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(54) **COLD SPRAY PROCESS USING TREATED METAL POWDER**

KALTSPRÜHVERFAHREN UNTER VERWENDUNG EINES BEHANDELTEN METALLPULVERS

PROCÉDÉ DE PULVÉRISATION À FROID METTANT EN OEUVRE UNE POUDRE MÉTALLIQUE TRAITÉE

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Description

BACKGROUND OF THE INVENTION

[0001] Thermal spray technologies such as the cold spray process can be used for various applications such as applying metal layers to non-metallic substrates to make metal layer-containing composite articles, applying metal outer layers to substrates of a different material, for example to obtain corrosion benefits of the outer layer metal with the processability of the substrate metal, field repair of metal components, and various other additive manufacturing technology applications.

[0002] Titanium and titanium alloys are widely used for various applications such as aircraft, motor vehicles, and countless other applications, where they provide beneficial properties including but not limited to strength, strength:weight ratio, corrosion resistance, high specific heat, and tolerance of extreme temperatures. However, the use of titanium alloys as metal powder used in the cold spray process has been limited by factors such as degradation of the nozzles used in the cold gas spray process and a tendency of the titanium alloys to clog nozzles used in the cold spray process. Conventional approaches for dealing with such nozzle problems typically involve the use of exotic (and expensive) materials such as quartz for the cold spray nozzles, or modification of cold spray process parameters to lower temperatures or other process modifications that can cause adverse impacts to the properties of cold spray-applied material.

[0003] WO 2011/132874 A2 discloses a method of nitriding a surface of aluminum or aluminum alloy by cold spraying, whereby a surface of aluminum or aluminum alloy is coated by cold spraying, and then a heat treatment is performed thereon at low temperature for a short time period. Its method is suitable for nitriding a surface of Al and Al alloy, which is very difficult to be nitrided, at low production costs. Its method includes removing a foreign material from a surface of a mother substrate comprising Al or Al alloy; cold spraying 15 to 50 wt% of a catalyst powder and 50 to 85 wt% of a coating agent powder on the surface of the mother substrate to form a coating layer; and heat treating the coating layer at a temperature of 450 to 630°C in a nitrogen atmosphere for 2 to 24 hours.

[0004] US 7,232,556 discloses nanoparticles comprising titanium, such as nanoscale doped titanium metal compounds, inorganic titanium compounds, and organic titanium compounds, their methods of manufacture, and methods of preparation of products from nanoparticles comprising titanium.

[0005] US 5,149,514 discloses a low temperature process for forming a coating or powder comprising one or more metals or metal compounds by first reacting one or more metal reactants with a halide-containing reactant to form one or more reactive intermediates capable of reacting, disproportionating, or decomposing to form a coating or powder comprising the one or more metal reactants. When one or more metal compounds are formed, either as powders or as coatings, a third reactant may be injected into a second reaction zone in the reactor to contact the one or more reactive intermediates formed in the first reaction zone to thereby form one or more metal compounds such as metal nitrides, carbides, oxides, borides, or mixtures of same.

[0006] US 5,320,686 discloses objects of titanium or titanium alloys having the surface converted to a hard and wear-resistant nitride layer with good adhesion, distributed uniformly and providing internal capillaries. The objects are produced by being treated in a vacuum furnace with an atmosphere of pure nitrogen gas at a temperature of 650-1000° C and at a pressure below atmospheric pressure. The thickness of the nitride layer can be controlled by controlling the treatment time and temperature.

BRIEF DESCRIPTION OF THE INVENTION

[0007] According the invention, there is a method of applying a metal comprising titanium to a substrate. The method comprises nitriding the surface of metal powder particles comprising titanium by contacting the particles with a first gas comprising nitrogen in a fluidized bed reactor, and depositing the nitrided metal powder particles onto the substrate with cold spray deposition using a second gas.

[0008] In some aspects of the invention, the metal powder particles comprise titanium or titanium alloys Ti-6Al-4V, Ti-3Al-2.5V, Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo, $\alpha+\beta$ Ti-6Al-4V, or near β Ti-10V-2Fe-3Al.

