



(51) International Patent Classification:

B22F 9/14 (2006.01) C22C 14/00 (2006.01)
B22F 1/00 (2006.01)

(21) International Application Number:

PCT/US2018/067024

(22) International Filing Date:

21 December 2018 (21.12.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15/869,064 12 January 2018 (12.01.2018) US

(71) Applicant: **GENERAL ELECTRIC COMPANY**
[US/US]; 1 River Road, Schenectady, New York 12345
(US).

(72) Inventors: **SUBRAMANIAN, Pazhayannur Ramanathan**; GENERAL ELECTRIC COMPANY, General Electric Company, Global Research, One Research Circle, Niskayuna, New York 12309 (US). **VINCIQUERRA, Anthony Joseph**; GENERAL ELECTRIC COMPAN-

NY, General Electric Company, Global Research, One Research Circle, Niskayuna, New York 12309 (US). **BE-WLAY, Bernard Patrick**; GENERAL ELECTRIC COMPANY, General Electric Company, Global Research, One Research Circle, Niskayuna, New York 12309 (US).

(74) Agent: **MARSHALL, Alan, R.** et al.; Dority & Manning, P.A., P.O. Box 1449, Greenville, SC 29602 (US).

(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.

(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,

(54) Title: METHODS OF FORMING SPHERICAL METALLIC PARTICLES

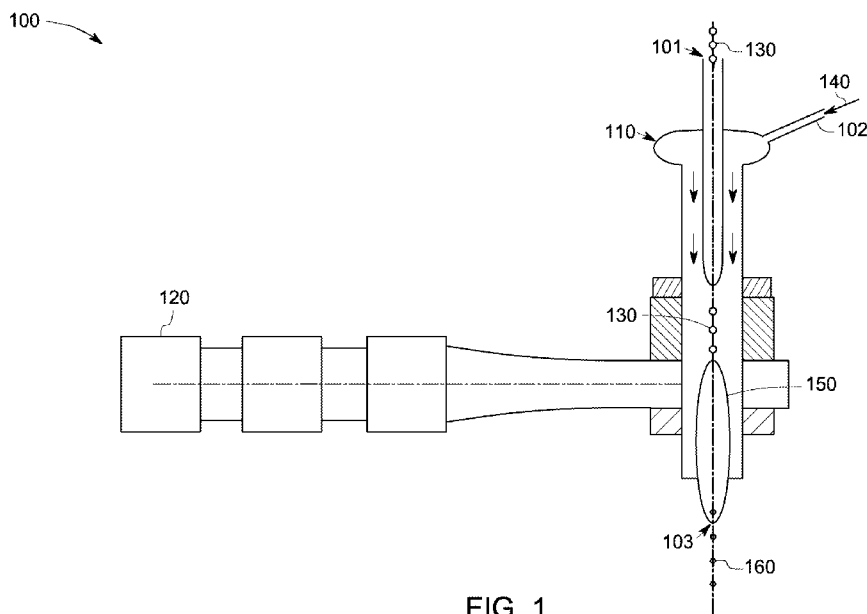


FIG. 1

(57) Abstract: A method of forming titanium-based spherical metallic particles includes performing a hydride-dehydride process on a meltless metallic sponge to form a feedstock material including a metallic powder. The method further includes introducing the feedstock material into a microwave plasma discharge to form the titanium-based spherical metallic particles.



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, 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).

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))*

Published:

- *with international search report (Art. 21(3))*

METHODS OF FORMING SPHERICAL METALLIC PARTICLES

BACKGROUND

[0001] Embodiments of the present disclosure generally relate to methods of forming spherical titanium-based metallic particles. More particularly, embodiments of the present disclosure relate to methods of forming spherical titanium alloy particles using microwave plasma.

[0002] An important aspect of preparing some forms of industrial powders is the spheroidization process, which transforms irregularly shaped or angular powders produced by conventional crushing methods, into spherical low-porosity particles. Spherical powders are homogenous in shape, dense, less porous, and exhibit better flowability. Such powders may exhibit superior properties in applications such as injection molding, thermal spray coatings, or additive manufacturing.

[0003] Titanium and titanium-alloy particles are particularly useful in additive manufacturing of industrial grade components. Additive manufacturing of titanium components may require high-quality, low-cost spherical titanium or titanium alloy powder as a feedstock for good flowability. Conventional methods for processing of titanium alloys to produce spherical powders typically involve multiple steps, such as, producing titanium ingots from sponges and utilizing melting and atomization processes on the titanium ingots to produce spherical powder. The formation of titanium powder can be facilitated by one of several approaches, such as, the Kroll process, the Hunter process, or the Armstrong process. However, most of these commercial processes are typically carried out as large-scale processes and are batch segregated, which increases the complexity and associated cost. Furthermore, the intermediate metallurgical processes for conversion to alloys may add to the cost of the resulting spherical titanium alloy powder.

