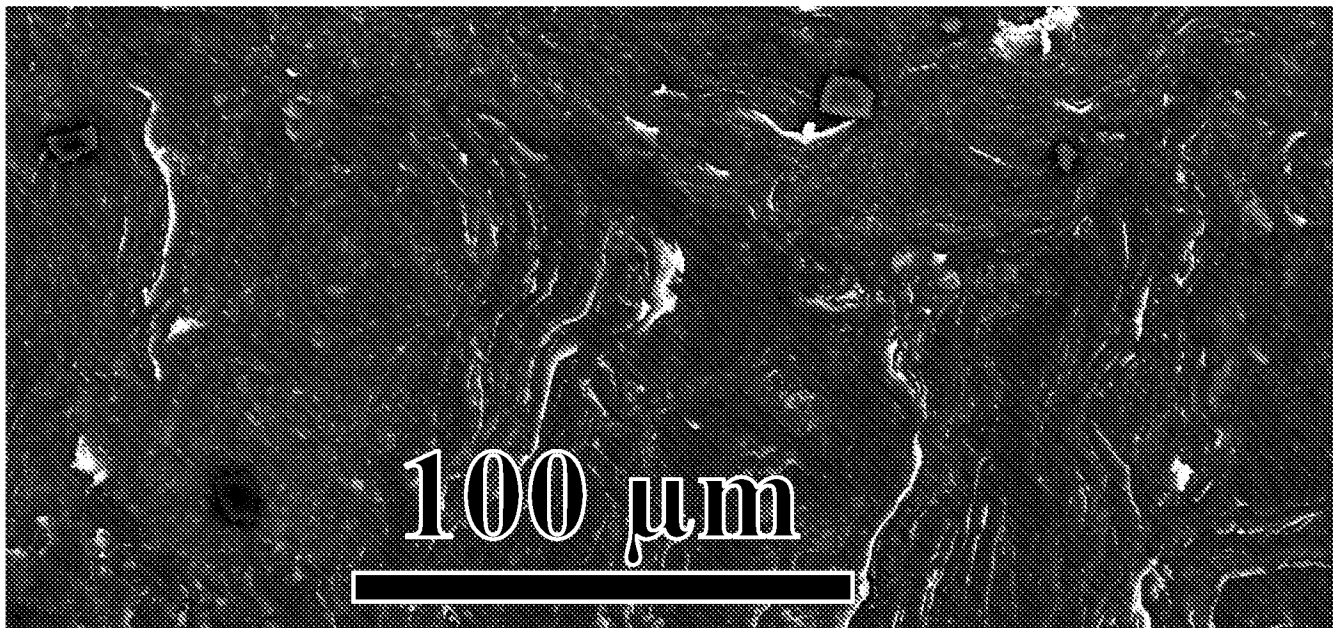


Figure 3

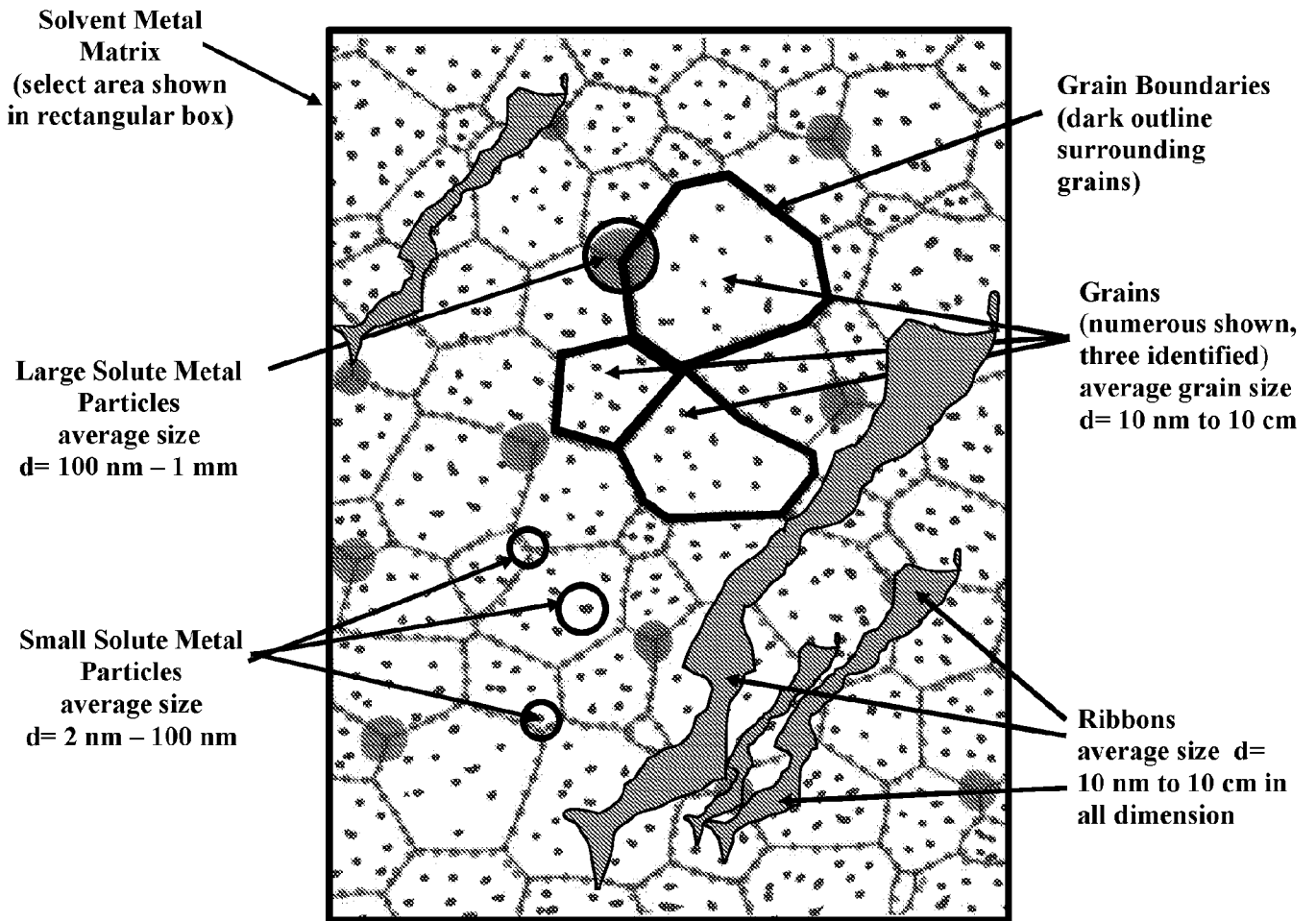


Figure 4

