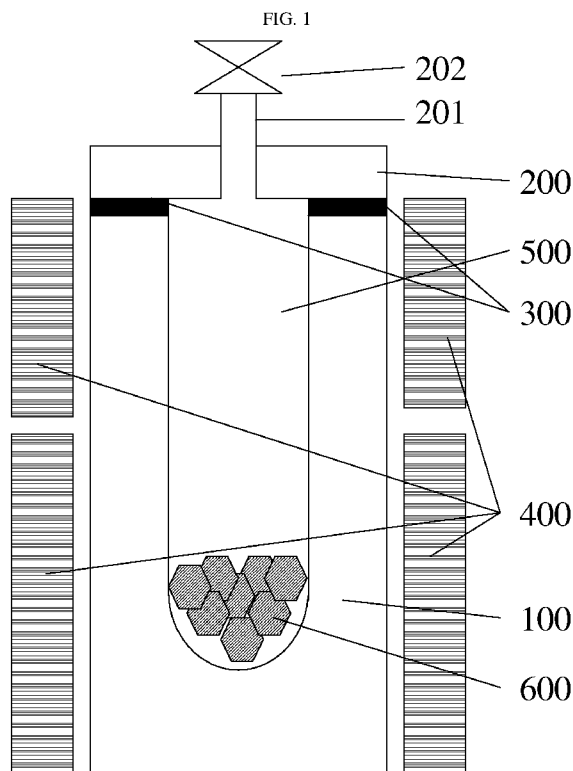




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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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.
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(54) Title: SYNTHESIS METHOD OF TRANSITION METAL NITRIDE AND TRANSITION METAL NITRIDE



(57) Abstract: The present invention discloses a method of synthesizing transition metal nitride by using supercritical ammonia. Transition metal nitride such as vanadium nitride, molybdenum nitride, titanium nitride, nickel nitride, neodymium nitride, iron nitride, etc. can be synthesized in supercritical ammonia with reducing mineralizers such as potassium, sodium, lithium, magnesium, calcium, and aluminum. Since supercritical ammonia has characteristics of both gas and liquid, it can cover complicated fine structure or fine particles. The new method is suitable for forming a protective coating on complicated structure or forming micro- to nano-sized particles.



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SYNTHESIS METHOD OF TRANSITION METAL NITRIDE AND TRANSITION METAL NITRIDE

PRIORITY CLAIM

5 This application claims priority to U.S. app. 61/501,656 filed June 27, 2011 with Tadao Hashimoto as inventor and entitled "SYNTHESIS METHOD FOR TRANSITION METAL NITRIDE AND TRANSITION METAL NITRIDE" and to U.S. app. 61/505,758 filed July 8, 2011 with Tadao Hashimoto as inventor and entitled "ULTRA CAPACITORS USING VANADIUM NITRIDE-CONTAINING ELECTRODE AND SYNTHESIS
10 METHOD OF TRANSITION METAL NITRIDE AND TRANSITION METAL NITRIDE." The contents of these patent applications are incorporated by reference herein as if put forth in full below.

FIELD OF THE INVENTION

15 The invention is related to transition metal nitrides and synthesis methods. The forms that the transition metal nitrides may take include thin film layers, micrometer-sized particles, and nanometer-sized particles. The applications include a thin film as a wear protective layer, particles for ultracapacitors, particles of catalysts, particles as an additive of a wear-resistant coating, and magnets.

20

BACKGROUND OF THE INVENTION

 Transition metal nitride has been used as wear-resistant coatings and thermal barriers, due to its strong mechanical and thermal property. Along with the development of structural and mechanical engineering, the coatings and barriers are required to cover
25 complicated and fine structures. In other words, the surface area relative to its volume is becoming larger in recent years.

 It is also reported that transition metal nitride is useful as a functional material for ultracapacitors, catalysts, and magnets. To use transition metal nitride as ultracapacitor, catalysts, or magnets, it is important to increase surface area of the material.
30 Nanotechnology using nano-sized particles has a potential of obtaining superior characteristics due to extremely large surface area relative to its weight. Functional

materials requiring large surface area such as ultracapacitors, catalyst, and magnets receives tremendous benefit from nanotechnology.

