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(54) Title: METHOD AND SYSTEM FOR PROCESSING METAL POWDERS, AND ARTICLES PRODUCED THEREFROM

(57) Abstract: A method and a system for converting irregular metal hydride powders to spherical metal powders, and to an article produced therefrom is provided. The method comprises preparing powder comprising metal hydride particles. The powder is passed through a plasma to thereby de-hydride the metal hydride particles, and the powder is spheroidized to provide spheroidized metallic particles.

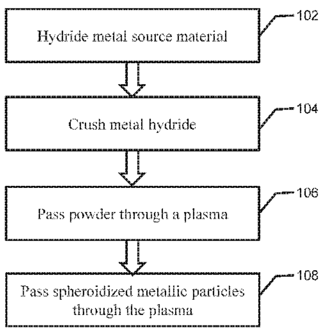

FIG. 1

WO 2020/009955 A1

[Continued on next page]

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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TITLE

METHOD AND SYSTEM FOR PROCESSING METAL POWDERS, AND ARTICLES PRODUCED THEREFROM

CROSS-REFERENCE

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/694,638, which was filed on July 6, 2018. The contents of which is incorporated by reference into this specification.

FIELD OF USE

[0002] The present disclosure relates to a method and a system for processing metal powders and to an article produced therefrom. In certain embodiments, the present disclosure relates to an additive manufacturing method and system.

BACKGROUND

[0003] In various powder bed additive manufacturing applications, the powder feedstocks have strict limits on properties like particle size (*e.g.*, average particle size, chemistry/composition, and morphology (particle shape)). Generally and in additive manufacturing, there are challenges in providing suitable powder metallic powder feedstocks.

SUMMARY

[0004] According to one aspect, the present disclosure provides a novel method for producing spheroidized metallic particles. The method comprises passing powder comprising metal hydride particles through a plasma to spheroidize the particles and to also de-hydride metal hydride particles in the powder, providing spheroidized metallic particles.

[0005] According to another aspect, the present disclosure provides a novel method for producing spheroidized metallic particles. The method comprises passing powder comprising metal hydride particles having an irregular shape through a plasma to produce spheroidized metallic particles. More specifically, as the powder is passed through the plasma, a hydrogen content of at least a portion of the metal hydride particles is reduced and

the metal hydride particles and any other particles present are spheroidized, providing spheroidized metallic particles. The spheroidized metallic particles are substantially spherical.

[0006] According to yet another aspect, the present disclosure provides novel spheroidized metallic particles. The novel spheroidized metallic particles may be used as powder material in an additive manufacturing system or method to produce a part.

[0007] According to a further aspect, the present disclosure provides a method for producing an additively manufactured part. The method comprises passing powder through a plasma to thereby spheroidize the powder and to de-hydride metal hydride particles in the powder, thereby providing spheroidized metallic particles. At least a portion of the spheroidized metallic particles are utilized as powder material in an additive manufacturing system or method to produce a part.

[0008] According to yet a further aspect, the present disclosure provides novel spheroidized metallic particles. The method of manufacturing the spheroidized metallic particles comprises passing powder comprising metal hydride particles through a plasma to produce spheroidized metallic particles. Passing the powder through the plasma also frees hydrogen from (de-hydrides) metal hydride particles in the powder. The spheroidized metallic particles may be used as powder material in an additive manufacturing system or method to produce a part.

[0009] It is understood that the inventions disclosed and described in this specification are not limited to the aspects summarized in this Summary. The reader will appreciate the foregoing details, as well as others, upon considering the following detailed description of various non-limiting and non-exhaustive aspects according to this specification.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The features and advantages of the examples, and the manner of attaining them, will become more apparent, and the examples will be better understood by reference to the following description taken in conjunction with the accompanying drawings, wherein:

[0011] FIG. 1 is a flow chart illustrating a non-limiting embodiment of a method to process powder according to the present disclosure;

[0012] FIG. 2 is a schematic representation of a non-limiting embodiment of a system to process powder according to the present disclosure; and

[0013] FIG. 3 presents photographs of non-limiting embodiments of experimental powder and experimental spheroidized metallic particles according to the present disclosure.

[0014] Corresponding reference characters indicate corresponding parts throughout the several views. The exemplifications set out herein illustrate certain embodiments, in one form, and such exemplifications are not to be construed as limiting the scope of the appended claims in any manner.

DETAILED DESCRIPTION OF NON-LIMITING EMBODIMENTS

[0015] Various embodiments are described and illustrated herein to provide an overall understanding of the structure, function, and use of the disclosed articles, systems, and methods. The various embodiments described and illustrated herein are non-limiting and non-exhaustive. Thus, the invention is not limited by the description of the various non-limiting and non-exhaustive embodiments disclosed herein. Rather, the invention is defined solely by the claims. The features and characteristics illustrated and/or described in connection with various embodiments may be combined with the features and characteristics of other embodiments. Such modifications and variations are intended to be included within the scope of this specification. As such, the claims may be amended to recite any features or characteristics expressly or inherently described in, or otherwise expressly or inherently supported by, this specification. Further, Applicant reserves the right to amend the claims to affirmatively disclaim features or characteristics that may be present in the prior art. The various embodiments disclosed and described in this specification can comprise, consist of, or consist essentially of the features and characteristics as variously described herein.

[0016] Any patent, publication, or other disclosure material identified herein is incorporated herein by reference in its entirety unless otherwise indicated, but only to the extent that the incorporated material does not conflict with existing definitions, statements, or other disclosure material expressly set forth in this specification. As such, and to the extent necessary, the express disclosure as set forth in this specification supersedes any conflicting material incorporated by reference herein. Any material, or portion thereof, that is said to be incorporated by reference into this specification, but which conflicts with existing definitions, statements, or other disclosure material set forth herein, is only incorporated to the extent that no conflict arises between that incorporated material and the existing disclosure material. Applicant reserves the right to amend this specification to expressly recite any subject matter, or portion thereof, incorporated by reference herein.

[0017] Any references herein to “various embodiments”, “some embodiments”, “one embodiment”, “an embodiment”, or like phrases, means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, appearances of the phrases “in various embodiments,” “in some embodiments,” “in one embodiment”, “in an embodiment”, or like phrases, in the specification do not necessarily refer to the same embodiment. Furthermore, the particular described features, structures, or characteristics may be combined in any suitable manner in one or more embodiments. Thus, the particular features, structures, or characteristics illustrated or described in connection with one embodiment may be combined, in whole or in part, with the features, structures, or characteristics of one or more other embodiments without limitation. Such modifications and variations are intended to be included within the scope of the present embodiments.

[0018] In this specification, unless otherwise indicated, all numerical parameters are to be understood as being prefaced and modified in all instances by the term “about”, in which the numerical parameters possess the inherent variability characteristic of the underlying measurement techniques used to determine the numerical value of the parameter. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter described herein should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0019] Also, any numerical range recited herein includes all sub-ranges subsumed within the recited range. For example, a range of “1 to 10” includes all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value equal to or less than 10. Any maximum numerical limitation recited in this specification is intended to include all lower numerical limitations subsumed therein and any minimum numerical limitation recited in this specification is intended to include all higher numerical limitations subsumed therein. Accordingly, Applicant reserves the right to amend this specification, including the claims, to expressly recite any sub-range subsumed within the ranges expressly recited. All such ranges are inherently described in this specification.