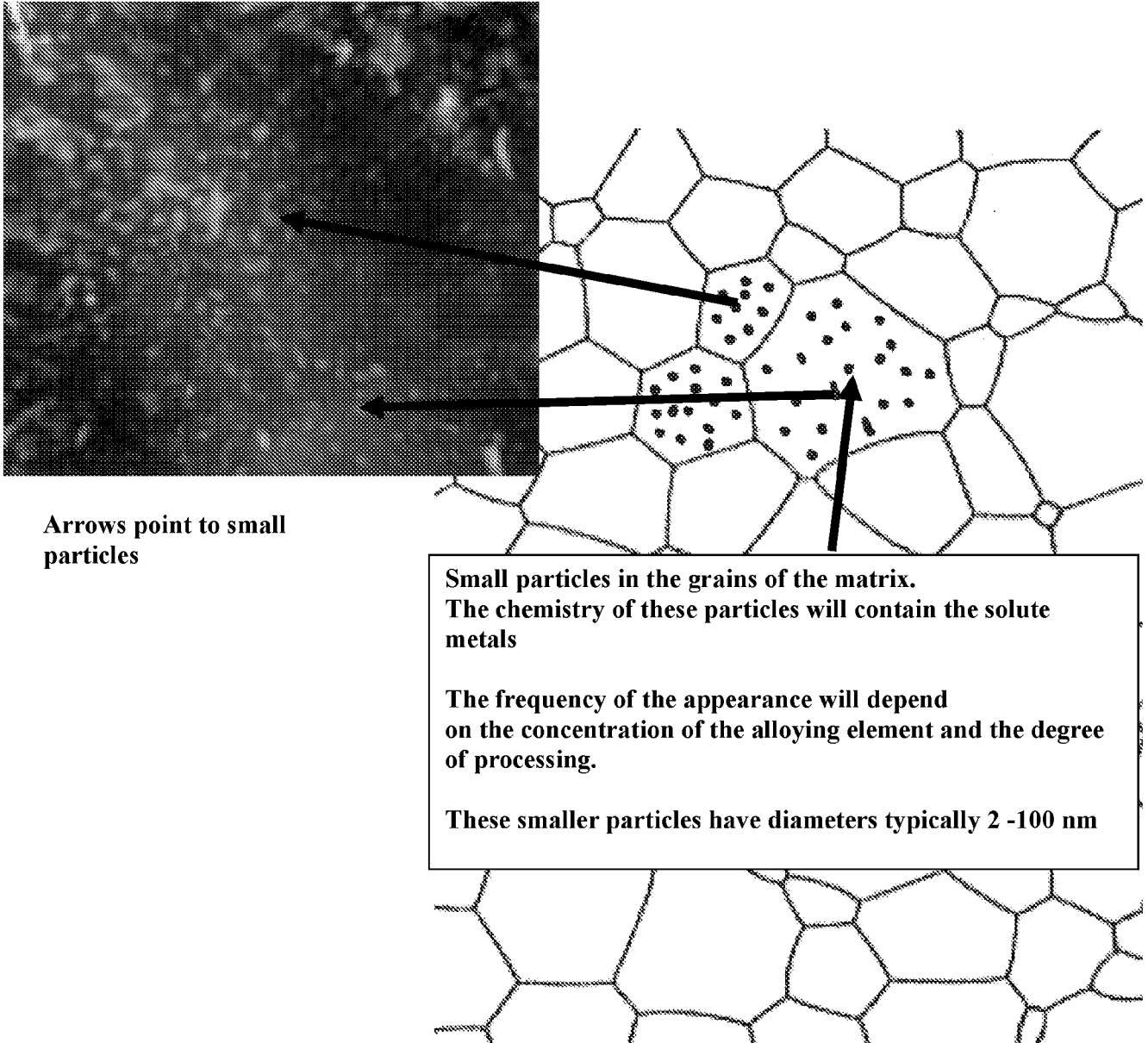


Figure 5

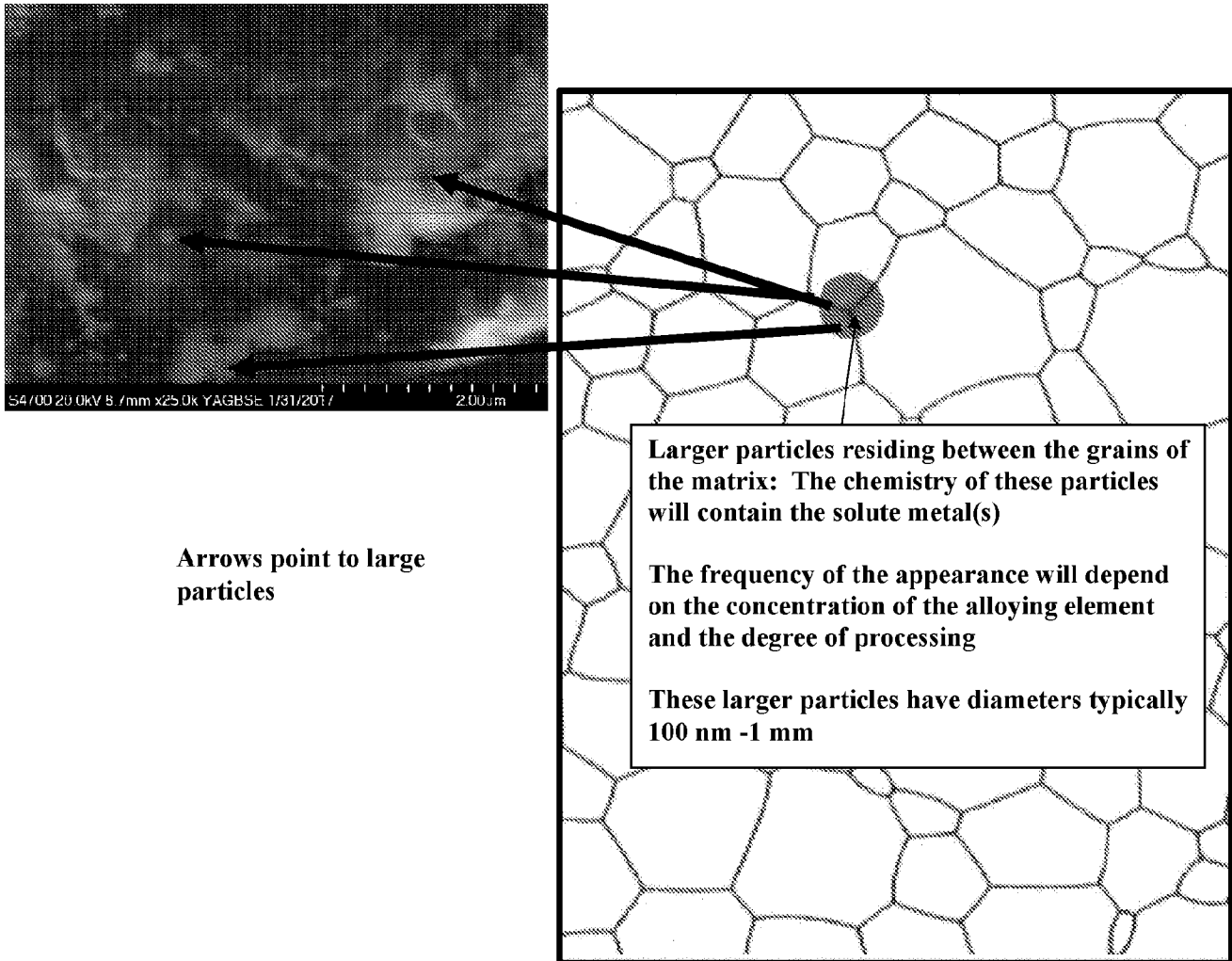


Figure 6