With increasing demand of covering small-sized material with large surface area, the existing synthesis method is facing several challenges. Since transition metal is more readily oxidized than nitridized, synthesis of transition metal nitride requires elimination of oxygen and moisture. Synthesis methods typically involve vapor phase reaction in vacuum/air tight reactors. To form a nitride layer on transition metal parts, physical vapor deposition or plasma deposition are used. However, these methods are unable to coat complicated structure having deep blind holes because vapor phase reactant does not reach the bottom surface of the deep holes.

In the case of particle synthesis, vapor phase method is even less efficient because of extremely high surface area to cover. When the particles have size less than 10 nm or specific surface area larger than $10 \text{ m}^2/\text{g}$, it becomes challenging for the gaseous agents to cover the entire surface. For example, vanadium nitride nanoparticles are synthesized using VCl_4 as precursor. The VCl_4 is dissolved and stirred in anhydrous chloroform inside a glovebox. The solution is then transferred to an Ar-filled glove bag, where the dissolved chloride is reacted with anhydrous ammonia gas over solution for 8 hours. The as-prepared powder is collected by evaporating the solvent at 100°C under continuous NH_3 gas flow. Final heat treatment for nitridization is conducted under an anhydrous ammonia atmosphere with a heating and cooling rate of $5^\circ\text{C}/\text{min}$. The temperature for heat treatment is 400°C [1]. As shown in this example, the final heat treatment involves vapor phase reaction with constant ammonia flow at high temperature. A high temperature such as this can cause sintering, resulting in larger particle size than what would be achieved using a lower-temperature process.

The challenges in the existing synthesis methods of transition metal nitride are summarized as follows: (1) the existing methods use vapor phase reaction which is unable to cover surfaces of complicated structures or small particles; (2) the existing methods require constant flow of source gas such as ammonia or nitrogen; (3) some existing methods use metal halide precursors, which leaves halogen impurities unfavorable to ultracapacitor applications; (4) some existing methods requires multiple steps to obtain transition metal nitride; (5) some existing methods requires high temperature which causes larger particle size or unfavorable phase.

SUMMARY OF THE INVENTION

To overcome above-mentioned challenges, the present invention provides a new approach to achieve a cost-competitive synthesis method of transition metal nitrides. The present invention utilizes supercritical ammonia to nitridize transition metals. A source material containing transition metal is supplied to a high-pressure reactor together with ammonia and mineralizers. Mineralizers, which act as reducing agents, are selected from alkali metal, alkali earth metals or aluminum. Then, the reactor is heated at 132 °C or higher to attain supercritical condition of ammonia. The reactor is typically sealed to attain self-pressurization of ammonia upon heating, however; a semi-open reactor which allows additional feeding of source, mineralizer or ammonia is also usable. The high reactivity of mineralized supercritical ammonia is very effective to nitridize transition metals at lower temperature than conventional method, thereby producing e.g. catalyst particles of smaller particle size than processes that sinter particles at higher temperatures.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

FIG. 1 is one construction of reactor.

- 100 High-pressure reactor
- 200 Lid of high-pressure reactor with gas inlet port
- 201 Gas inlet port
- 202 High-pressure valve
- 300 Gasket seal
- 400 External heater
- 500 Ammonobasic solution (ammonia with dissolved mineralizer)
- 600 Source material containing transition metal

FIG. 2 is a standard process flow of current invention.

DETAILED DESCRIPTION OF THE INVENTION

In the following description of the preferred embodiment, reference is made to the accompanying drawings which form a part hereof, and in which is shown by way of

illustration a specific embodiment in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural changes may be made without departing from the scope of the present invention.

A source material containing transition metal contains an amount of transition metal effective to accomplish a particular purpose. For instance, a substrate may be coated with a layer of transition metal that is to be converted to a nitride, so that the surface layer may be effective as a heat barrier or wear protective surface. Another example is that particles may contain an amount of a transition metal that, upon conversion to nitride, are catalytically active, will bear a certain amount of electrical charge when formed into an ultracapacitor, or shows sufficient magnetic property. The source material may contain more than 10 percent of transition metal by weight.