[0009] In some aspects of the invention, the metal powder particles comprises titanium or titanium alloy grades 5 (Ti-6Al-4V) or 23(Ti-6Al-4V) according to ASTM B861-10.

[0010] In some aspects of the invention, the metal powder particles after nitriding comprise elemental nitrogen at the particle surface and also comprise an internal particle portion that is free of elemental nitrogen.

[0011] In some aspects of the invention, the metal powder particles after nitriding have a surface nitrogen content ranging from 5.96 wt.% to 12.22 wt.% as determined by x-ray photoelectron spectroscopy.

[0012] In some aspects of the invention, the metal powder particles after nitriding have a nitrogen:oxygen surface wt.% ratio of from 5.96:26.20 to 12.22:16.75 as determined by x-ray photoelectron spectroscopy.

[0013] In some aspects of the invention, the first gas comprises at least 1 vol.% nitrogen.

[0014] In some aspects of the invention, the first gas consists essentially of nitrogen.

[0015] In some aspects of the invention, the fluidized bed reactor is operated at a temperature of 500°C to 850°C.

[0016] In some aspects of the invention, the first gas is at a pressure of 0.11 to 0.12 MPa.

[0017] In some aspects of the invention, the space ve-

locity of the first gas in the fluidized bed reactor is from 1 min^{-1} to 30 min^{-1}.

[0018] In some aspects of the invention, the metal powder particles are contacted with the first gas in the fluidized bed reactor for at least 1 minute.

[0019] In some aspects of the invention, the second gas comprises helium or argon.

[0020] In some aspects of the invention, the second gas comprises helium or argon and nitrogen.

[0021] In some aspects of the invention, the second gas consists essentially of helium or argon.

[0022] In some aspects of the invention, the second gas is at a temperature of 20°C to 850°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] The subject matter which is regarded as the invention is claimed in the appended claims at the conclusion of the specification. The foregoing and other features, and advantages of the invention are apparent from the following detailed description taken in conjunction with the accompanying figures, in which:

FIG. 1 is a schematic depiction of a fluidized bed reactor assembly;

FIG. 2 is a schematic depiction of a cold spray system; and

FIG. 3 is a bar chart showing the results of surface elemental analysis of titanium alloy powders processed as described herein.

DETAILED DESCRIPTION OF THE INVENTION

[0024] An exemplary fluidized bed reactor assembly for nitriding titanium alloys is depicted in FIG. 1. As shown in FIG. 1, the assembly includes a fluidized bed reactor 12 having inlet openings 14 disposed at one end of the reactor 12 and an outlet opening 16 disposed at the opposite end of the reactor 12. The fluidized bed reactor 12 is disposed inside of an outer tubing 18, with outlet 16 extending to the outside of outer tubing 18. During operation, the fluidized bed assembly is disposed in a furnace (not shown) to provide heat. Thermocouples 17 and 19 are disposed to monitor temperature in the reactor 12 and outer tubing 18, respectively. An inlet 20 is connected to a gas feed line 22. A gas source 24 such as a storage tank or a gas-generating reactor is connected to gas feed line 22 to supply a gas feed to the fluidized bed reactor 12. Other components, such as mass flow controller 26, pressure regulating valve 28, pressure sensor 30, and shut-off valves 32 and 34 are also disposed in the gas feed line 22 for monitoring and controlling the flow rate and pressure of the gas delivered to the reactor 12. Reactor outlet 16 is connected to outlet line 36, which is connected to a water or other liquid bubbler 38. A bleed line 40 with shut-off valve 42 also connects feed line 22 to the bubbler 38, which is vented to atmosphere through exhaust port 44.

[0025] In operation, a gas comprising nitrogen from gas source 24 is fed through feed line 22, with the flow rate and gas pressure controlled by mass flow controller 26 and pressure regulating valve 28. The nitrogen-containing gas enters the outer tubing 18 through inlet 20. The gas is heated as it passes through the space between fluidized bed 12 and outer tubing 18 to enter the fluidized bed reactor 12 through inlet 14. The fluidized bed reactor 12 has metal particles 46 comprising titanium disposed therein, and the upward gas flow rate through the reactor applies sufficient upward force to the particles 46 to counteract the force of gravity acting on the particles so that they are suspended in a fluid configuration in the reactor space. The gas flow is generally maintained below levels that would carry entrained particles out of the reactor 16 through outlet 16, and outlet 16 can also be fitted with a filter or screen to further assist in keeping metal powder particles 46 from exiting the reactor 12. Nitrogen-containing gas exits the reactor 12 through outlet 16 and flows via outlet line 36 to the bubbler 38, from which it is exhausted to the atmosphere through exhaust port 44.