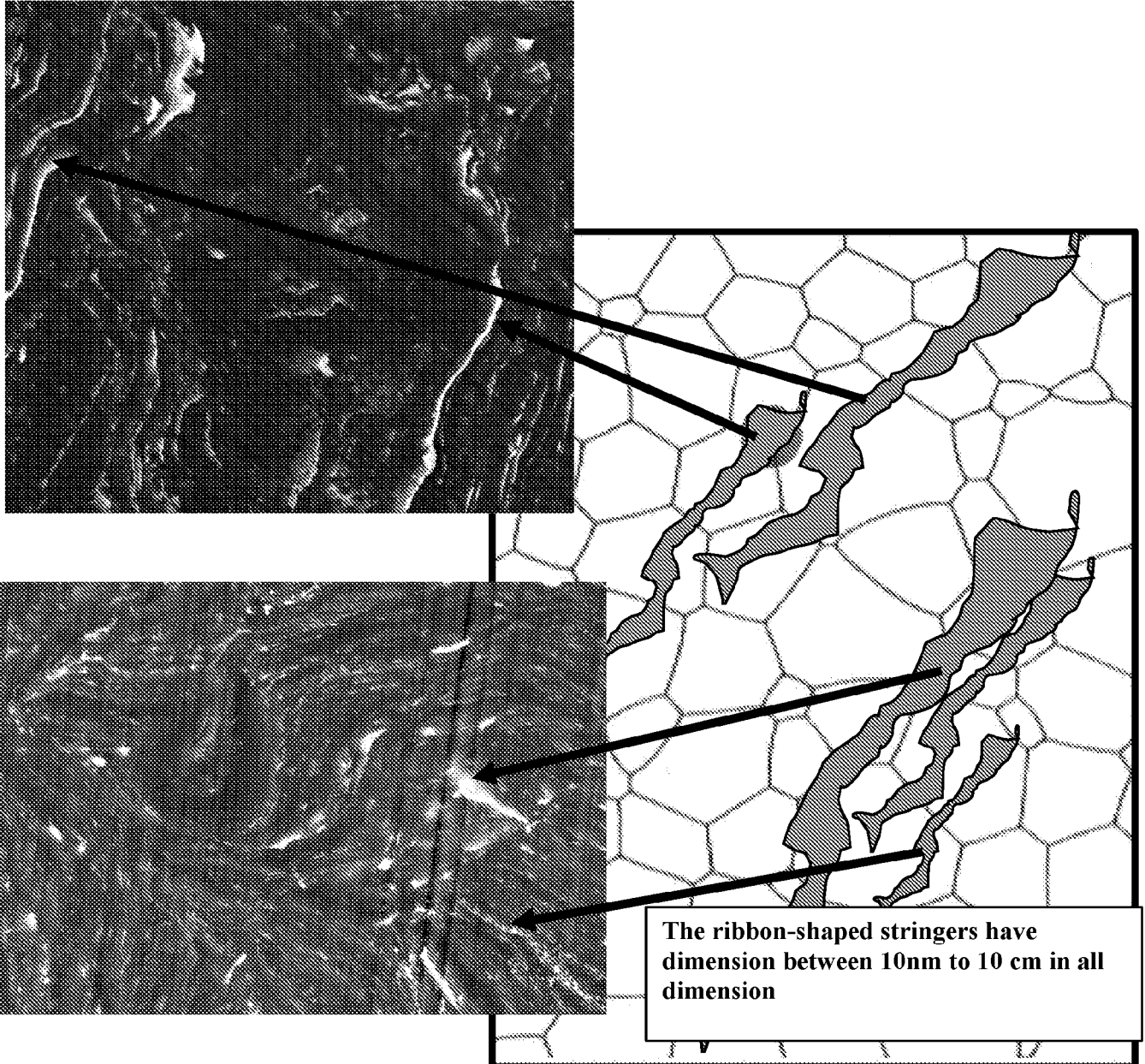


Figure 7

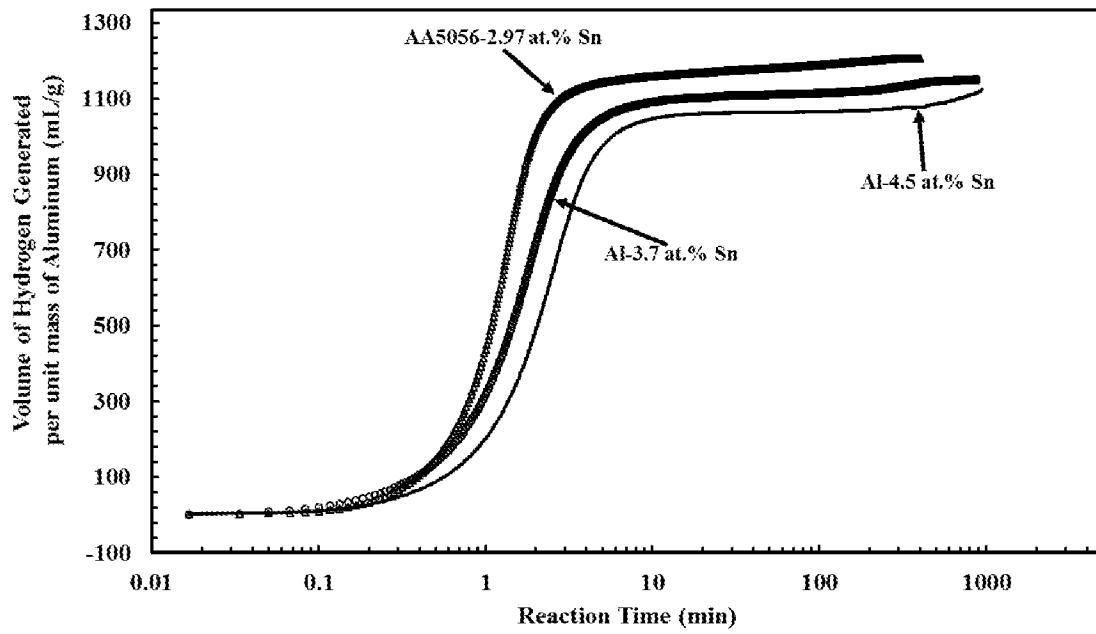


Figure 8