Technical description of the invention

The method of synthesizing transition metal nitrides in the current invention may utilize supercritical ammonia. Over the critical point of 132.4 °C and 11.28 MPa, ammonia becomes the supercritical condition, which is a state between liquid and gas. We found that supercritical ammonia with, optionally but desirably, a strong reducing mineralizer such as alkali metals, alkali earth metals or aluminum is capable of forming transition metal nitride.

This process may in one instance be a one-step process in a closed reactor and does not require constant flow of ammonia. By changing process temperature, pressure, mineralizer and time, the layer thickness or particle size is expected to be controlled from nano-scale to micron-scale. A batch process such as this may therefore enable all of the reaction materials to be placed into the high-pressure reactor and the product to be separated from the reactor after the reaction has concluded.

The process may in another instance be conducted with either constant flow of ammonia or with periodic addition of ammonia to the high-pressure reactor. A semi-batch process such as this may therefore allow some of the reaction materials such as the source material and optional mineralizer to be added to the reactor first and ammonia added either continuously or periodically during the reaction. Further, either source or mineralizer may instead or additionally be continuously or periodically added to the reactor during the reaction.

A standard process as diagramed in Fig. 2 is depicted in Fig. 1. A standard process as described uses high-pressure reactor 100. A source material containing transition metal 600 is placed in the high-pressure reactor 100 together with a mineralizer. Since mineralizer is highly reactive with oxygen, it is favorable to work in a glovebox filled with nitrogen or argon. The lid 200 has a gas inlet port 201 which is connected to a high-pressure valve 202. After charging the source material 600 and a mineralizer in the high-pressure reactor 100, the lid 200 is closed using a gasket 300 to prevent leaking of ammonia at high pressure. The high-pressure valve 202 is also closed. Then, the high-pressure reactor 100 is taken out of the glovebox and the high-pressure valve 202 is connected to a gas/vacuum line. The high-pressure reactor 100 is pumped through the gas inlet port 201 by opening the high-pressure valve 202. After attaining sufficient vacuum level, the high-pressure reactor 100 is externally chilled with liquid nitrogen and filled with gaseous ammonia through the gas inlet port 201. The gaseous ammonia is condensed to the liquid phase in the high-pressure reactor 100. After filling predetermined amount of liquid ammonia, the high-pressure valve 202 is closed and disconnected from the gas/vacuum line. The high-pressure reactor 100 is transferred to a furnace and externally heated. Since the high-pressure reactor 100 is sealed, it is self pressurized with heated ammonia and the ammonia reaches supercritical condition. The mineralizer is dissolved in ammonia creating ammonobasic solution 500. The source material containing transition metal 600 inside the high-pressure reactor 100 is nitridized with the ammonobasic solution 500. After predetermined time, the ammonia is released by opening the high-pressure valve 202. The transition metal nitride is taken out of the high-pressure reactor 100 after the high-pressure reactor 100 is cooled. The transition metal nitride is rinsed with water to remove mineralizers. The last step creates a thin oxide layer on the top surface of the transition metal nitride.

Mineralizer can be selected based on the metal nitride to synthesize. Sodium metal is commonly used, but if higher reactivity is needed, one may choose potassium-based mineralizer. Conversely, if milder reactivity is favored one may choose lithium-based mineralizers. If even milder reactivity is favored, magnesium or calcium based mineralizers may be selected. Also, if removal of oxygen is the primary purpose of mineralizer, metallic calcium, aluminum or magnesium may be suited for a mineralizer. Mixture of these materials may also be used to control the reaction.