[0020] The grammatical articles “a”, “an”, and “the”, as used herein, are intended to include “at least one” or “one or more”, unless otherwise indicated, even if “at least one” or “one or more” is expressly used in certain instances. Thus, the foregoing grammatical articles are used herein to refer to one or more than one (*i.e.*, to “at least one”) of the particular identified elements. Further, the use of a singular noun includes the plural, and the use of a plural noun includes the singular, unless the context of the usage requires otherwise.

[0021] As used herein, “powder” refers to a material comprising a plurality of particles. Powder may be used, for example, in a powder bed in an additive manufacturing system or process to produce a tailored alloy product via additive manufacturing.

[0022] As used herein, “median particle size” refers to the diameter at which 50% of the volume of the particles have a smaller diameter than the given value (*e.g.*, D_{50}).

[0023] As used herein, particle size was determined in accordance with ASTM standard B822.

[0024] As used herein, “substantially comprise” means at least 50% by weight. In various embodiments, substantially comprise can be 50% to 100% by weight such as, for example, at least 60% by weight, at least 70% by weight, at least 80% by weight, at least 90% by weight, at least 95% by weight, or at least 99% by weight.

[0025] As used herein, “substantially free” means no more than 1% by weight. In various embodiments, substantially free of can be 0 to 1% by weight such as, for example, less than 0.5% by weight, less than 0.1% by weight, less than 0.01% by weight, less than 0.001% by weight, or 0.

[0026] As used herein, “substantially removed” means at least 50% by weight has been removed. In various embodiments, “substantially removed” can refer to removal of 50% to 100% by weight such as, for example, removal of at least 60% by weight, removal of at least 70% by weight, removal of at least 80% by weight, removal of at least 90% by weight, removal of at least 95% by weight, or removal of at least 99% by weight.

[0027] As used herein, “substantially spherical” means a shape having a sphericity of at least 0.8, such as, for example, at least 0.85 or at least 0.92.

[0028] When producing metallic powders for use in additive manufacturing, a metal or metal alloy source material (*e.g.*, metal sponge, bar, etc.) may be hydrided to increase hydrogen content of and thereby embrittle the material. For example, the metal source material can be contacted with a gas containing hydrogen at an elevated temperature (*e.g.*, 400°C to 700°C). The resulting brittle metal hydride (*i.e.*, a hydride of a metal or metal alloy) can be crushed to break the material into irregularly shaped metal hydride particles. The irregularly shaped metal hydride particles are then de-hydrided to substantially remove hydrogen from the particles and increase ductility. In certain de-hydriding processes, the metal hydride particles are heated at a temperature greater than 700°C. The de-hydrided particles can then be milled to a desired particle size. The milled material can be subjected to de-oxygenation, additional milling, and spheroidization to produce spheroidized metallic particles that can be substantially free from hydrogen and can be suitable for use as a powder feedstock.

[0029] Typically, the process to produce spheroidized metallic particles having a low hydrogen content and that have a morphology generally suitable to flow in an additive manufacturing apparatus or system involves multiple energy-intensive steps such as heating and reducing pressure. In the present disclosure, a method and system are provided that can reduce energy input requirements and increase the efficiency of producing spheroidized metallic particles having low or substantially no hydrogen content. In various embodiments according to the present disclosure, the de-hydriding process for freeing hydrogen from previously hydrided metals or metal alloys can be combined with spheroidization. In various embodiments, de-oxygenation can be combined with spheroidization/de-hydriding.

[0030] According to an aspect of the present disclosure, powder comprising metal hydride particles which may be generally irregularly shaped are passed through a plasma to thereby de-hydride metal hydride particles in the powder and to spheroidize the powder. This process results in spheroidized metallic particles, and the hydrogen content in the powder has been reduced.

[0031] When producing metallic powders as powder feed material for powder metallurgy applications, including additive manufacturing applications, a metal or metal alloy source material (*e.g.*, metal sponge, bar, etc.) may be used. For example, the metal or metal alloy source material can comprise at least one of titanium, titanium alloy, aluminum, aluminum alloy, tantalum, tantalum alloy, niobium, niobium alloy, zirconium, zirconium alloy, hafnium, hafnium alloy, molybdenum, molybdenum alloy, vanadium, and vanadium alloy. In various embodiments, the metal source material can comprise at least one of titanium and a titanium alloy, for example, a titanium alloy comprising, in weight percentages based on total alloy weight, 87 to 91 titanium, 3.5 to 4.5 vanadium, 5.5 to 6.75 aluminum, and incidental impurities. In various embodiments, the metal source material can comprise Ti-6Al-4V alloy.

[0032] Referring to FIG. 1, a flow chart illustrating a non-limiting embodiment of a method to process powder according to the present disclosure is provided. The metal source material can be hydrided to increase its hydrogen content and thereby convert the material to a metal hydride 102. This conversion embrittles the material. (As used herein, a "metal hydride" refers to both a hydrided metal and a hydrided metal alloy.) For example, the metal source material can be hydrided by heating the source material at an elevated temperature (*e.g.*, 400°C to 700°C) and exposing the heated material to a gas comprising hydrogen (*i.e.*, a hydriding gas). The resulting metal hydride can be or comprise titanium hydride, titanium alloy hydride, aluminum hydride, aluminum alloy hydride, tantalum hydride, tantalum alloy hydride, niobium hydride, niobium alloy hydride, zirconium hydride, zirconium alloy hydride, hafnium hydride, hafnium alloy hydride, molybdenum hydride, molybdenum alloy hydride, vanadium hydride, and vanadium alloy hydride. In certain embodiments, the metal hydride comprises at least one of titanium hydride and titanium alloy hydride. In various embodiments, the metal hydride can comprise a titanium alloy hydride produced by hydriding a titanium alloy comprising, in weight percentages based on total alloy weight, 87 to 91 titanium, 3.5 to 4.5 vanadium, 5.5 to 6.75 aluminum, and incidental impurities. In certain embodiments, the metal source material can be produced by hydriding a titanium alloy comprising Ti-6Al-4V alloy. In various embodiments, the metal hydride can comprise at least 2 weight % hydrogen, such as, for example, at least 4 weight % hydrogen or at least 5 weight % hydrogen. In some embodiments, the metal hydride can comprise a hydrogen content in a range of 2 weight % to 10 weight % hydrogen. For example, titanium hydride particles or titanium alloy hydride particles can comprise 4 weight % hydrogen. In various embodiments, niobium hydride particles or niobium alloy hydride particles can comprise 5 weight % hydrogen. In other embodiments, aluminum hydride particles or aluminum alloy hydride particles can comprise 10 weight % hydrogen.

[0033] In various embodiments, the resulting metal hydride can be crushed to break up the material into smaller pieces (*e.g.*, irregularly shaped metal hydride particles) 104. Crushing can include various means of size reduction such as, for example, milling, grinding, pulverizing, and attriting. In various embodiments, the metal hydride particles can comprise a median particle size of less than 325 μm such as, for example, less than 300 μm, less than 275 μm, less than 250 μm, less than 225 μm, less than 200 μm, less than 175 μm, less than 150 μm, less than 125 μm, less than 100 μm, less than 90 μm, less than 70 μm. In some embodiments, the metal hydride particles can comprise a median particle size in a range of 5 μm to 100 μm, 10 μm to 100 μm, 105 μm to 180 μm, 20 μm to 50 μm, 10 μm to 50 μm, 60 μm to 90 μm, or 50 μm to 100 μm. In various embodiments, fractions of the crushed metal hydride having an undesirable particle size (*e.g.*, too small, too large) can be removed from the metal hydride particles by sieving, air separation, or other known techniques. Crushing the metal hydride can increase the surface area of the metal hydride.