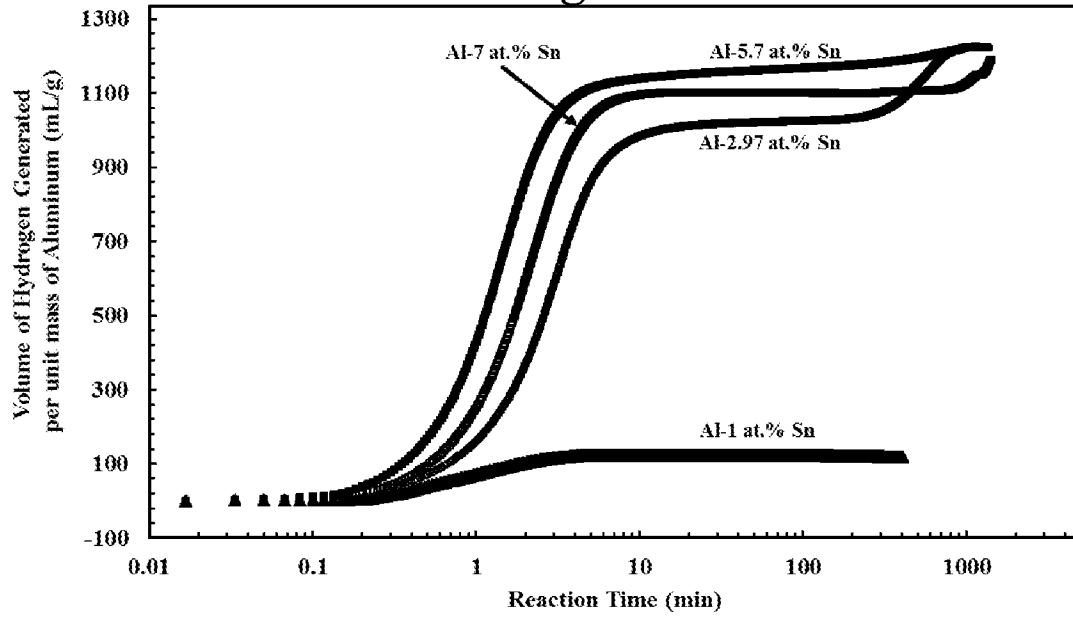


Figure 9

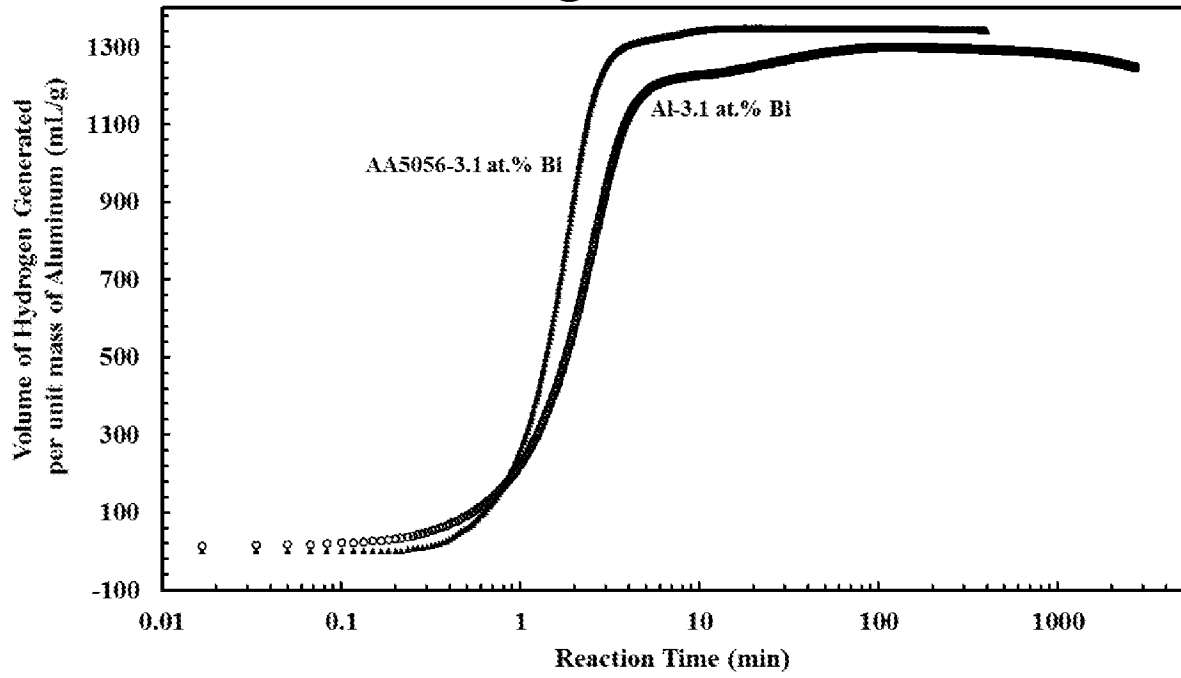


Figure 10