[0026] The invention can utilize any titanium metal or titanium metal alloy, including any of the grades of titanium alloys specified in ASTM B861-10. Alpha titanium alloys, near-alpha titanium alloys, alpha-beta titanium alloys, and beta titanium alloys. In some embodiments, the titanium alloy comprises from 0 to 10 wt.% aluminum and from 0 to 10 wt.% vanadium. In some embodiments, the titanium alloy is an alpha-beta titanium alloy such as Ti-6Al-4V (e.g., grades 5 or 23 according to ASTM B861-10), Ti-Al-Sn, Ti-Al-V-Sn, Ti-Al-Mo, Ti-Al-Nb, Ti-V-Fe-Al, Ti-8Al-1Mo-1V, Ti-6Al-2Sn-4Zr-2Mo, $\alpha+\beta$ Ti-6Al-4V or near β Ti-10V-2Fe-3Al. In some embodiments, the titanium alloy is a Ti-6Al-4V alloy such as grade 5 or grade 23 according to ASTM B861-10.

[0027] The nitrogen-containing gas can contain from 1 vol.% to 100 vol.% nitrogen, more specifically from 5 vol.% to 100 vol.% nitrogen, and more specifically from 25 vol.% to 75 vol.% nitrogen. In some embodiments, the nitrogen-containing gas consists essentially of nitrogen, and in some embodiments the nitrogen-containing gas is pure. The nitriding reaction conducted in the fluidized bed reactor is typically conducted at elevated temperature, compared to ambient conditions. The reaction temperature in the reactor can range from 500°C to 800°C, more specifically from 600°C to 750°C, and even more specifically from 600°C to 700°C. Pressures in the reactor can range from from 0.11 MPa to 0.12 MPa, and more specifically from 0.11 MPa to 0.115 MPa. The flow rate of nitrogen to the reactor can vary based on factors such as reactor dimension, with exemplary flow rates of 0.0069 m/min to 0.013 m/min, more specifically from 0.0097 m/min to 0.011 m/min, and even more specifically from 0.010 m/ min to 0.0105 m/min. The metal powder particles can be nitrided for periods (i.e., contact time with the nitrogen-containing gas) of at least 1 minute, for example, time periods ranging from 1 minute to 30 min-

utes, more specifically from 1 minute to 10 minutes, and even more specifically from 1 minute to 5 minutes. In batch mode, such as depicted in the reaction scheme shown in FIG. 1, the reactor is operated for the specified amount of time to achieve the desired contact time. In a continuous mode, throughput of the particles through the reactor can be adjusted to achieve an average residence time equal to the desired contact time.

[0028] After processing the titanium-containing metal particles in the nitrogen-containing fluidized bed reactor, the particles can have a surface nitrogen content ranging from 5.96 wt.% to 12.22 wt.%, more specifically from 5.96 wt.% to 7.90 wt.%, or from 7.90 wt.% to 9.77 wt.%, or from 9.77 wt.% to 12.22 wt.%, as determined by x-ray photoelectron spectroscopy. As used herein, x-ray photoelectron spectroscopy and the values specified herein are according to the protocols of according to ASTM E2735-14, Standard Guide for Selection of Calibrations Needed for X-ray Photoelectron Spectroscopy (XPS) Experiments, ASTM International, West Conshohocken, PA, 2014. Surface nitrogen on titanium or titanium alloy metal particles can bond with titanium or other metals in the alloy such as aluminum, and in doing so can displace oxygen from metal oxide at the particle surface, thus reducing the material's oxygen content at the surface. In some embodiments, after nitriding the metal powder particles can have a nitrogen:oxygen surface wt.% ratio of from 5.96:26.20 to 7.90:21.83 as determined by x-ray photoelectron spectroscopy, and more specifically can have a nitrogen:oxygen surface wt.% ratio of from 9.77:19.99 to 12.22:16.75. The use of pure titanium nitride as a cold spray applied metal can result in undesirable porosity levels in the applied material. Accordingly, in some embodiments, the nitriding reaction is conducted under conditions (e.g., contact time, temperature, space velocity) so that nitriding occurs on the surface of the metal particles but not throughout the interior of the particles, resulting in particles with a surface layer comprising nitrogen and at least a portion of the particles' interior being free of nitrogen.