[0034] The powder subjected to the succeeding steps can comprise or substantially comprise metal hydride particles. In various embodiments, the powder can consist of or consist essentially of metal hydride particles. In various examples, the powder comprises, substantially comprises, or consists essentially of particles have an irregular shape. For example, irregularly shaped powder may include at least one sharp edge having an acute exterior angle. The metal hydride particles can be at least one of titanium hydride particles, titanium alloy hydride particles, aluminum hydride particles, aluminum alloy hydride particles, tantalum hydride particles, tantalum alloy hydride particles, niobium hydride particles, niobium alloy hydride particles, zirconium hydride particles, zirconium alloy hydride particles, hafnium hydride particles, hafnium alloy hydride particles, molybdenum hydride particles, molybdenum alloy hydride particles, vanadium hydride particles, and vanadium alloy hydride particles. In certain embodiments, the metal hydride particles comprise at least one of titanium hydride particles and titanium alloy hydride particles.

[0035] The powder can comprise at least one additional material. For example, the powder can comprise non-hydride metallic particles, spheroidized metallic particles, a ceramic, or combinations of any of those materials. The non-hydride metallic particles are metal or metal alloy particles that are substantially free of hydrogen. The non-hydride metallic particles can comprise, for example, at least one of titanium particles, titanium alloy particles, aluminum particles, aluminum alloy particles, tantalum particles, tantalum alloy particles, niobium particles, niobium alloy particles, zirconium particles, zirconium alloy particles, hafnium particles, hafnium alloy particles, molybdenum particles, molybdenum alloy particles, vanadium particles, and vanadium alloy particles, all of which are substantially free of hydrogen. The non-hydride metallic particles can be produced from de-hydriding metal hydride particles, for example, or may be particles of material that was not previously subjected to a hydriding treatment. In various embodiments, the powder can comprise a blend of metal hydride particles and non-hydride metallic particles.

[0036] The powder is passed through a plasma to produce spheroidized metallic particles from the powder 106. In addition, metal hydride particles within the powder that are subjected to the plasma can be de-hydrided and thus converted to non-hydride metallic particles. Thus, the plasma treatment can both spheroidize and de-hydride metal hydride particles included in the powder. In various embodiments, particles within the powder have not been de-hydrided prior to passing the powder through the plasma. In various embodiments, however, powder is simultaneously de-hydrided and spheroidized in a single process while passing through the plasma, providing spheroidized metallic particles having a reduced (*e.g.*, lowered or substantially no) hydrogen content as compared to the powder prior to passing the powder through the plasma. In various embodiments, the spheroidized metallic particles can be substantially spherical. In various embodiments, crushing the metal hydride to increase surface area thereof can enable a lower content of hydrogen and/or oxygen in the spheroidized metallic particles.

[0037] In various embodiments, the spheroidized metallic particles can comprise less than 4 weight % hydrogen based on the total weight of the spheroidized metallic particles. In certain embodiments the hydrogen content of the spheroidized particles can be, for example, less than 2 weight %, less than 1 weight %, less than 0.1 weight %, or less than 0.01 weight %. In some embodiments, the spheroidized metallic particles can be substantially free of hydrogen. In certain embodiments, passing the powder through the plasma can reduce a weight percentage hydrogen content of the powder by at least 30%, such as, for example, by at least 40%, by at least 50%, by at least 70%, or by at least 90%. In some embodiments, passing the powder through the plasma can reduce a weight percentage hydrogen content of the powder in a range of 40% to 90%, or 50% to 100%.

[0038] Passing the powder through the plasma also can reduce an oxygen content of the powder. In various embodiments, the spheroidized metallic particles can comprise less than 1 weight % oxygen or less than 0.5 weight % oxygen, based on the total weight of the spheroidized metallic particles. In certain embodiments, the spheroidized metallic particles can be substantially free of oxygen. In various embodiments, passing the powder through the plasma can reduce a weight percentage oxygen content of the powder by at least 15%, such as, for example, by at least 30%, by at least 50%, by at least 70%, or by at least 90%. In some embodiments, passing the powder through the plasma can reduce a weight percentage oxygen content of the powder in a range of 40% to 90%, or 50% to 100%.

[0039] In various embodiments, at least a portion of the spheroidized metallic particles can be passed through a plasma (*e.g.*, passed through the plasma a second time) 108, thereby reducing or further reducing a hydrogen content and/or an oxygen content in the spheroidized metallic particles. For example, the spheroidized metallic particles can be passed through a plasma a plurality of (*i.e.*, two or more) times. The several passes through the plasma can reduce a weight percentage hydrogen content of the spheroidized metallic particles by at least 30%, such as, for example, by at least 40%, by at least 50%, by at least 70%, or by at least 90%. In some embodiments, the several passes through the plasma can reduce a weight percentage hydrogen content of the spheroidized metallic particles in a range of 40% to 90%, or 50% to 100%. In various embodiments, the several passes through the plasma can reduce a weight percentage oxygen content of the spheroidized metallic particles by at least 15%, such as, for example, by at least 30%, by at least 50%, by at least 70%, or by at least 90%. In some embodiments, the several passes through the plasma can reduce a weight percentage oxygen content of the spheroidized metallic particles in a range of 40% to 90%, or 50% to 100%. In various embodiments, the plurality of passes through the plasma can improve a spherical shape (*e.g.*, sphericity) of the previously spheroidized metallic particles.

[0040] Referring to FIG. 2, a schematic representation of a non-limiting embodiment of a system 200 to process powder is shown. Chamber 202 is provided with an inlet 204 and an outlet 206. The inlet 204 is adapted to receive powder 208 and convey it into the chamber 202. In various embodiments of the system 200, the inlet 204 also is adapted to receive an additional material such as, for example, a gas.

[0041] The chamber 202 is adapted to receive the powder 208 and convert the powder 208 to spheroidized metallic particles 210. For example, the chamber 202 can be configured to produce a plasma 212, and the powder 208 is brought into contact with the plasma 212 in the chamber 202. In certain embodiments, the chamber 202 is adapted to operate with a pressure therein of at least atmospheric pressure (*e.g.*, 1 atmosphere (atm) absolute). In various other embodiments, the chamber 202 is adapted to operate with a pressure less than atmospheric pressure (*e.g.*, less than 1 atm absolute) therein. The spheroidization can reduce the number of faces, edges, and/or features otherwise out of round in the powder 208.

[0042] Spheroidized metallic particles 210 formed in the chamber 202 pass into outlet 206 and can be collected or, in certain embodiments of system 200, may be recycled by passing back into the chamber 202 where they are contacted by the plasma 212. In certain embodiments, outlet 206 can be adapted to receive an additional material, such as, for example, an inert gas and/or one or more additional products of the reaction that occurs in the chamber 202. The additional reaction product(s) can be, for example, hydrogen and/or water. Water may be produced in the chamber 202, for example, when hydrogen is freed from metal hydride particles in chamber 202 and reacts with oxygen from particles in the chamber 202 and/or present in the atmosphere provided in the chamber 202. In various examples, the plasma 212 also can facilitate removal of nitrides from powder 208.