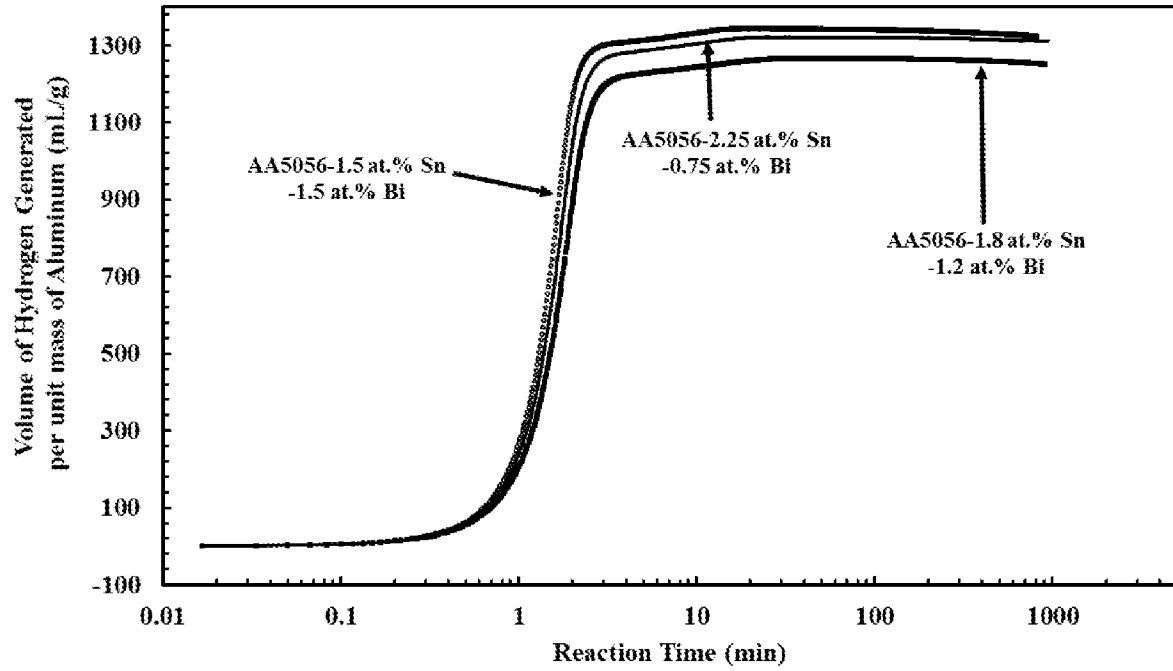


Figure 11

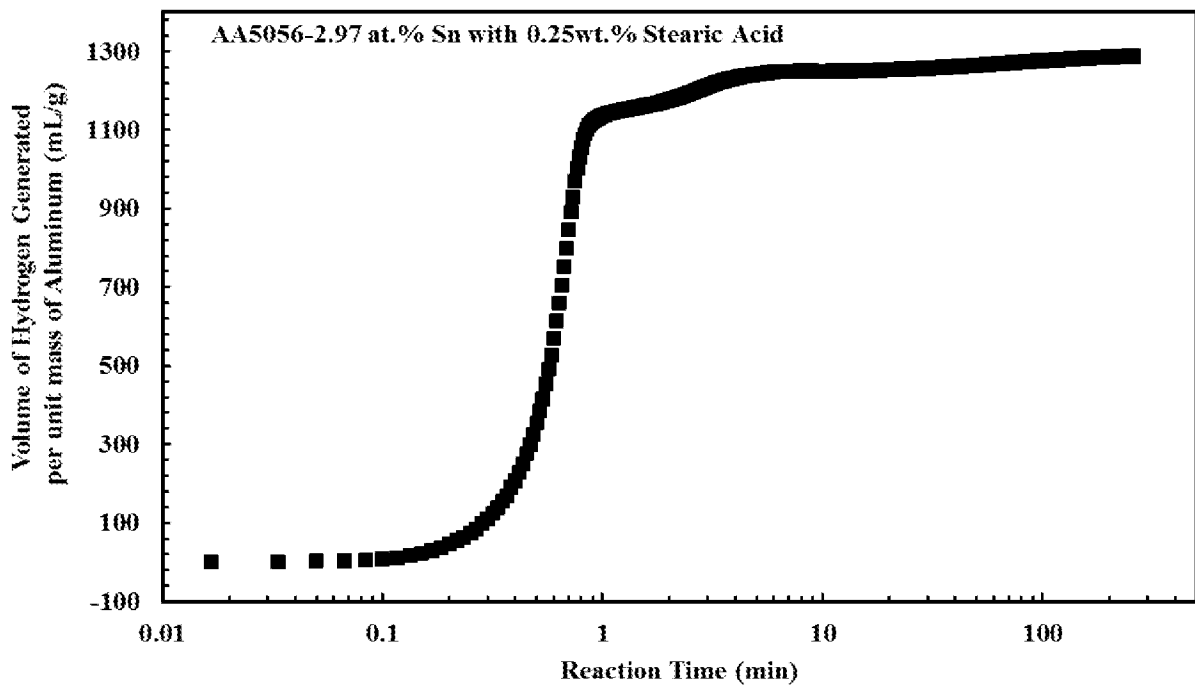