[0029] As mentioned above, the nitride titanium or titanium alloy metal powder is applied to a substrate with a cold spray deposition process. In a cold spray process, unmelted metal particles are introduced into a high velocity gas stream being projected out of a high velocity (e.g., supersonic) nozzle toward the coating substrate target. The particles' kinetic energy provides sufficient heat on impact with the coating substrate such that the particles plastically deform and fuse with the substrate and surrounding deposited metal material. As the particles impact the substrate, they rapidly cool even as the particles are deforming. The particles change shape dramatically from relatively round to very thin flat splats on the surface.

[0030] An exemplary system is depicted in FIG. 2. As shown in FIG. 2, metal powder is fed from powder feeder 48 through conduit 49 to spray gun 50, which includes nozzle 52 and gun heater 54. Powder particle diameter sizes can range from 1 to 120 microns, more specifically from 5 to 75 microns. Pressurized gas is fed from gas pre-heater 56 to gun heater 54 through conduit 55. Exemplary gases for use in the system include helium, nitrogen, or a mixture of helium and nitrogen. Helium can provide greater gas velocities than nitrogen and has the additional technical effect of being benefited by the nitriding process because unlike a nitrogen-based gas stream, helium does not provide any opportunity for nitriding to occur in the spray gun 50. The powder and the gas streams are mixed in the gun and accelerated to supersonic speeds as the gas/powder mixture exits the nozzle 52. The system also includes a controller or control console 58, which receives input from gun pressure sensor 60 and gun temperature sensor 62 and provides control signals to the gas pre-heater and powder feeder. The term "cold" in "cold spray deposition" refers to the fact that the gas is maintained at a temperature below the melting point of the metal powder; however, as described above the gas is heated in both the gas pre-heater 56 and the gun heater 54. The temperature of the gas used in the process can range from 0°C to 1200°C, more specifically from 200°C to 1000°C, and even more specifically from 200°C to 800°C. Gas pressure can range from 5 bar to 60 bar, more specifically from 15 bar to 45 bar, and even more specifically from 20 bar to 40 bar.

[0031] The invention is further described in the following Examples.

Examples

[0032] Ti-6Al-4V alloy powder materials were nitrided in a fluidized bed reactor as shown in FIG. 1. Approximately, 25 - 40g of Ti-6Al-4-V powder, particle size of 10 to 88 microns was loaded into the fluidized bed reactor. The reactor was then placed in a Model K-3-18 reactor furnace (CM Furnaces, Inc.). Prior to nitridation, argon gas (Praxair) was introduced into the reactor at flow rates equivalent to the N_2 rates to be used for nitridation. This was done by using an MKS type 247 mass flow controller. In each case, the furnace temperature was increased at a rate of about 4.5°C/min to the target nitridation temperature as shown in Table 1. A control sample was also prepared in which argon gas was used for the entire process without any nitrogen gas.

Table 1

Temperature (°C)	700	800
N_2 flow rate (ml/min)	286	260
Duration (min)	30	30

[0033] After the target temperature was reached using an argon gas flow in the reactor, the gas flow was switched to nitrogen (Matheson) and the temperature was held for the times indicated in Table 1. After treating the powder samples in nitrogen at the designated tem-