[0043] The plasma 212 produced in chamber 202 can be generated by any of various means known in the art. For example, the plasma 212 can be any of a glow discharge plasma, a capacitive discharge plasma, a cascaded arc plasma, an inductively coupled plasma, a microwave plasma, a wave heated plasma, an arc discharge plasma, a corona discharge plasma, a dielectric barrier discharge plasma, and a piezoelectric direct discharge plasma. The system 200 can be designed so that the plasma 212 is generated in one or more of various regions within the chamber 202. In certain embodiments, the plasma 212 is generated so that powder introduced into chamber 202 contacts the plasma 212 in a manner that facilitates spheroidization and de-hydriding of the powder 208 to form the spheroidized metallic particles 210 with reduced (*e.g.*, low or substantially no) hydrogen content. For example, the system 200 can be designed so that the plasma 212 is generated axially with respect to the flow of the powder 208 through the chamber 202. The positioning of the plasma 212 within the chamber 202 also can be arranged to enhance the de-oxygenation effects of the plasma 212, so as to reduce oxygen content of powder introduced into chamber 202 along with reducing hydrogen content of and spheroidizing the particles. In various embodiments, the plasma 212 comprises inductively coupled plasma. In certain embodiments, the plasma 212 comprises microwave plasma. In various embodiments, the plasma can be a thermal plasma or a non-thermal plasma.

[0044] The plasma 212 can comprise a temperature suitable to promote de-hydriding of the powder 208 and/or suitable to melt the powder 208 to promote spheroidization. For example, in various embodiments, an electron temperature of the plasma 212 is at least 3,000 K

(Kelvin) such as, for example, at least 4,000 K, at least 5,000 K, at least 6,000 K, at least 7,000 K, 4,000 K to 10,000 K, or 6,000 K to 10,000 K.

[0045] A gas feed line 214 can supply a gas to the chamber 202. The gas feed line 214 can communicate with the inlet 204, which then feeds the gas into the chamber 202 along with the powder 208, or, alternatively, the gas feed line 214 can directly communicate with the chamber 202. The plasma 212 can be produced from gas fed to the system 200 by the gas feed line 214. In various embodiments, the gas can comprise an inert gas. In various embodiments, the gas can comprises at least one of helium, argon, nitrogen, hydrogen, oxygen, carbon tetrachloride, and an alkane. In various embodiments, the gas is supplied to the chamber 202 with the powder 208 in the inlet 204.

[0046] In certain embodiments, the gas introduced into the chamber 202 comprises hydrogen. For example, the gas introduced into the chamber 202 can comprise 1% to 20% hydrogen by volume, such as, for example, 2% to 15% hydrogen by volume, 1% to 4% hydrogen by volume, or 8% to 12% hydrogen by volume. The addition of hydrogen to the gas can facilitate the removal of oxygen from the powder 208 given that the oxygen can react with the hydrogen in the chamber 202.

[0047] In other embodiments, the gas introduced into the chamber 202 can comprise at least one of oxygen, nitrogen, and an alkane. The oxygen, nitrogen, and/or alkane can react with the powder and produce spheroidized metallic particles comprising at least one surface bound group of an oxide, a nitride, and a carbide. The surface bound group can differ depending on the nature of the gas introduced into the chamber 202. In various embodiments, the inner portion below the surface of the spheroidized metallic particles can be substantially free of the surface bound group.

[0048] The surface bound group can be used to indicate that the spheroidized metallic particles were created by the process according to the present disclosure. For example, the surface bound group on the spheroidized metallic particles can be identified by x-ray photoelectron spectroscopy, auger electron spectroscopy, or other suitable identification technique. The identification of the surface bound group can indicate that the spheroidized metallic particles were created by the process according to the present disclosure. In various embodiments, the surface bound group can form a shell around the spheroidized metallic particles and the thickness of the shell can be used to indicate the spheroidized metallic particles were created by the process according to the present disclosure.

[0049] In various embodiments, a recycle line 216 can be in fluid communication with the outlet 210 and adapted to receive the spheroidized metallic particles 210. The recycle line 216 can be suitable to output at least a portion of the spheroidized metallic particles 210 into the inlet 208, in which they are then conveyed into the chamber 202 to pass through the plasma 212. The spheroidized metallic particles 210 can be recycled into the chamber 202 through recycle line 216 as many times as necessary to remove the desired levels of hydrogen and/or oxygen from the spheroidized metallic particles 210.

[0050] The spheroidized metallic particles produced according to the present disclosure can be used to produce a part. For example, the spheroidized metallic particles can be used as powder material in a powder metallurgy system and/or process such as, for example, an additive manufacturing system and/or process. The part produced by the system and/or process can comprise, for example, at least one of an aerospace component, an automotive component, an industrial component, a consumer product, and a building component.

[0051] As used herein, "additive manufacturing" refers to a process of joining materials to make objects from three dimensional model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies, as defined in ASTM F2792-12a entitled "Standard Terminology for Additively Manufacturing Technologies". Non-limiting examples of additive manufacturing processes useful in producing products from metallic feedstock include, for instance, DMLS (direct metal laser sintering), SLM (selective laser melting), SLS (selective laser sintering), and EBM (electron beam melting), among others. Any suitable feedstock may be used, including a powder, a wire, and combinations thereof. In some embodiments the additive manufacturing feedstock is comprised of powder.

<u>EXAMPLES</u>

[0052] Irregularly shaped metal hydride particles were produced by hydriding Ti-6Al-4V alloy source material and crushing the metal hydride. The irregularly shaped metal hydride particles were passed through a plasma in a commercially available powder spheroidization system and were simultaneously de-hydrided and spheroidized to produce experimental spheroidized metallic particles utilizing suitable operating parameters. The commercially available system used was the TEKSPHERO 15 plasma powder spheroidization system, available form Tekna, Sherbrooke, Quebec. The irregularly shaped metal hydride particles were passed through the spheroidization system once to produce experimental spheroidized metallic particles. The metal hydride particles were not subjected to a de-hydriding treatment prior to passage through the powder spheroidization system. The compositions of the irregularly shaped metal hydride particles and the spheroidized metallic particles produced by passage once through the plasma in the powder spheroidization system are provided in Table 1. The oxygen content of the particles was measured according to ASTM E1408. The hydrogen content of the particles was measured according to ASTM E1447 with a sample size adjustment. The aluminum, vanadium, and titanium contents of the particles was measured according to ASTM E-2371.

Table 1:

	Shape	Median Particle Size (µm)	Hydrogen Content (weight percent)	Oxygen Content (weight percent)	Aluminum Content (weight percent)	Vanadium Content (weight percent)	Titanium Content (weight percent)
Metal hydride Particles	Irregular	29.2	3.2	1.2	5.7	3.8	Balance
Experimental Spheroidized Particles	Spherical	43	2.0	1.0	5.2	3.8	Balance

[0053] As illustrated in Table 1, passing the irregularly shaped metal hydride particles through the plasma spheroidized the particles and also reduced both hydrogen and oxygen content of the particles. More specifically, the plasma process reduced the hydrogen content of the particles to 2.0 weight %, and reduced the oxygen content of the particles to 1.0 weight %. This represents an approximately 37% reduction in hydrogen weight percentage content, and an approximately 16% reduction in oxygen weight percentage content in the powder for this composition.