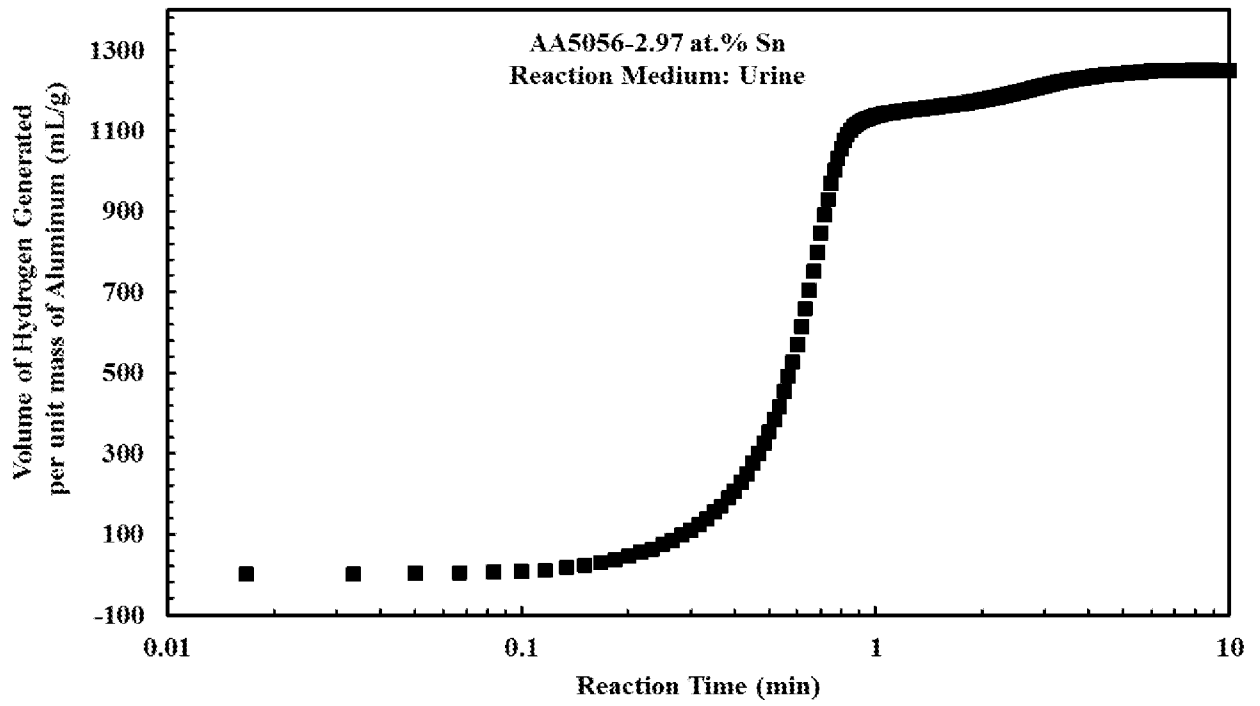
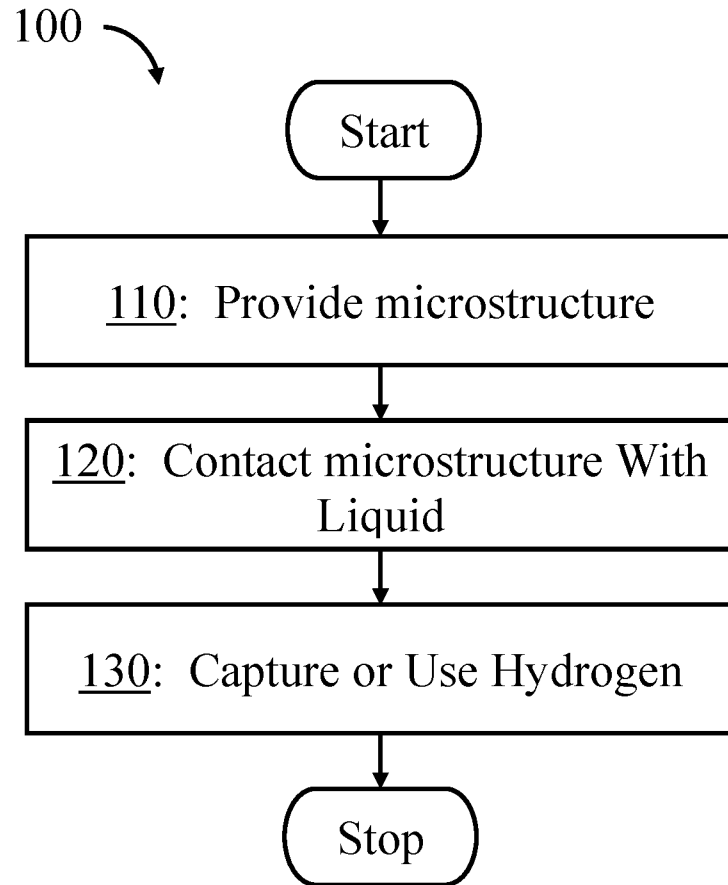
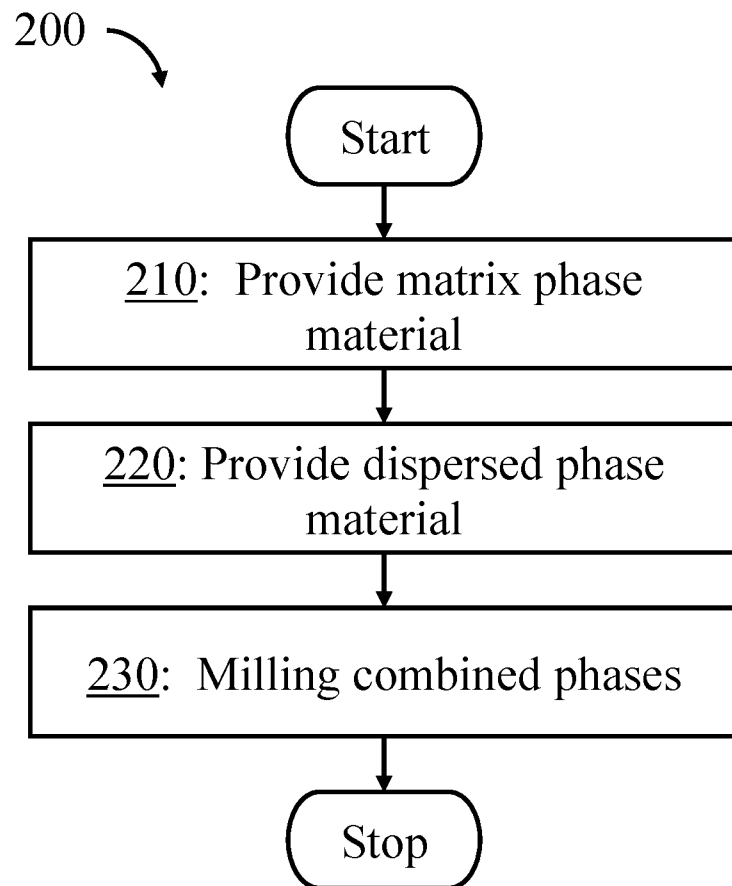