perature and time, the gas flow was switched to argon and the reactor was allowed to cool down. This was done primarily to isolate the soak time and to prevent any further nitridation that might occur at the higher temperatures during the slow cooling process. Once the powder temperature reached a low enough temperature (about 300°C), the gas flow was switched again, back to nitrogen and the furnace continued to cool down to ambient temperature. The resulting metal powders, along with samples of the untreated powder, were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX). Identification of bulk phase structures and the extent of nitridation were conducted by X-ray diffraction (XRD) using Rigaku and JADE software from MDI. Surface elemental composition was determined by X-ray photoelectron spectroscopy (XPS) using a PHI VersaProbe. Elemental surface analysis was conducted by x-ray photoelectron spectroscopy, the results of which are shown in FIG. 3. As shown in FIG. 3, nitridation at 700°C and 800°C each resulted in an increase in surface nitrogen on the particles and a decrease in surface oxygen for the particles, with nitridation at 800°C producing a greater effect than nitridation at 700°C. Surface carbon detected by XPS is believed to result from surface contamination during preparation of the metal powders.

[0034] The metal powders were used in a system as shown in FIG. 2 using helium at 700° and 30 bar as the gas or a 50/50 blend of helium and nitrogen at 800°C and 40 bar. The nitrided titanium alloy powders exhibited significantly reduced nozzle clogging (and resulting higher quality metal deposits) than either the untreated powder or the control powder.

[0035] The suffix "(s)" is intended to include both the singular and the plural of the term that it modifies, thereby including at least one of that term (e.g., the colorant(s) includes at least one colorants). "Optional" or "optionally" means that the subsequently described event or circumstance can or can not occur, and that the description includes instances where the event occurs and instances where it does not. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs.

[0036] While the invention has been described in detail in connection with only a limited number of embodiments, it should be readily understood that the invention is not limited to such disclosed embodiments. Additionally, while various embodiments of the invention have been described, it is to be understood that aspects of the invention may include only some of the described embodiments. Accordingly, the invention is not to be seen as limited by the foregoing description, but is only limited by the scope of the appended claims.

Claims

1. A method of applying a metal comprising titanium to a substrate, the method comprising:

   nitriding the surface of metal powder particles (46) comprising titanium by contacting the particles (46) with a first gas comprising nitrogen in a fluidized bed reactor; and
   depositing the metal powder particles (46) onto the substrate with cold spray deposition using a second gas.

2. The method of claim 1, wherein the metal powder particles (46) comprise at least one titanium or titanium alloy selected from grades 5 (Ti 6Al 4V) and 23(Ti 6Al 4V), according to ASTM B861-10.

3. The method of claim 2, wherein the metal powder particles (46) comprise at least one titanium or titanium alloy selected from Ti 6Al 4V, Ti-3Al-2.5V, Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V, Ti 6Al 2Sn 4Zr 2Mo, $\alpha+\beta$ Ti-6Al-4V, and near β Ti-10V-2Fe-3Al.

4. The method of any of claims 1-3,, wherein the first gas comprises at least 1 vol.% nitrogen.

5. The method of any of claims 1-4, wherein the first gas consists essentially of nitrogen.

6. The method of any of claims 1-5, wherein the fluidized bed reactor is operated at a temperature of 500°C to 850°C.

7. The method of any of claims 1-6, wherein the first gas is at a pressure of 0.11 to 0.12 MPa.

8. The method of any of claims 1-7, wherein the space velocity of the first gas in the fluidized bed reactor is from 1 min^{-1} to 30 min^{-1}.

9. The method of any of claims 1-8, wherein the metal powder particles (46) are contacted with the first gas in the fluidized bed reactor (12) for at least 1 minute.

10. The method of any of claims 1-9, wherein the second gas comprises helium.

11. The method of claim 10, wherein the second gas further comprises nitrogen, or wherein the second gas consists essentially of helium.

12. The method of any of claims 1-11, wherein the second gas is at a temperature of 20°C to 850°C.

13. The method of any of claims 1-3, wherein the first gas comprises at least 1 vol.% nitrogen,
    wherein the fluidized bed reactor is operated at a

temperature of 500°C to 800°C, even more preferably 600°C to 750°C, even more preferably 600°C to 700°C,
wherein the pressure in the reactor can range from 0.11 to 0.12 MPa, more preferably from 0.11 MPa to 0.115 MPa,
wherein the metal powder particles (46) are contacted with the first gas in the fluidized bed reactor (12) for at least 1 minute, more preferably from 1 minute to 30 minutes, more preferably from 1 minute to 10 minutes, and even more preferably from 1 minute to 5 minutes, and
wherein the metal powder particles (46) after nitriding comprise nitrogen at the particle surface and also comprise an internal particle portion that is free of nitrogen.