[0054] Surprisingly, it was observed that passing irregularly shaped metal hydride particles through a plasma concomitantly spheroidized and de-hydrided the particles, thus forming a spheroidized metallic powder having a tailored composition (*e.g.*, lowered hydrogen, lowered oxygen) and suitable characteristics (appropriate morphology) for further applications (*e.g.*, utilization as an additive manufacturing feedstock). In view of the experimental results presented herein, it is believed that other alloy compositions would experience an improvement (reduction) in hydrogen and oxygen contents if subjected to the same process.

[0055] It is believed that the hydrogen and oxygen contents of the experimental spheroidized metallic particles could be further reduced by subjecting the particles to one or more additional passes through the plasma (*e.g.*, recycling the particles through the spheroidization system). In particular, it is believed that recycling the spheroidized metallic powder through the plasma powder spheroidization system in the present example may reduce the hydrogen content of the spheroidized metallic particles to less than 2.0 weight %, and may reduce the oxygen content of the spheroidized metallic particles to less than 1.0 weight %.

[0056] FIG. 3 provides scanning electron microscope images of the metal hydride particles 302 and the experimental spheroidized particles 304 of the present example. As shown in FIG. 3, the metal hydride particles 302 produced by hydriding the Ti-6Al-4V alloy and crushing the hydride generally had an irregular, angular shape. After passing through the plasma, the particles 304 were generally substantially spherical in shape. Also, as shown in Table 1, the spheroidization process also reduced both the hydrogen and oxygen contents of the irregularly shaped metal hydride particles comprising Ti-6Al-4V alloy. Thus, the plasma process can convert metal hydride particles into spheroidized metallic particles having a morphology and chemistry suitable for use as powder material for further applications such as, for example, additive manufacturing.

[0057] In some embodiments, the products produced by these methods have commercial end-uses in industrial applications, consumer applications (e.g. consumer electronics and/or appliances) or other areas. For example, the components or resulting products can be utilized in the aerospace field, automotive field, transportation field, building and construction field, in a variety of forms: fasteners, sheet, plate, castings, forgings, extrusions, post processed additive manufacturing forms, among others, including various applications (e.g. structural applications and components like beams, frames, rails, brackets, bulkheads, spars, ribs, among others.

[0058] Various aspects of the invention according to the present disclosure include, but are not limited to, the aspects listed in the following numbered clauses.

1. A method comprising:

passing a powder comprising metal hydride particles through a plasma to thereby de-hydride the metal hydride particles and spheroidize the powder to provide spheroidized metallic particles.

2. The method of clause 1, further comprising crushing a metal hydride to provide the metal hydride particles.

3. The method of clause 2, wherein the metal hydride particles comprise a median particle size less than 200 microns after crushing.

4. The method of clause 1-3, wherein the spheroidized metallic particles are substantially spherical.

5. The method of clause 1-4, wherein the spheroidized metallic particles comprise 30 weight percentage hydrogen content less than the powder.

6. The method of clause 1-5, wherein the passing the powder through a plasma reduces an oxygen content of the powder.

7. The method of clause 1-6, wherein the spheroidized metallic particles comprise less than 1 weight percent oxygen based on the total weight of the spheroidized metallic particles.

8. The method of clause 1-7, wherein the metal hydride particles comprise at least one of titanium hydride particles, titanium alloy hydride particles, aluminum hydride particles, aluminum alloy hydride particles, tantalum hydride particles, tantalum alloy hydride particles, niobium hydride particles, niobium alloy hydride particles, zirconium hydride particles, zirconium alloy hydride particles, hafnium hydride particles, hafnium alloy hydride particles, molybdenum hydride particles, molybdenum alloy particles, vanadium hydride particles, and vanadium alloy hydride particles.

9. The method of clause 1-8, further comprising hydriding at least one of a metal source material and a metal alloy source material to produce the metal hydride particles.

10. The method of clause 9, wherein the hydriding at least one of a metal source material and a metal alloy source material comprises hydriding a titanium alloy comprising, in

weight percentages based on total alloy weight, 87 to 91 titanium, 3.5 to 4.5 vanadium, and 5.5 to 6.75 aluminum.

11. The method of clause 1-10, further comprising hydriding a Ti-6Al-4V alloy and crushing the hydrided Ti-6Al-4V alloy to produce the metal hydride particles.

12. The method of clause 1-11, wherein the powder has an irregular shape.

13. The method of clause 1-12, wherein the plasma comprises an inductively coupled plasma.

14. The method of clause 1-13, wherein the plasma comprises a microwave plasma.

15. The method of clause 1-14, wherein the plasma is produced from a gas comprising at least one of helium, argon, nitrogen, hydrogen, oxygen, carbon tetrachloride, and an alkane.

16. The method of clause 15, wherein the spheroidized metallic particles comprises at least one surface bound group of an oxide, a nitride, and a carbide.

17. The method of clause 1-16, further comprising passing at least a portion of the spheroidized metallic particles through a plasma, thereby reducing a hydrogen content and an oxygen content in the spheroidized metallic particles.

18. The method of clause 17, wherein spheroidized metallic particles are passed through a plasma a plurality of times to thereby reduce a weight percentage hydrogen content of the powder by at least 30 percent.

19. The method of clause 17-18, wherein spheroidized metallic particles are passed through a plasma a plurality of times to thereby reduce a weight percentage oxygen content of the powder by at least 15 percent.

20. The method of clause 1-19, further comprising passing at least a portion of the spheroidized metallic particles through a plasma one or more times to improve a spherical shape of the spheroidized metallic particles.

21. The method of clause 1-20, wherein a temperature of the plasma is suitable to melt the powder.

22. The method of clause 1-21, further comprising processing at least a portion of the spheroidized metallic particles by an additive manufacturing method to produce a part.

23. The method of clause 1-22, wherein the powder consists essentially of the metal hydride particles.

24. The method of clause 23, further comprising:

hydriding a titanium alloy comprising, in weight percentages based on total alloy weight, 87 to 91 titanium, 3.5 to 4.5 vanadium, and 5.5 to 6.75 aluminum to provide a hydrided source material; and

crushing the hydrided source material to provide the metal hydride particles.

25. The method of clause 24, wherein the titanium alloy is Ti-6Al-4V alloy.

26. The method of clause 1-25, wherein the powder is not de-hydrided prior to passing the powder through the plasma.

27. A method for producing spheroidized metallic particles comprising:

passing a powder comprising metal hydride particles, through a plasma in a reactor to produce spheroidized metallic particles, wherein passing the powder through the plasma:

reduces a hydrogen content of at least a portion of the metal hydride particles so that a hydrogen content of the spheroidized metallic particles is less than 4 percent by weight based on the total weight of the spheroidized metallic particles; and

spheroidizes the metal hydride particles, wherein the spheroidized metallic particles are substantially spherical.

28. The method of clause 27, wherein the metal hydride particles comprise at least one of titanium hydride particles, titanium alloy hydride particles, aluminum hydride particles, aluminum alloy hydride particles, tantalum hydride particles, tantalum alloy hydride particles, niobium hydride particles, niobium alloy hydride particles, zirconium hydride particles, zirconium alloy hydride particles, hafnium hydride particles, hafnium alloy hydride particles, molybdenum hydride particles,

molybdenum alloy hydride particles, vanadium hydride particles, and vanadium alloy hydride particles.