[0004] Other methods of forming spherical titanium particles employ thermal arc plasma or radio-frequency (RF) generated plasma for spheroidization of titanium-based feedstock material. However, these two methods may present limitations inherent to the thermal non-uniformity of radio-frequency and thermal arc plasmas. Some other spheroidization methods employ inductively coupled plasma (ICP), where angular powder obtained from a hydride-dehydride (HDH) process is entrained within a gas and injected through a hot plasma environment to melt the powder particles. However, this method also suffers from non-uniformity of the microwave plasma, which leads to incomplete spheroidization of feedstock.

BRIEF DESCRIPTION

[0005] In one aspect, the present disclosure relates to method of forming spherical metallic particles including titanium. The method includes performing a hydride-dehydride process on a meltless metallic sponge to form a feedstock material including a metallic powder. The method further includes introducing the feedstock material into a microwave plasma discharge to form the spherical metallic particles.

[0006] In another aspect, the present disclosure relates to a plurality of spherical metallic particles including titanium. The plurality of spherical metallic particles is formed by performing a hydride-dehydride process on a meltless metallic sponge to form a feedstock material including a metallic powder; and introducing the feedstock material into a microwave plasma discharge.

[0007] In yet another aspect, the present disclosure relates to a method of forming spherical titanium alloy particles. The method includes performing a hydride-dehydride process on a meltless titanium alloy sponge to form a feedstock material including acicular titanium alloy powder. The method further includes introducing the feedstock material into a microwave plasma discharge to form the spherical titanium alloy particles.

DRAWINGS

[0008] These and other features, aspects, and advantages of the present disclosure will become better understood when the following detailed description is read with reference to the accompanying drawings, wherein:

[0009] FIG. 1 illustrates a schematic of an apparatus for forming spherical metallic particles, in accordance with some embodiments of the present disclosure;

[0010] FIG. 2 is a flow-chart for a method of forming spherical metallic particles, in accordance with some embodiments of the present disclosure; and

[0011] FIG. 3 is a flow-chart for a method of forming spherical titanium alloy particles, in accordance with some embodiments of the present disclosure.

DETAILED DESCRIPTION

[0012] In the following specification and the claims, which follow, reference will be made to a number of terms, which shall be defined to have the following meanings. The singular forms “a”, “an” and “the” include plural referents unless the context clearly dictates otherwise. As used herein, the term “or” is not meant to be exclusive and refers to at least one of the referenced components being present and includes instances in which a

combination of the referenced components may be present, unless the context clearly dictates otherwise.

[0013] Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value solidified by a term or terms, such as “about”, and “substantially” is not to be limited to the precise value specified. In some instances, the approximating language may correspond to the precision of an instrument for measuring the value. Similarly, “free” may be used in combination with a term, and may include an insubstantial number, or trace amounts, while still being considered free of the solidified term. Here and throughout the specification and claims, range limitations may be combined and/or interchanged, such ranges are identified and include all the sub-ranges contained therein unless context or language indicates otherwise.

[0014] As mentioned earlier, conventional methods for producing spherical titanium-based particles may involve multiple intermediate metallurgical steps and batch processing of the feedstock material, which in turn may affect the cost and consistency of the final product. Embodiments of the present disclosure described herein address the noted shortcomings in the art.

[0015] A method of forming spherical metallic particles including titanium is presented. The method includes performing a hydride-dehydride process on a meltless metallic sponge to form a feedstock material including a metallic powder. The feedstock material is introduced into a microwave plasma discharge to form the spherical metallic particles.

[0016] The term “metallic particles” as used herein refers to a plurality of particles including an elemental metal, a metal alloy, or a combination thereof. Therefore, the term metallic particles as used herein includes elemental titanium, a titanium-based metal alloy, or a combination thereof. The term “elemental metal” as used herein means that an amount of a base metal in the metallic particles is greater than 97 weight percent. In certain embodiments, an amount of the base metal in the metallic particles is greater than 99 weight percent. Therefore, the term “elemental titanium” as used herein means that an amount of titanium in the metallic particles is greater than 97 weight percent. In certain embodiments, the spherical metallic particles include a metal alloy including titanium. The metal alloy may further include aluminum, vanadium, or a combination thereof. In certain embodiments, the spherical metallic particles include titanium alloy particles, such as, Ti6Al4V. In some such

instances, the amount of aluminum in the titanium alloy may be in a range of from about 4 weight percent to about 7 weight percent, and the amount of vanadium in the titanium alloy may be in a range from about 3 weight percent to about 5 weight percent.