14. The method of any of claims 1-3 and 13, wherein the first gas comprises at least 1 vol.% nitrogen,
wherein the fluidized bed reactor is operated at a temperature of 500°C to 800°C, even more preferably 600°C to 750°C, even more preferably 600°C to 700°C,
wherein the pressure in the reactor can range from 0.11 to 0.12 MPa, more preferably from 0.11 MPa to 0.115 MPa,
wherein the metal powder particles (46) are contacted with the first gas in the fluidized bed reactor (12) for at least 1 minute, more preferably from 1 minute to 30 minutes, more preferably from 1 minute to 10 minutes, and even more preferably from 1 minute to 5 minutes, and
wherein the metal powder particles (46) after nitriding have a surface nitrogen content ranging from 5.96 wt.% to 12.22 wt.% as determined by x-ray photoelectron spectroscopy.

15. The method of any of claims 1-3, 13, and 14, wherein the first gas comprises at least 1 vol.% nitrogen,
wherein the fluidized bed reactor is operated at a temperature of 500°C to 800°C, even more preferably 600°C to 750°C, even more preferably 600°C to 700°C,
wherein the pressure in the reactor can range from 0.11 to 0.12 MPa, more preferably from 0.11 MPa to 0.115 MPa,
wherein the metal powder particles (46) are contacted with the first gas in the fluidized bed reactor (12) for at least 1 minute, more preferably from 1 minute to 30 minutes, more preferably from 1 minute to 10 minutes, and even more preferably from 1 minute to 5 minutes, and
wherein the metal powder particles (46) after nitriding have a nitrogen:oxygen surface wt.% ratio of from 5.96:26.2 to 12.26:16.75 as determined by x-ray photoelectron spectroscopy.

Patentansprüche

1. Verfahren zum Auftragen eines Metalls, umfassend Titan, auf ein Substrat, wobei das Verfahren Folgendes umfasst:

Nitrieren der Oberfläche aus Metallpulverpartikeln (46), umfassend Titan, durch Inkontaktbringen der Partikel mit einem ersten stickstoffumfassenden Gas in einem Wirbelbettreaktor; und Abscheiden der Metallpulverpartikel (46) auf das Substrat durch Kaltsprühabscheidung unter Verwendung eines zweiten Gases.

2. Verfahren nach Anspruch 1, wobei die Metallpulverpartikel (46) zumindest ein Titan oder eine Titanlegierung umfassen, ausgewählt aus Grad 5 (Ti 6AL 4V) und 23 (Ti 6Al 4V) gemäß der ASTM B861-10.

3. Verfahren nach Anspruch 2, wobei die Metallpulverpartikel (46) zumindest ein Titan oder eine Titanlegierung umfassen, ausgewählt aus Ti 6Al 4V, Ti-3Al-2,5V, Ti-5Al-2,5Sn, Ti-8Al-1Mo-1V, Ti 6Al 2Sn 4Zr 2Mo, $\alpha+\beta$ Ti-6Al-4V und nahe β Ti-10V-2Fe-3Al.

4. Verfahren nach einem der Ansprüche 1-3, wobei das erste Gas zumindest 1 Vol.-% Stickstoff umfasst.

5. Verfahren nach einem der Ansprüche 1-4, wobei das erste Gas im Wesentlichen aus Stickstoff besteht.

6. Verfahren nach einem der Ansprüche 1-5, wobei der Wirbelbettreaktor bei einer Temperatur von 500 °C bis 850 °C betrieben wird.

7. Verfahren nach einem der Ansprüche 1-6, wobei das erste Gas einen Druck von 0,11 bis 0,12 MPa aufweist.

8. Verfahren nach einem der Ansprüche 1-7, wobei die Raumgeschwindigkeit des ersten Gases in dem Wirbelbettreaktor 1 min^{-1} bis 30 min^{-1} beträgt.

9. Verfahren nach einem der Ansprüche 1-8, wobei die Metallpulverpartikel (46) in dem Wirbelbettreaktor (12) zumindest 1 Minute mit dem ersten Gas in Kontakt gebracht werden.