29. The method of clause 27-28, further comprising:

hydriding a titanium alloy comprising, in weight percentages based on total alloy weight, 87 to 91 titanium, 3.5 to 4.5 vanadium, and 5.5 to 6.75 aluminum to provide a hydrided source material; and

crushing the hydrided source material to provide the metal hydride particles.

30. The method of clause 27-29, further comprising hydriding a Ti-6Al-4V alloy (UNS R56400) and crushing the hydrided Ti-6Al-4V to produce the metal hydride particles.

31. Spheroidized metallic particles produced by a process comprising a method according to any one or more of clauses 1 to 30.

32. A part produced by an additive manufacturing system or method utilizing the spheroidized metallic particles made by the method of any one or more of clauses 1 to 30.

33. The part of clause 32, wherein the part is at least one of an aerospace component, an automotive component, an industrial component, a consumer product, and a building component.

34. A method for producing an additively manufactured part, the method comprising:

passing the powder through a plasma to thereby de-hydride the metal hydride particles and spheroidizing the powder to provide spheroidized metallic particles

processing at least a portion of the spheroidized metallic particles using an additive manufacturing system or method to produce a part.

35. The method of clause 34, wherein the part is at least one of an aerospace component, an automotive component, an industrial component, a consumer product, and a building component.

[0059] One skilled in the art will recognize that the herein described components, devices, operations/actions, and objects, and the discussion accompanying them, are used as examples for the sake of conceptual clarity and that various configuration modifications are contemplated. Consequently, as used herein, the specific examples/embodiments set forth and the accompanying discussion are intended to be representative of their more general classes. In general, use of any specific exemplar is intended to be representative of its class, and the non-inclusion of specific components, devices, operations/actions, and objects should not be taken limiting. While the present disclosure provides descriptions of various specific aspects for the purpose of illustrating various aspects of the present disclosure and/or its potential applications, it is understood that variations and modifications will occur to those skilled in the art. Accordingly, the invention or inventions described herein should be understood to be at least as broad as they are claimed and not as more narrowly defined by particular illustrative aspects provided herein.

CLAIMS

What is claimed is:

1. A method comprising:

   passing a powder comprising metal hydride particles through a plasma to thereby de-hydride the metal hydride particles and spheroidize the powder to provide spheroidized metallic particles.

2. The method of claim 1, further comprising crushing a metal hydride to provide the metal hydride particles.

3. The method of claim 2, wherein the metal hydride particles comprise a median particle size less than 200 microns after crushing.

4. The method of any one of claims 1-3, wherein the spheroidized metallic particles are substantially spherical.

5. The method of any one of claims 1-4, wherein the spheroidized metallic particles comprise 30 weight percentage hydrogen content less than the powder.

6. The method of any one of claims 1-5, wherein the passing the powder through a plasma reduces an oxygen content of the powder.

7. The method of any one of claims 1-6, wherein the spheroidized metallic particles comprise less than 1 weight percent oxygen based on the total weight of the spheroidized metallic particles.

8. The method of any one of claims 1-7, wherein the metal hydride particles comprise at least one of titanium hydride particles, titanium alloy hydride particles, aluminum hydride particles, aluminum alloy hydride particles, tantalum hydride particles, tantalum alloy hydride particles, niobium hydride particles, niobium alloy hydride particles, zirconium hydride particles, zirconium alloy hydride particles, hafnium hydride particles, hafnium hydride hydride particles, molybdenum hydride particles, molybdenum alloy hydride particles, vanadium hydride particles, and vanadium alloy hydride particles.

9. The method of any one of claims 1-8, further comprising hydriding at least one of a metal source material and a metal alloy source material to produce the metal hydride particles.

10. The method of claim 9, wherein the hydriding at least one of a metal source material and a metal alloy source material comprises hydriding a titanium alloy comprising, in weight percentages based on total alloy weight, 87 to 91 titanium, 3.5 to 4.5 vanadium, and 5.5 to 6.75 aluminum.

11. The method of any one of claims 1-10, further comprising hydriding a Ti-6Al-4V alloy and crushing the hydrided Ti-6Al-4V alloy to produce the metal hydride particles.

12. The method of any one of claims 1-11, wherein the powder have an irregular shape.

13. The method of any one of claims 1-12, wherein the plasma comprises an inductively coupled plasma.

14. The method of any one of claims 1-13, wherein the plasma comprises a microwave plasma.

15. The method of any one of claims 1-14, wherein the plasma is produced from a gas comprising at least one of the following: helium, argon, nitrogen, hydrogen, oxygen, carbon tetrachloride, and an alkane.

16. The method of claim 15, wherein the spheroidized metallic particles comprises at least one surface bound group of an oxide, a nitride, and a carbide.

17. The method of any one of claims 1-16, further comprising passing at least a portion of the spheroidized metallic particles through a plasma, thereby reducing a hydrogen content and an oxygen content in the spheroidized metallic particles.

18. The method of claim 17, wherein spheroidized metallic particles are passed through a plasma a plurality of times to thereby reduce a weight percentage hydrogen content of the powder by at least 30 percent.

19. The method of any one of claims 17-18, wherein spheroidized metallic particles are passed through a plasma a plurality of times to thereby reduce a weight percentage oxygen content of the powder by at least 15 percent.

20. The method of any one of claims 1-19, further comprising passing at least a portion of the spheroidized metallic particles through a plasma one or more times to improve a spherical shape of the spheroidized metallic particles.

21. The method of any one of claims 1-20, wherein a temperature of the plasma is suitable to melt the powder.

22. The method of any one of claims 1-21, further comprising processing at least a portion of the spheroidized metallic particles by an additive manufacturing method to produce a part.

23. The method of any one of claims 1-22, wherein the powder consists essentially of the metal hydride particles.

24. The method of claim 23, further comprising:

hydriding a titanium alloy comprising, in weight percentages based on total alloy weight, 87 to 91 titanium, 3.5 to 4.5 vanadium, and 5.5 to 6.75 aluminum to provide a hydrided source material; and

crushing the hydrided source material to provide the metal hydride particles.

25. The method of claim 24, wherein the titanium alloy is Ti-6Al-4V alloy.

26. The method of any one of claims 1-25, wherein the powder is not de-hydrided prior to passing the powder through the plasma.

27. A method for producing spheroidized metallic particles comprising:

passing powder having an irregular shape through a plasma to produce spheroidized metallic particles, wherein passing the powder through the plasma:

reduces a hydrogen content of at least a portion of the metal hydride particles so that a hydrogen content of the spheroidized metallic particles is less than 4 percent by weight based on the total weight of the spheroidized metallic particles; and spheroidizes the metal hydride particles, wherein the spheroidized metallic particles are substantially spherical.

28. The method of claim 27, wherein the metal hydride particles comprise at least one of titanium hydride particles, titanium alloy hydride particles, aluminum hydride particles, aluminum alloy hydride particles, tantalum hydride particles, tantalum alloy hydride particles, niobium hydride particles, niobium alloy hydride particles, zirconium hydride particles, zirconium alloy hydride particles, hafnium hydride particles, hafnium alloy hydride particles, molybdenum hydride particles, molybdenum alloy hydride particles, vanadium hydride particles, and vanadium alloy hydride particles.