[0017] The term “spherical metallic particles” as used herein refers to a plurality of particles having an average aspect ratio that is less than 1.1. In some embodiments, the spherical metallic particles may have an average aspect ratio that is less than 1.05. The spherical metallic particles may have an average diameter in a range of from about 1 micron to about 500 microns. In some embodiments, the spherical metallic particles may have an average diameter in a range of from about 10 microns to about 150 microns.

[0018] As noted herein, the method includes performing a hydride-dehydride process on the meltless metallic sponge to form the feedstock material. In some embodiments, where the spherical metallic particles include elemental titanium, the meltless metallic sponge includes elemental titanium. Also, in some embodiments, where the spherical metallic particles include a metal alloy, the meltless metallic sponge includes a metal alloy including titanium. In such instances, the metal alloy may further include aluminum, vanadium, or a combination thereof. In certain embodiments, the meltless metallic sponge includes a titanium-based metal alloy.

[0019] The term “meltless metallic sponge” refers to a metallic material present in the form of a sponge that has been produced without melting of the metallic material. In some embodiments, the meltless metallic sponge may be produced by chemically reducing suitable precursors for the metallic material, without melting the metallic material. As used herein, “without melting,” “no melting,” and related concepts mean that the material is not macroscopically or grossly melted, so that it liquefies and loses its shape. There may be, for example, some minor amount of localized melting as low-melting-point elements melt and are diffusionally alloyed with the higher-melting-point elements that do not melt. Even in such cases, the gross shape of the material remains unchanged.

[0020] In some embodiments, the Hunter Process or the Armstrong Process may be used to form the meltless metallic sponge by reduction of metal halide precursors with sodium. In some embodiments, the Kroll Process may be used to produce the meltless metallic sponge by reducing titanium tetrachloride with magnesium.

[0021] In certain embodiments, the method of forming a meltless metallic sponge of a metal alloy includes contacting a chemically reducible nonmetallic base-metal precursor compound with a chemically reducible nonmetallic alloying-element precursor compound. “Nonmetallic precursor compounds” are nonmetallic compounds of the metals that eventually

constitute the metal alloy. Any operable nonmetallic precursor compounds may be used. For example, oxides of the metals may be employed as nonmetallic precursor compounds in solid-phase reduction, but other types of nonmetallic compounds such as sulfides, carbides, halides, and nitrides may also be employed. The “base-metal” is a metal that is present in a greater percentage by weight than any other element in the metal alloy. In certain embodiments, the base-metal is titanium, and the chemically reducible nonmetallic base-metal precursor compound includes titanium oxide, TiO₂. The alloying element may be any element that is available in the chemically reducible form of the precursor compound. A few illustrative examples are aluminum and vanadium.

[0022] The chemically reducible nonmetallic precursor compounds are selected to provide the desired metals in the final meltless metallic sponge, and are mixed together in the proper proportions to yield the desired proportions of these metals in the meltless metallic sponge. For example, if the final meltless metallic sponge was to have particular proportions of titanium, aluminum, and vanadium, the chemically reducible nonmetallic precursor compounds may include titanium oxide, aluminum oxide, and vanadium oxide, for solid-phase reduction in the particular proportions. Chemically reducible nonmetallic precursor compounds that serve as a source of more than one of the metals in the final meltless metallic sponge may also be used. These precursor compounds are furnished and mixed together in the correct proportions such that the ratio of titanium, aluminum, and vanadium in the mixture of chemically reducible nonmetallic precursor compounds is equivalent to the one desired in the meltless metallic sponge. In certain embodiments, the final meltless metallic sponge includes a titanium-base alloy, which has more titanium by weight than any other element.

[0023] The chemically reducible nonmetallic base-metal precursor compound and the chemically reducible nonmetallic alloying-element precursor compound may be in the form of finely divided solids to ensure that they are chemically reacted in the subsequent step. The finely divided chemically reducible nonmetallic base-metal precursor compound and the chemically reducible nonmetallic alloying-element precursor compound may be in the form of, for example, powders, granules, flakes, liquids, or the like.

[0024] The chemically reducible nonmetallic base-metal precursor compound and the chemically reducible nonmetallic alloying-element precursor compound may be mixed to form a compound mixture. The mixing may be performed by conventional procedures used to mix powders in other applications, for solid-phase reduction. After, or, during mixing, the compound mixture may be compacted to form a preform. The compacting may be conducted

by cold or hot pressing of the compound mixture, but not at such a high temperature that there is any melting of the compound mixture. The compacted shape may be sintered in the solid-state to temporarily bind the particles together. The compacting desirably forms a shape similar to, but larger in dimensions than, the shape of the final meltless metallic sponge.