10. Verfahren nach einem der Ansprüche 1-9, wobei das zweite Gas Helium umfasst.

11. Verfahren nach Anspruch 10, wobei das zweite Gas ferner Stickstoff umfasst oder wobei das zweite Gas im Wesentlichen aus Helium besteht.

12. Verfahren nach einem der Ansprüche 1-11, wobei das zweite Gas eine Temperatur von 20 °C bis 850 °C aufweist.

13. Verfahren nach einem der Ansprüche 1-3, wobei das erste Gas zumindest 1 Vol.-% Stickstoff umfasst,
wobei der Wirbelbettreaktor bei einer Temperatur von 500 °C bis 800 °C, bevorzugter von 600 °C bis 750 °C oder noch bevorzugter von 600 °C bis 700 °C betrieben wird,
wobei der Druck in dem Reaktor im Bereich von 0,11 bis 0,12 MPa, bevorzugter von 0,11 bis 0,115 MPa, liegen kann,
wobei die Metallpulverpartikel (46) in dem Wirbelbettreaktor (12) zumindest 1 Minute, bevorzugter 1 Minute bis 30 Minuten, bevorzugter 1 Minute bis 10 Minuten und noch bevorzugter 1 Minute bis 5 Minuten mit dem ersten Gas in Kontakt gebracht werden, und
wobei die Metallpulverpartikel (46) nach dem Nitrieren auf der Partikeloberfläche Stickstoff umfassen und ebenso einen Innenpartikelanteil umfassen, der kein Stickstoff aufweist.

14. Verfahren nach einem der Ansprüche 1-3 und 13, wobei das erste Gas zumindest 1 Vol.-% Stickstoff umfasst,
wobei der Wirbelbettreaktor bei einer Temperatur von 500 °C bis 800 °C, bevorzugter von 600 °C bis 750 °C oder noch bevorzugter von 600 °C bis 700 °C betrieben wird,
wobei der Druck in dem Reaktor im Bereich von 0,11 bis 0,12 MPa, bevorzugter von 0,11 bis 0,115 MPa, liegen kann,
wobei die Metallpulverpartikel (46) in dem Wirbelbettreaktor (12) zumindest 1 Minute, bevorzugter 1 Minute bis 30 Minuten, bevorzugter 1 Minute bis 10 Minuten und noch bevorzugter 1 Minute bis 5 Minuten mit dem ersten Gas in Kontakt gebracht werden, und
wobei die Metallpulverpartikel (46) nach dem Nitrieren einen Stickstoffoberflächengehalt von 5,96 Gew.-% bis 12,22 Gew.-% aufweisen, wie durch Röntgenphotoelektronenspektroskopie bestimmt.

15. Verfahren nach einem der Ansprüche 1-3, 13 und 14, wobei das erste Gas zumindest 1 Vol.-% Stickstoff umfasst,
wobei der Wirbelbettreaktor bei einer Temperatur von 500 °C bis 800 °C, bevorzugter von 600 °C bis 750 °C oder noch bevorzugter von 600 °C bis 700 °C betrieben wird,
wobei der Druck in dem Reaktor im Bereich von 0,11 bis 0,12 MPa, bevorzugter von 0,11 bis 0,115 MPa, liegen kann,
wobei die Metallpulverpartikel (46) in dem Wirbelbettreaktor (12) zumindest 1 Minute, bevorzugter 1 Minute bis 30 Minuten, bevorzugter 1 Minute bis 10 Minuten und noch bevorzugter 1 Minute bis 5 Minuten mit dem ersten Gas in Kontakt gebracht werden, und
wobei die Metallpulverpartikel (46) nach dem Nitrieren ein Oberflächen-Gew.-%-Verhältnis zwischen Stickstoff und Sauerstoff von 5,96:26,2 bis 12,26:16,75 aufweisen, wie durch Röntgenphotoelektronenspektroskopie bestimmt.