Example 1

A vanadium foil of approximately 13 mm in diameter and 2.6 g of Na were placed in a high-pressure reactor having an internal volume of 127 cc in a glove box in which the oxygen and moisture concentration is regulated below 0.1 ppm. Then, the high-pressure reactor was sealed and nitrogen in the reactor was evacuated with turbo molecular pump through a gas inlet port. After pumping the reactor to less than 10^{-6} mbar, the reactor was chilled by immersing it in liquid nitrogen and gaseous anhydrous ammonia was introduced in the reactor through the gas inlet port. Approximately 43.7 g of liquid anhydrous ammonia was condensed in the reactor. The sealed reactor was then transferred to a furnace and heated at 530~535 °C for 5 days. The resulting pressure was 167 MPa (24,170 psi). After the process, the vanadium foil showed goldish color, indicating the surface of the vanadium foil was nitridized. When yellowish V_2O_5 powders were used instead of the foil, blackish powder, which is expected to be VN, were obtained.

Example 2

Similar experiment as example 1 was conducted for molybdenum and titanium, and confirmed color change in of these metals.

Example 3

Similar experiment as example 1 is conducted with a high-pressure reactor having gas inlet port and high-pressure valve. During the process, pressurized ammonia is supplied to supplement ammonia consumed during the process.

Example 4

Using similar high-pressure reactor, vanadium-containing tools or parts are coated with transition metal nitride by nitridizing the surface of the metal. Also, these tools or parts are coated with metallic vanadium prior to the ammonothermal process to form thicker protective layer of transition metal nitride.

Example 5

A high-pressure reactor has the following particles placed in it sequentially along with a mineralizer and ammonia: niobium, tin, indium, platinum, tantalum, zirconium,

copper, iron, tungsten, chromium, molybdenum, hafnium, titanium, vanadium, cobalt, manganese, cerium, mercury, plutonium, gold, silver, iridium, palladium, yttrium, ruthenium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and nickel. The reactor is heated, and the ammonia is placed in supercritical state within the high-pressure reactor. The respective niobium nitride, tin nitride, indium nitride, platinum nitride, tantalum nitride, zirconium nitride, copper nitride, iron nitride, tungsten nitride, chromium nitride, molybdenum nitride, hafnium nitride, titanium nitride, vanadium nitride, cobalt nitride, manganese nitride, cerium nitride, mercury nitride, plutonium nitride, gold nitride, silver nitride, iridium nitride, palladium nitride, yttrium nitride, ruthenium nitride, lanthanum nitride, cerium nitride, praseodymium nitride, neodymium nitride, promethium nitride, samarium nitride, europium nitride, gadolinium nitride, terbium nitride, dysprosium nitride, holmium nitride, erbium nitride, thulium nitride, ytterbium nitride, lutetium nitride and nickel nitride nanoparticles are obtained. Desired phase such as Fe_{16}N_2 of iron nitride, which is useful for magnet applications, could be obtained by adjusting process temperature, pressure, time, etc.

Advantages and Improvements

The present invention discloses a new method of producing transition metal nitride having one or more of the following advantages:

- 1) Highly cost-competitive due to closed reactor system.
- 2) Capable of forming nitride layer on surfaces of complicated structure due to high reactivity of supercritical ammonia.
- 3) Capable of forming nitride particles due to high reactivity of supercritical ammonia.
- 4) Free from unfavorable impurities such as halogens.
- 5) Capable of selecting desired phase, particularly low-temperature phase, which is difficult to obtain in other high-temperature process.

References

All references discussed in the application are incorporated by reference herein,

[1] D. Choi, G.E. Blomgren, and P.N. Kumta, Advanced Materials 18 (2006) pp.1178.

Conclusion

5 This concludes the description of preferred embodiments of the invention. The following describes some alternative embodiments for accomplishing the present invention.

 Although the examples describe a method of synthesizing vanadium nitride, molybdenum nitride and titanium nitride, other transition metal nitrides such as iron nitride, chromium nitride, scandium nitride, zirconium nitride can be synthesized with the same
10 method. Also, alloy of transition metal nitrides can be synthesized with the same method.

 Although the examples describe synthesis of foil of vanadium nitride, molybdenum nitride, and titanium nitride, other forms of transition metal nitrides such as nanocrystalline particles, microcrystalline particles, thin layers, and bulk single crystals can be produced
15 with the same method.