29. The method of any one of claims 27-28, further comprising:

hydriding a titanium alloy comprising, in weight percentages based on total alloy weight, 87 to 91 titanium, 3.5 to 4.5 vanadium, and 5.5 to 6.75 aluminum to provide a hydrided source material; and

crushing the hydrided source material to provide the metal hydride particles.

30. The method of any one of claim 27-29, further comprising hydriding a Ti-6Al-4V alloy and crushing the hydrided Ti-6Al-4V to produce the metal hydride particles.

31. Spheroidized metallic particles produced by a process comprising a method according to any one or more of claims 1 to 30.

32. A part produced by an additive manufacturing system or method utilizing the spheroidized metallic particles made by the method of any one or more of claims 1 to 30.

33. The part of claim 32, wherein the part is at least one of an aerospace component, an automotive component, an industrial component, a consumer product, and a building component.

34. A method for producing an additively manufactured part, the method comprising:

passing powder comprising metal hydride particles through a plasma to thereby de-hydride the metal hydride particles and spheroidizing the powder to provide spheroidized metallic particles processing at least a portion of the spheroidized metallic particles using an additive manufacturing system or method to produce a part.

35. The method of claim 34, wherein the part is at least one of an aerospace component, an automotive component, an industrial component, a consumer product, and a building component.

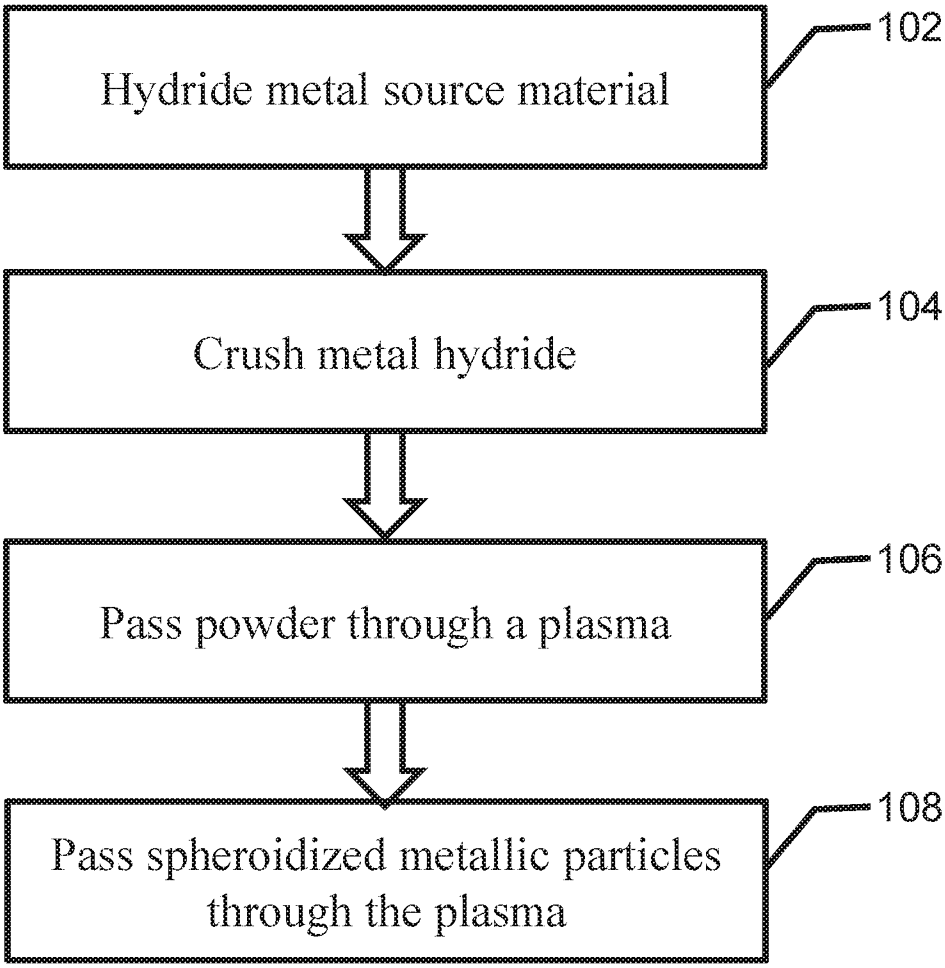
Hydride metal source material
102
Crush metal hydride
104
Pass powder through a plasma
106
Pass spheroidized metallic particles through the plasma
108