Figure 12



**FIG. 13**

**FIG. 14**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/43267

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - C22C 21/00, E21B 23/06, E21B 33/12 (2018.01)
 CPC - E21B 33/128, B23K 1/06, B23K 1/20

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2002/0048548 A1 (CHAKLADER) 25 April 2002 (25.04.2002) Abstract, para[0019]-[0023], [0028], [0055], [0066], [0071], [0128]; Table 14	1-17, 20-26, 28-34 ----- 18-19, 27
X -- Y	ZHANG et al. "Hydrogen generation from pure water using Al-Sn powders consolidated through high-pressure torsion" Journal of Materials Research. Vol 31(6), March 28, 2016; Abstract, Page 776 Col 1 para[0001], [0003]; Page 781 Col 1 para[0002], Col 2 para[0002]; Table I; Figure 9	35-43, 45-46 ----- 44, 47
Y	ABBAS et al. "Hydrogen production using Al-Sn alloys prepared by rapid solidification" Journal of Advances in Physics. Vol 13(6), June 2017; Page 4980 para[0003]; Page 4981 para[0002]; Figures 12, 13b	44, 47
Y	US 2016/0059214 A1 (HELTON) 03 March 2016 (03.03.2016) para[0028]	18
Y	US 2015/0360941 A1 (CLEAN WAVE ENERGY CORP) 17 December 2015 (17.12.2015) para[0039], [0079], [0097]	19
A	US 7441717 B1 (MAJKA et al.) 28 October 2008 (28.10.2008) Col 1 lines 18-21; Col 3 lines 61-64;	27
A	US 2007/0199410 A1 (SCHOLL et al.) 30 August 2007 (30.08.2007) para[0010]	10-13
A	WIKIPEDIA "Cryogenics" 13 July 2016 (13.07.2016) Page 1 para[0001]; Retrieved from https://en.wikipedia.org/w/index.php?title=Cryogenics&oldid=729654110 on 14 September 2018 (14.09.2018).	13