[0025] The compacted compound mixture may be then reduced using solid-phase reduction. A non-limiting example of a suitable method to perform the solid-phase reduction includes fused salt electrolysis. Briefly, in fused salt electrolysis, the compound mixture is immersed in an electrolysis cell in a fused salt electrolyte, such as a chloride salt, at a temperature below the melting temperatures of the metals that form the compound mixture. The compound mixture is made the cathode of the electrolysis cell, with an inert anode. The oxygen, in the case of oxide nonmetallic precursor compounds, is removed from the mixture by chemical reduction (i.e., the reverse of chemical oxidation). The reaction is performed at an elevated temperature to accelerate the diffusion of the oxygen or other gases away from the cathode. The cathodic potential is controlled to ensure that the reduction of the nonmetallic precursor compounds occurs, rather than other possible chemical reactions such as the decomposition of the molten salt. The electrolyte is typically a salt that is more stable than the equivalent salt of the metals being refined and suitably stable to remove the oxygen. In some embodiments, the chemical reduction may be carried to completion, so that the nonmetallic precursor compounds are completely reduced. In some other embodiments, the chemical reduction may instead be partial, such that some nonmetallic precursor compounds remain.

[0026] The physical form of the metallic material at the completion of the solid-phase reduction process depends upon the physical form of the mixture of chemically reducible nonmetallic precursor compounds at the beginning of the solid-phase reduction process. As noted herein, as the mixture of chemically reducible nonmetallic precursor compounds is a compressed mass. Therefore, the final physical form of the metallic material is typically in the form of a porous metallic sponge.

[0027] The process for forming a meltless metallic sponge is described above in the context of forming a meltless metal alloy sponge. A similar method may be employed for forming a meltless metallic sponge composed primarily of an elemental metal. In such instances, a non-metallic precursor compound (e.g., TiO_2) may be compacted and chemically reduced using a suitable solid-phase reduction process, e.g., fused salt electrolysis, to form the meltless metallic sponge.

[0028] The meltless metallic sponge may be further characterized by a packing density. The term “packing density” as used in this context refers to the percentage volume of the total volume of the meltless metallic sponge, occupied by the metallic material. In some embodiments, the meltless metallic sponge has a packing density less than 20%. In certain embodiments, the meltless metallic sponge has a packing density in a range from about 10% to about 20%.

[0029] The term “hydride-dehydride” process as used herein refers to a process in which a metallic material (e.g., the meltless metallic sponge) is first subjected to a hydrogenation step, followed by milling and a dehydrogenation step, resulting in the feedstock material. In some embodiments, the feedstock material includes acicular or angular metallic powder. In certain embodiments, the feedstock material includes acicular or angular titanium-based metal alloy powder.

[0030] The acicular metallic powder may be further characterized by a packing density. The term “packing density” as used in this context refers to the percentage volume of the total volume of the acicular metallic powder, occupied by the metallic material. In some embodiments, the acicular metallic powder has a packing density greater than 50%. In certain embodiments, the acicular metallic powder has a packing density in a range from about 50% to about 90%.

[0031] The microwave plasma discharge may be generated using a suitable microwave plasma torch. The method may include introducing the feedstock material into the microwave plasma torch using any suitable means, for example, a suitable powder feeder. Within the microwave plasma torch, the feedstock material is exposed to a plasma discharge causing the materials to melt. Because of the uniformity of the microwave plasma discharge, the feedstock material may be exposed to a substantially uniform temperature profile, and rapidly heated and melted. In one example, the feedstock material may be exposed to a uniform temperature profile in a range from about 4,000 K to about 8,000 K, within the microwave plasma.

[0032] In certain embodiments, the feedstock material is introduced into the microwave plasma discharge in the presence of a non-reactive gas. The term “non-reactive gas” as used herein refers to a gas or a gas mixture that does not react with the feedstock material or the spherical metallic particles, in the presence of the microwave plasma discharge. A non-limiting example of a suitable non-reactive gas may include argon. Thus, in contrast to conventional methods of forming spherical particles using thermal arc/RF

plasma, the methods, as described herein, may not require use of additional reductants along with the microwave plasma, such as, magnesium or hydrogen.

[0033] After the melting of the feedstock material within the microwave plasma discharge, the melted metals may be inherently spheroidized, at least in part, due to liquid surface tension. As the microwave generated plasma exhibits a substantially uniform temperature profile, greater than 90% spheroidization of particles may be achieved.

[0034] Various parameters of the microwave plasma discharge, as well as feedstock material parameters, may be adjusted in order to achieve the desired results. These parameters may include one or more of microwave power, feedstock material size, feedstock material insertion rate, gas flow rates, plasma temperature, and cooling rates.

[0035] After the spheroidization step in the microwave plasma discharge, the plurality of spherical metallic particles may exit the microwave plasma discharge, resulting in cooling and further solidification of the particles. In some embodiments, the spherical metallic particles exiting from the microwave plasma discharge may be further subjected to one or more additional cooling steps to facilitate solidification and collection. The cooled and solidified spherical metallic particles may be subsequently collected using appropriate collection mechanisms, e.g., collection bins.