FIG. 1

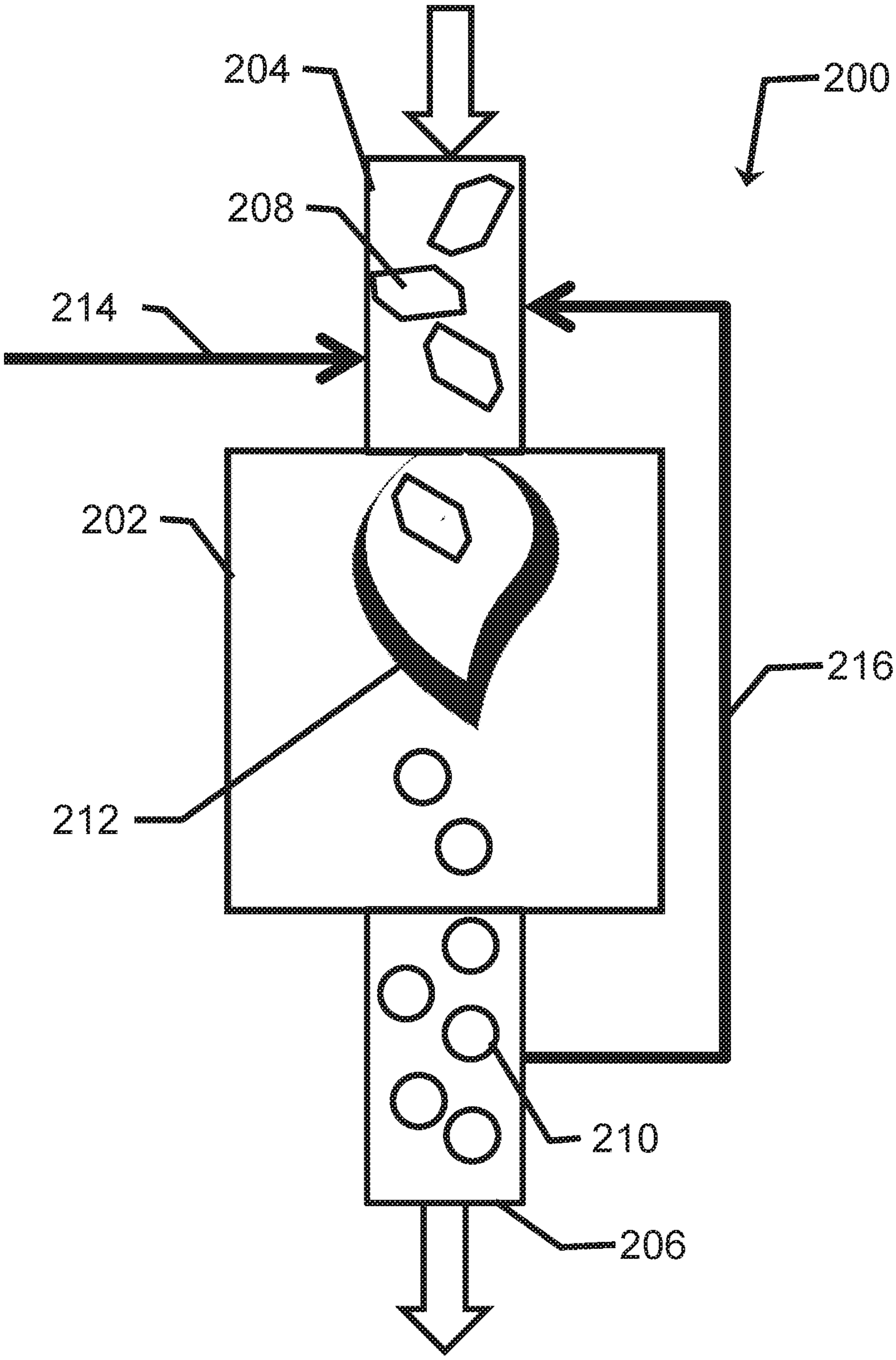

FIG. 2

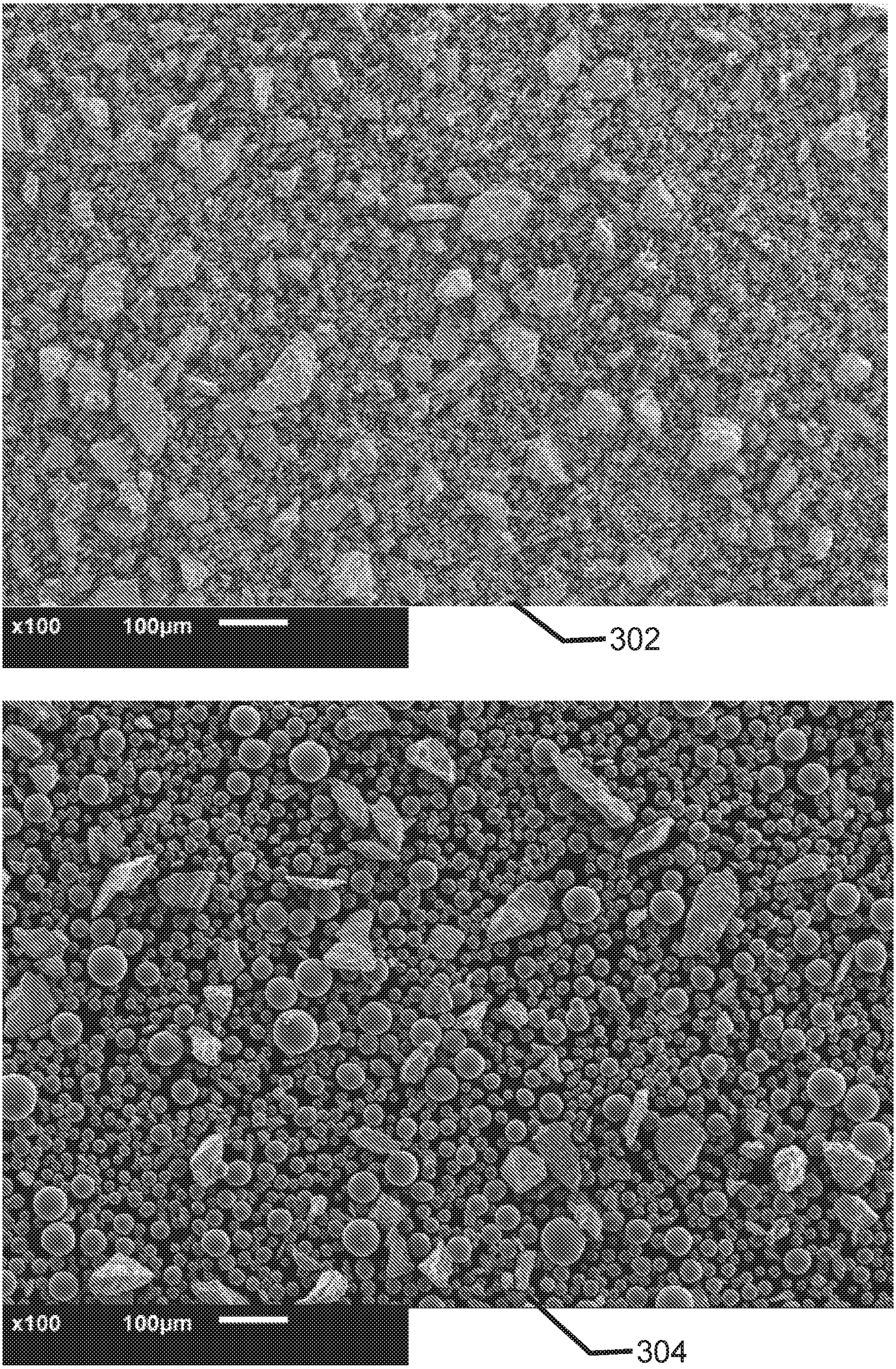

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/040053

A. CLASSIFICATION OF SUBJECT MATTER

B22F 1/00(2006.01)i, B22F 3/105(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)
B22F 1/00; B22F 1/02; B22F 9/04; B22F 9/14; B22F 9/30; B33Y 70/00; H01J 37/32; B22F 3/105

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: plasma, powder, de-hydride, metal hydride particle, spheroidize

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 2017-0173699 A1 (AMASTAN TECHNOLOGIES L.L.C. et al.) 22 June 2017 See paragraphs [0007], [0022], [0030], [0038] and claims 1, 3-5, 15, 28-29.	1-15,17-35 16
Y	JP 63-266001 A (SUMITOMO METAL MINING CO., LTD.) 02 November 1988 See claim 1.	16
X Y	KR 10-2017-0118302 A (RESEARCH INSTITUTE OF INDUSTRIAL SCIENCE & TECHNOLOGY) 25 October 2017 See paragraphs [0055]-[0062], [0066] and claim 1.	1-15,17-35 16
X Y	KR 10-1421244 B1 (KOREA INSTITUTE OF MACHINERY & MATERIALS) 18 July 2014 See paragraphs [0040]-[0046] and claim 1.	1-15,17-35 16
A	CN 102554242 A (XI`AN BAODE POWDER METALLURGY CO., LTD.) 11 July 2012 See paragraphs [0025]-[0031] and claims 1-2.	1-35
A	CN 101716686 A (UNIVERSITY OF SCIENCE AND TECHNOLOGY BEIJING) 02 June 2010 See paragraphs [0022]-[0031] and claims 1-6.	1-35

☐ 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	Date of mailing of the international search report
24 October 2019 (24.10.2019)	**24 October 2019 (24.10.2019)**

Name and mailing address of the ISA/KR	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2019/040053

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2017-0173699 A1	22/06/2017	AU 2016-370962 A1	05/07/2018
		CA 3009630 A1	22/06/2017
		CN 108883407 A	23/11/2018
		EP 3389862 A1	24/10/2018
		EP 3389862 A4	10/07/2019
		WO 2017-106601 A1	22/06/2017
		WO 2017-106601 A8	27/07/2017
JP 63-266001 A	02/11/1988	None	
KR 10-2017-0118302 A	25/10/2017	KR 10-1883403 B1	31/07/2018
KR 10-1421244 B1	18/07/2014	KR 10-2014-0040477 A	03/04/2014
CN 102554242 A	11/07/2012	CN 102554242 B	11/12/2013
CN 101716686 A	02/06/2010	CN 101716686 B	16/02/2011
		WO 2011-082596 A1	14/07/2011