 Although the examples describe a synthesis method using Na as a mineralizer, other alkali metal, alkali earth metal or aluminum can be used as a mineralizer. Also, mixture of two or more mineralizers can be used.

 Although the preferred embodiment describes a synthesis method in a specific
20 temperature and pressure, other temperature and pressure setting can be used as long as the ammonia is in the supercritical condition.

 Although the preferred embodiment describes a synthesis method using high-pressure reactor of a specific shape, other types of high-pressure reactor such as one with two lids, one with external high-pressure pump, one with high-pressure inlet port
25 which enables constant feeding of source, mineralizer or ammonia can be used.

 The method may be particularly useful in forming a nitride of a single transition metal (and particularly a relatively pure form of such a nitride) such as e.g. vanadium nitride, molybdenum nitride, titanium nitride, or iron nitride or an alloy of such nitrides rather than a nitride of a non-transition element and a transition metal element together as
30 one compound.

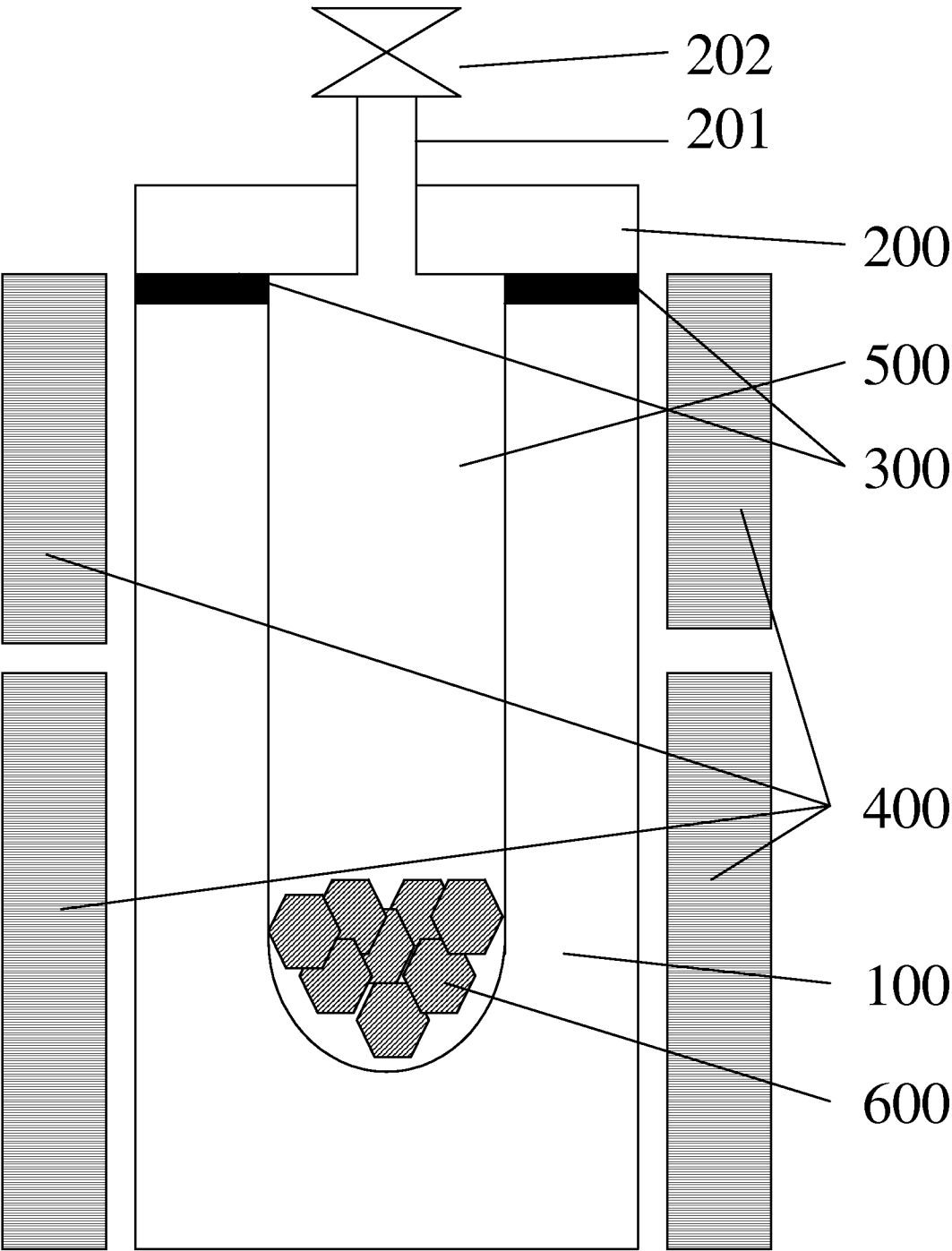
WHAT IS CLAIMED IS:

1. A method of synthesizing a nitride of a transition metal or transition metal alloy comprising:
 - 5 (a) Supplying one or more source materials containing one or more transition metals in a reactor;
 - (b) Supplying ammonia in the reactor;
 - (c) Optionally supplying a mineralizer which enhances the reaction between the source material and the ammonia;
 - 10 (d) Heating the reactor to attain supercritical condition of the ammonia.
2. A method of synthesizing a nitride of transition metal or transition metal alloy according to claim 1, wherein the mineralizer contains at least one selected from Li, Na, K, Ca, Mg and Al.
3. A method of synthesizing a nitride of a transition metal or transition metal alloy according to claim 1 or claim 2, wherein the reactor is made of Ni-Cr based alloy.
4. A method of synthesizing a nitride of a transition metal or transition metal alloy according to any of claims 1-3, wherein the reactor is heated to a temperature of 132°C or higher.
5. A method of synthesizing a nitride of a transition metal or transition metal alloy according to any of claims 1-4, wherein the reactor is a batch reactor which is sealed and self pressurized with heated ammonia.
6. A method of synthesizing a nitride of a transition metal or transition metal alloy according to any of claims 1-4, wherein the reactor is a semi-batch reactor which enables supply of the source material, the ammonia, or the mineralizer or exhaust of gas, products, or byproducts during the synthesis.
7. A method of synthesizing a nitride of a transition metal or transition metal alloy according to any of claims 1-6, wherein the transition metal is V.
8. A method of synthesizing a nitride of a transition metal or transition metal alloy according to any of claims 1-7, wherein the source material is metallic vanadium, vanadium oxide, vanadium pentoxide, ammonium metavanadate, or a mixture of one or more thereof.

9. A method according to any of claims 1-8 wherein the transition metal nitride does not incorporate a substantial amount of the mineralizer into the transition metal nitride.
- 5 10. Vanadium nitride particles synthesized by a method of any of claims 1-9, wherein the particle size is less than 10 nm.
11. Vanadium nitride particles according to claim 10 or as synthesized by a method of any of claims 1-9, wherein the specific surface area of the particles is greater than 10 m²/g.
- 10 12. Vanadium nitride particles of any of claims 10-11, wherein the surface of the particles is oxidized.
13. Vanadium nitride particles of any of claims 10-12, wherein the particles do not contain halogen impurities.
14. Nitride particles of transition metal or transition metal alloy synthesized by a method according to any of claims 1-9, wherein the particle size is less than 10 nm.
- 15 15. Nitride particles according to claim 14 or as synthesized by a method according to any of claims 1-9, wherein the specific surface area of the particles is greater than 10 m²/g.
16. Nitride particles of transition metal or transition metal alloy of any of claims 14-15, wherein the surface of the particles is oxidized.
- 20 17. Nitride particles of transition metal or transition metal alloy of any of claims 14-16, wherein the particles do not contain halogen impurities.
18. A compound having particles as specified in any of claims 10-17 or as made by a method of any of claims 1-9 wherein the compound comprises a nitride of a single transition metal and not a nitride of a non-transition element and a transition metal element together as one compound.
- 25