[0036] Fig. 1 illustrates a schematic of an apparatus 100 for forming spherical metallic particles, in accordance with some embodiments of the present disclosure. The apparatus includes a plasma torch 110 having a first inlet 101 and a second inlet 102. The microwave plasma torch 110 is configured to generate and sustain a microwave plasma discharge 150 upon ignition from a suitable microwave radiation source 120. A feedstock material 130 is fed into the microwave plasma torch 110 via the first inlet 101 and a non-reactive gas 140 is fed into the microwave plasma torch 110 via the second inlet 102. As further illustrated in Fig. 1, the feedstock material 130 is introduced into the microwave plasma discharge 150 in the presence of the non-reactive gas 140. The feedstock material 130 melts within the microwave plasma discharge 150, and the melted metals are inherently spheroidized, at least in part, due to liquid surface tension. Spherical metallic particles 160 are discharged from the microwave plasma torch 110 via an outlet 103. As noted earlier, the discharged spherical metallic particles 160 may be subjected to one or more cooling steps and subsequently collected (not shown in Fig. 1).

[0037] A flow chart for a method of forming spherical metallic particles is further illustrated in Fig. 2. The method 200 includes, at step 210, performing a hydride-dehydride process on a meltless metallic sponge to form a feedstock material including a metallic

powder. The method 200 further includes, at step 220, introducing the feedstock material into a microwave plasma discharge to form the spherical metallic particles.

[0038] A method of forming spherical titanium alloy particles is also presented in flow chart 300 illustrated in Fig. 3. The method 300 includes, at step 310, performing a hydride-dehydride process on a meltless titanium alloy sponge to form a feedstock material including acicular titanium alloy powder. The method 300, at step 320, further includes introducing the feedstock material into a microwave plasma discharge to form the spherical titanium alloy particles.

[0039] A plurality of spherical metallic particles including titanium, formed by the methods described herein, is also presented. The plurality of spherical metallic particles includes an elemental metal, a metal alloy, or a combination thereof. In some embodiments, the spherical metallic particles include elemental titanium, a titanium alloy, or a combination thereof. In certain embodiments, the plurality of spherical metallic particles includes a titanium alloy. The titanium alloy may further include aluminum, vanadium, or a combination thereof.

[0040] The spherical titanium-based metallic particles and methods of producing such particles, in accordance with embodiments of the present disclosure, may provide a number of advantages. For example, the methods as described herein may allow for fewer number of processing steps for spheroidization of the meltless metallic sponge, using a microwave plasma discharge. Reduction in the number of intermediate steps may reduce the cost of the resulting spherical metallic particles.

[0041] The methods as described herein can further achieve additional improvements in consistency due to the homogeneity and control of the energy source (i.e., microwave plasma). Specifically, if the microwave plasma conditions are well controlled, particle agglomeration can be reduced, if not eliminated, thus leading to a better particle size distribution, which could result in high-quality, low-cost, high flowability titanium-based powder. As mentioned earlier, high-quality, low-cost, high flowability titanium-based powder may be particularly desirable for additive manufacturing of titanium-based components.

[0042] The appended claims are intended to claim the invention as broadly as it has been conceived and the examples herein presented are illustrative of selected embodiments from a manifold of all possible embodiments. Accordingly, it is the Applicants' intention that the appended claims are not to be limited by the choice of examples utilized to illustrate features of the present disclosure. As used in the claims, the word "comprises" and its

grammatical variants logically also subtend and include phrases of varying and differing extent such as for example, but not limited thereto, “consisting essentially of” and “consisting of.” Where necessary, ranges have been supplied; those ranges are inclusive of all sub-ranges there between. It is to be expected that variations in these ranges will suggest themselves to a practitioner having ordinary skill in the art and where not already dedicated to the public, those variations should where possible be construed to be covered by the appended claims. It is also anticipated that advances in science and technology will make equivalents and substitutions possible that are not now contemplated by reason of the imprecision of language and these variations should also be construed where possible to be covered by the appended claims.

CLAIMS

1. A method of forming spherical metallic particles, comprising:
performing a hydride-dehydride process on a meltless metallic sponge to form a feedstock material comprising a metallic powder; and
introducing the feedstock material into a microwave plasma discharge to form the spherical metallic particles, wherein the spherical metallic particles comprise titanium.
2. The method of claim 1, wherein the meltless metallic sponge comprises elemental titanium.
3. The method of claim 1, wherein the meltless metallic sponge comprises a metal alloy comprising titanium.
4. The method of claim 3, wherein the metal alloy further comprises aluminum, vanadium, or a combination thereof.
5. The method of claim 1, wherein the meltless metallic sponge has a packing density less than 10%.
6. The method of claim 1, wherein the feedstock material comprises acicular metallic powder.
7. The method of claim 6, wherein the acicular metallic powder has a packing density greater than 50%.
8. The method of claim 1, wherein the feedstock material is introduced into the microwave plasma discharge in the presence of a non-reactive gas.
9. The method of claim 1, wherein the spherical metallic particles comprise an elemental metal, a metal alloy, or a combination thereof.
10. The method of claim 1, wherein the spherical metallic particles comprise a metal alloy comprising titanium.
11. The method of claim 10, wherein the metal alloy further comprises aluminum, vanadium, or a combination thereof.
12. plurality of spherical metallic particles comprising titanium, formed by:
performing a hydride-dehydride process on a meltless metallic sponge to form a feedstock material comprising a metallic powder; and