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

"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

07 November 2018

Date of mailing of the international search report

19 NOV 2018

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
 P.O. Box 1450, Alexandria, Virginia 22313-1450
 Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/43267

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-34, directed to a method of forming an aluminum, an aluminum alloy or other aluminum-based composition that generates hydrogen gas upon contact with water or other aqueous compositions, the method comprising: providing aluminum, providing a second metal, milling the aluminum and second metal, producing a milled, powder composition that comprises grains or subgrains of aluminum with individual grains or subgrains of the dispersed second metal, having atomic to nano-scale or micro-scale dimensions.

Continued in supplemental box

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
1-47
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

- Remark on Protest**
- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
 - The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
 - No protest accompanied the payment of additional search fees.

Continuation of:

Box NO. III: Observations where unity of invention is lacking

Group II: Claims 35-47, directed to a galvanic metal microstructure comprising: an anodic matrix comprising aluminum; a cathodic disperse phase comprising a second metal selected from the group consisting of: tin(Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C), and mixtures and alloys thereof wherein said cathodic disperse phase forms galvanic couples with the anodic matrix and produce hydrogen gas when said galvanic metal microstructure contacts with water, a water containing liquid or another electrolyte.

Group III: Claim 48, directed to a method for producing a nanogalvanic microstructure, comprising: providing at least one matrix phase material comprising aluminum; providing at least one dispersed phase material selected from the group consisting of tin(Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C), and mixtures and alloys thereof: producing a powder composition that comprises grains or subgrains of aluminum with individual grains or subgrains of the dispersed second metal, having nano- or micro-dimensions by milling the at least one matrix phase material with the at least one dispersed phase material.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I requires a method of forming an aluminum composition that generates hydrogen gas upon contact with water, not required by groups II-III.

Group II requires an anodic matrix, and a cathode disperse phase, not required by groups I and III.

Group III requires a method for producing a nanogalvanic microstructure, not required by groups I-II.

Common Technical Features:

Groups I-III share the technical feature of: using aluminum.

However, the share technical feature does not represent a contribution over prior art because the shared technical feature is being anticipated by US 2002/0048548 A1 to CHAKLADER (hereinafter "Chaklader"). Chaklader discloses using aluminum (Abstract, ...a method of producing hydrogen by reacting a metal selected from the group consisting of Aluminum (Al)).

Groups I-II share the technical features of a second metal, second alloy or other second metal-based composition and producing hydrogen gas when the metal composition from combining the aluminum and the second metal contacts water.

However, the share technical feature does not represent a contribution over prior art because the shared technical feature is being anticipated by Chaklader. Chaklader discloses a second metal, second alloy or other second metal-based composition (para[0128], ...the system of Al+Mg...) and producing hydrogen gas when the metal composition from combining the aluminum and the second metal contacts water (para[0128], ...the system of Al+Mg...was studied to evaluate the effect of mechanically alloying two metals on hydrogen generated from water...).

Groups I and III share the technical features of producing a powder composition that comprises grains or subgrains of the dispersed second metal, second alloy or other second-metal based composition having nano- or micro-dimensions by milling the aluminum with the second metal.

However, the share technical feature does not represent a contribution over prior art because the shared technical feature is being anticipated by Chaklader. Chaklader discloses producing a powder composition comprising grains or substrates of the dispersed second metal, second alloy or other second-metal based composition by milling the aluminum with the second metal (para[0055], ...pulverizing Al + additive in closed environments...the surface of Al remains substantially free of oxides during milling...para[0128], ...the system of Al+Mg metals and aluminum oxide...mechanically alloying two metals on hydrogen generation from water. The powder mixtures were produced following the same procedure as described before...) having nano- or micro-dimensions (para[0021], ...preferably, the metal and catalyst are each in the form of particles having a size between .01 microns and 1000 microns...).

Groups II-III share the technical features of: a galvanic microstructure comprising using material selected from the group consisting of: in(Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C), and mixtures and alloys thereof.

However, these technical features do not represent a contribution over prior art because the shared technical features are being anticipated by US 5494538 A to KIRILLOV et al. (hereinafter "Kirillov"). Kirillov discloses a galvanic microstructure comprising using material selected from the group consisting of: in(Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), carbon (C), and mixtures and alloys thereof (Col 3 lines 47-51, the hydroreactive metal mixture of the invention has a crystalline structure incorporating micro-galvanic cells...Magnesium constitutes the micro-anodes of these cells...).

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-III lack unity under PCT Rule 13.

Notes:

Regarding claim 17, this claim lacks clarity as presented. For the purposes of completing this opinion, the first mention of "tin" has been omitted and the claim has been assumed to be the following: "The method of claim 1, wherein the milled, powder composition comprises between about 0.1 atomic percent and about 49.99 atomic percent tin (Sn), magnesium (Mg), silicon (Si), bismuth (Bi), lead (Pb), gallium (Ga), indium (In), zinc (Zn), or carbon (C), or a mixture thereof."