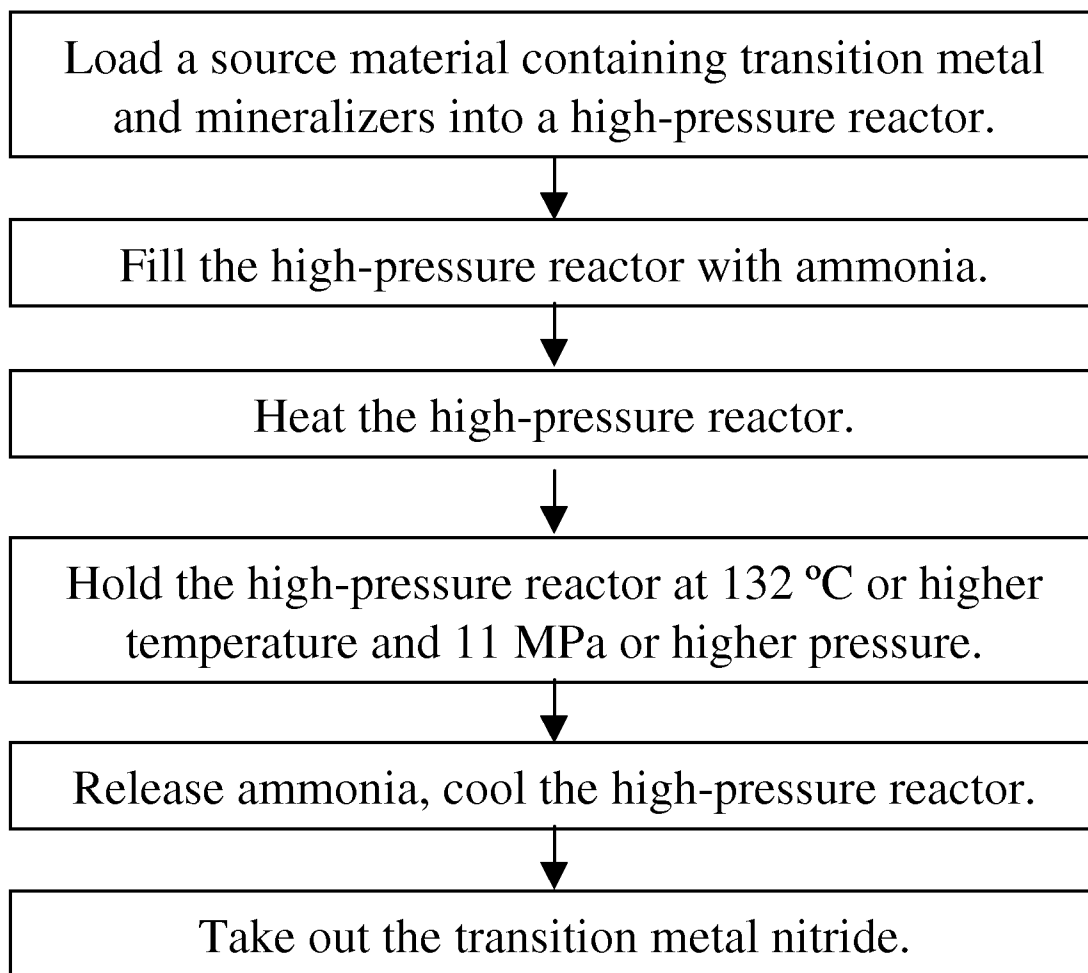
1/2

FIG. 1



2/2

FIG. 2



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B21/06
ADD.

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)
C01B

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

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

EPO-Internal, COMPENDEX, INSPEC, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PIETRO CHIRICO ET AL: "Solvothermal synthesis of group 5 and 6 nitrides via reactions using LiNH₂ and ammonia nitrogen sources", DALTON TRANSACTIONS, vol. 39, no. 26, 1 January 2010 (2010-01-01), page 6092, XP55041398, ISSN: 1477-9226, DOI: 10.1039/c0dt00120a the whole document ----- -/-	1-18



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

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"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

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/042689

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International application No

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