introducing the feedstock material into a microwave plasma discharge to form the spherical metallic particles.

13. The plurality of spherical metallic particles of claim 12, wherein the plurality of spherical metallic particles comprises elemental titanium, a titanium alloy, or a combination thereof.

14. The plurality of spherical metallic particles of claim 12, wherein the plurality of spherical metallic particles comprises a titanium alloy.

15. The plurality of spherical metallic particles of claim 14, wherein the titanium alloy further comprises aluminum, vanadium, or a combination thereof.

16. A method of forming spherical titanium alloy particles, comprising:
performing a hydride-dehydride process on a meltless titanium alloy sponge to form a feedstock material comprising acicular titanium alloy powder; and
introducing the feedstock material into a microwave plasma discharge to form the spherical titanium alloy particles.

17. The method of claim 16, wherein the feedstock material is introduced into the microwave plasma discharge in the presence of a non-reactive gas.

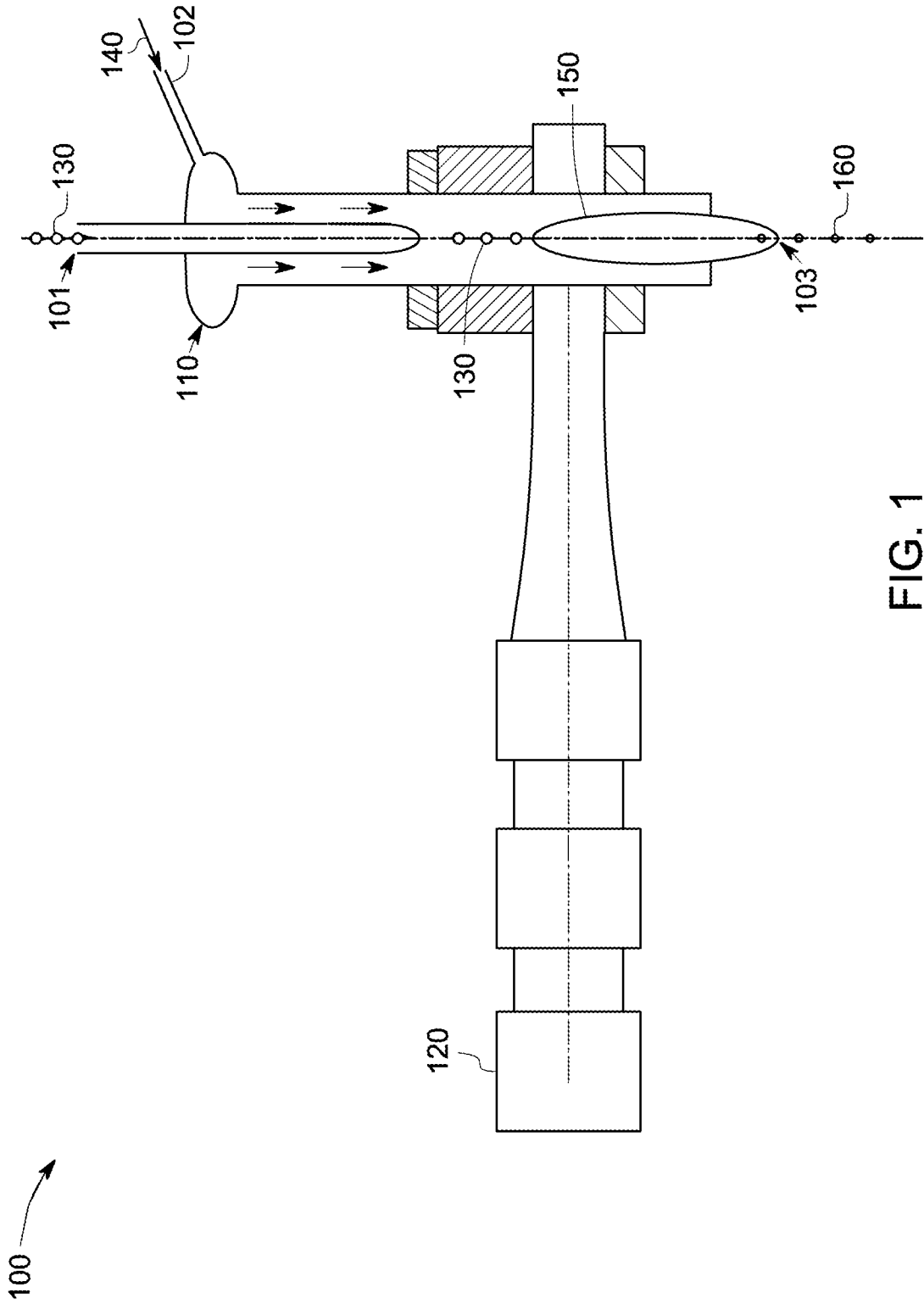


FIG. 1

2/2

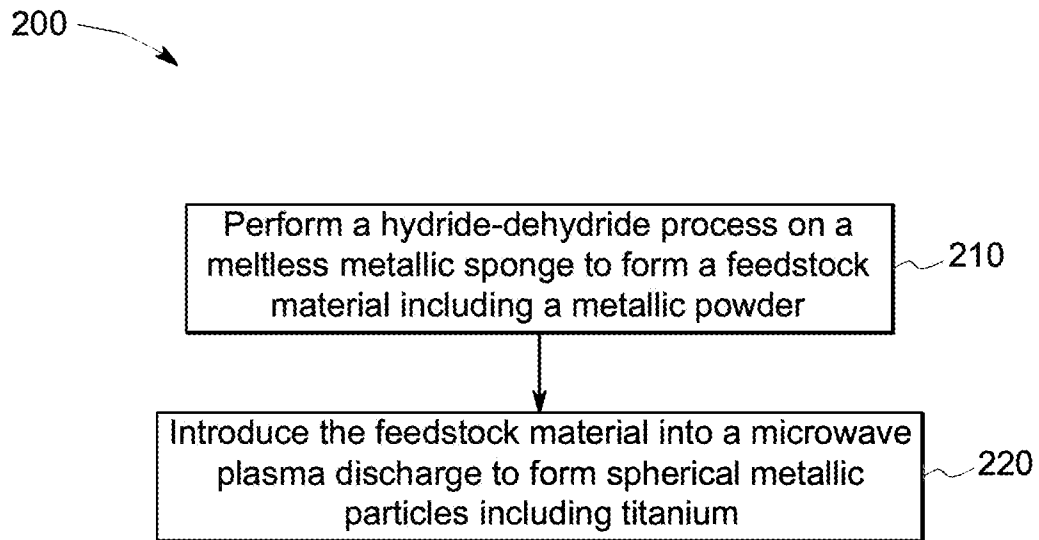


FIG. 2

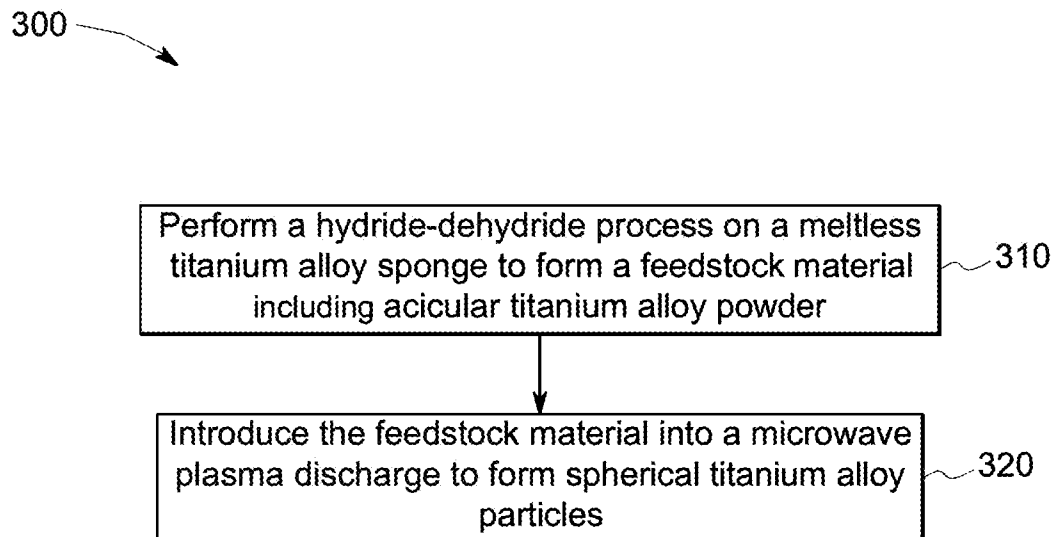


FIG. 3

A. CLASSIFICATION OF SUBJECT MATTER**B22F 9/14(2006.01)i, B22F 1/00(2006.01)i, C22C 14/00(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 9/14; B22F 1/00; B22F 5/12; B22F 9/28; B22F 9/30; C04B 35/56; C22B 34/12; H01J 37/32; C22C 14/00

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: pherical, hydride, dehydride, titanium, plasma

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012-0289395 A1 (LEE, ROBERT G.) 15 November 2012 See paragraph [0041].	1-17
A	US 2017-0173699 A1 (AMASTAN TECHNOLOGIES L.L.C. et al.) 22 June 2017 See paragraphs [0007], [0030]-[0039]; and figures 1-4.	1-17
A	WO 2017-132322 A2 (H.C. STARCK PLACE) 03 August 2017 See claims 1-18.	1-17
A	US 2002-0148327 A1 (ARMSTRONG et al.) 17 October 2002 See paragraphs [0021]-[0034]; and claim 1.	1-17
A	US 2010-0180724 A1 (GROHOWSKI, JR., JOSEPH A.) 22 July 2010 See paragraphs [0045], [0068].	1-17

 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

02 April 2019 (02.04.2019)

Date of mailing of the international search report

03 April 2019 (03.04.2019)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

LEE, Se Gyoung

Telephone No. +82-42-481-8740



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/067024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date		
US 2012-0289395 A1	15/11/2012	AU 2010-351588 A1	07/06/2012		
		AU 2010-351588 B2	13/08/2015		
		AU 2010-351588 C1	03/12/2015		
		EP 2555891 A1	13/02/2013		
		EP 2555891 A4	07/05/2014		
		EP 2555891 B1	27/09/2017		
		IL 222155 A	30/06/2016		
		NZ 599937 A	26/09/2014		
		US 2012-0276393 A1	01/11/2012		
		US 2014-0154126 A1	05/06/2014		
		US 7687023 B1	30/03/2010		
		US 8608822 B2	17/12/2013		
		US 8936751 B2	20/01/2015		
		US 9707623 B2	18/07/2017		
		WO 2011-133132 A1	27/10/2011		
		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				
US 2018-0297122 A1	18/10/2018				
WO 2017-106601 A1	22/06/2017				
WO 2017-106601 A8	27/07/2017				
WO 2017-132322 A2	03/08/2017	EP 3408047 A2	05/12/2018		
		TW 201728388 A	16/08/2017		
		US 2017-0209908 A1	27/07/2017		
		US 2017-0209963 A1	27/07/2017		
		WO 2017-132322 A3	26/07/2018		
US 2002-0148327 A1	17/10/2002	AU 3320195 A	04/03/1996		
		AU 686444 B2	05/02/1998		
		BR 9508497 A	23/12/1997		
		CA 2196534 A1	15/02/1996		
		CA 2196534 C	10/04/2001		
		CN 1076759 C	26/12/2001		
		CN 1161064 A	01/10/1997		
		DE 69521432 T2	29/05/2002		
		EP 0777753 A1	11/06/1997		
		EP 0777753 A4	26/11/1997		
		EP 0777753 B1	20/06/2001		
		ES 2161297 T3	01/12/2001		
		JP 10-502418 A	03/03/1998		
		JP 3391461 B2	31/03/2003		
		KR 10-0241134 B1	02/03/2000		
		MX 9700827 A	30/09/1997		
		NO 970444 A	26/03/1997		
		RU 2152449 C1	10/07/2000		
		US 2002-0005090 A1	17/01/2002		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/067024

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 2002-0152844 A1	24/10/2002
		US 2003-0061907 A1	03/04/2003
		US 2003-0145682 A1	07/08/2003
		US 2004-0166045 A1	26/08/2004
		US 2008-0187455 A1	07/08/2008
		US 2008-0199348 A1	21/08/2008
		US 5779761 A	14/07/1998
		US 5958106 A	28/09/1999
		US 6409797 B2	25/06/2002
		US 6861038 B2	01/03/2005
		US 7435282 B2	14/10/2008
		US 7445658 B2	04/11/2008
		WO 2005-023725 A2	17/03/2005
		WO 2005-023725 A3	16/06/2005
		WO 96-04407 A1	15/02/1996
		ZA 200307069 B	02/07/2004
US 2010-0180724 A1	22/07/2010	EP 1781437 A1	09/05/2007
		EP 1781437 A4	14/07/2010
		US 2006-0002810 A1	05/01/2006
		US 2006-0228247 A1	12/10/2006
		US 2010-0094420 A1	15/04/2010
		US 2012-0065739 A1	15/03/2012
		US 2013-0289735 A1	31/10/2013
		US 2015-0328685 A1	19/11/2015
		US 7674426 B2	09/03/2010
		US 8500843 B2	06/08/2013
		US 9089427 B2	28/07/2015
		US 9089431 B2	28/07/2015
		WO 2006-014294 A1	09/02/2006
		WO 2007-146063 A1	21/12/2007