Revendications

1. Procédé d'application d'un métal comprenant du titane sur un substrat, le procédé comprenant :

la nitruration de la surface de particules de poudre métallique (46) comprenant du titane par mise en contact des particules (46) avec un premier gaz comprenant de l'azote dans un réacteur à lit fluidisé ; et
le dépôt des particules de poudre métallique (46) sur le substrat par dépôt par pulvérisation à froid à l'aide d'un second gaz.

2. Procédé selon la revendication 1, dans lequel les particules de poudre métallique (46) comprennent au moins un titane ou un alliage de titane choisi parmi les classes 5 (Ti 6Al 4V) et 23 (Ti 6Al 4V), selon la norme ASTM B861-10.

3. Procédé selon la revendication 2, dans lequel les particules de poudre métallique (46) comprennent au moins un titane ou un alliage de titane choisi parmi Ti 6Al 4V, Ti-3Al-2.5V, Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V, Ti 6Al 2Sn 4Zr 2Mo, $\alpha+\beta$ Ti-6Al-4V, et quasi β Ti-10V-2Fe-3Al.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le premier gaz comprend au moins 1 % en volume d'azote.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le premier gaz est constitué essentiellement d'azote.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le réacteur à lit fluidisé fonctionne à une température située dans la plage allant de 500 °C à 850 °C.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le premier gaz est à une pression située dans la plage allant de 0,11 à 0,12 MPa.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la vitesse spatiale du premier gaz dans le réacteur à lit fluidisé se situe dans la plage allant de 1 min^{-1} à 30 min^{-1}.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel les particules de poudre métallique (46) sont mises en contact avec le premier gaz dans

le réacteur à lit fluidisé (12) pendant au moins 1 minute.

10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel le second gaz comprend de l'hélium.

11. Procédé selon la revendication 10, dans lequel le second gaz comprend en outre de l'azote, ou dans lequel le second gaz est constitué essentiellement d'hélium.

12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel le second gaz est à une température située dans la plage allant de 20 °C à 850 °C.

13. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le premier gaz comprend au moins 1 % en volume d'azote,
dans lequel le réacteur à lit fluidisé fonctionne à une température située dans la plage allant de 500 °C à 800 °C, plus préférablement encore de 600 °C à 750 °C, et plus préférablement encore de 600 °C à 700 °C,
dans lequel la pression dans le réacteur peut se situer dans la plage allant de 0,11 à 0,12 MPa, plus préférablement de 0,11 MPa à 0,115 MPa,
dans lequel les particules de poudre métallique (46) sont mises en contact avec le premier gaz dans le réacteur à lit fluidisé (12) pendant au moins 1 minute, plus préférablement de 1 minute à 30 minutes, plus préférablement de 1 minute à 10 minutes, et plus préférablement encore de 1 minute à 5 minutes, et
dans lequel les particules de poudre métallique (46) après nitruration comprennent de l'azote à la surface des particules et comprennent également une partie interne de particule exempte d'azote.

14. Procédé selon l'une quelconque des revendications 1 à 3 et 13, dans lequel le premier gaz comprend au moins 1 % en volume d'azote,
dans lequel le réacteur à lit fluidisé fonctionne à une température située dans la plage allant de 500 °C à 800 °C, plus préférablement encore de 600 °C à 750 °C, et plus préférablement encore de 600 °C à 700 °C,
dans lequel la pression dans le réacteur peut se situer dans la plage allant de 0,11 à 0,12 MPa, plus préférablement de 0,11 MPa à 0,115 MPa,
dans lequel les particules de poudre métallique (46) sont mises en contact avec le premier gaz dans le réacteur à lit fluidisé (12) pendant au moins 1 minute, plus préférablement de 1 minute à 30 minutes, plus préférablement de 1 minute à 10 minutes, et plus préférablement encore de 1 minute à 5 minutes, et
dans lequel les particules de poudre métallique (46) après nitruration présentent une teneur en azote en surface située dans la plage allant de 5,96 % en poids à 12,22 % en poids, telle que déterminée par spectroscopie de photoélectrons induite par rayons X.

15. Procédé selon l'une quelconque des revendications 1 à 3, 13 et 14, dans lequel le premier gaz comprend au moins 1 % en volume d'azote,
dans lequel le réacteur à lit fluidisé fonctionne à une température située dans la plage allant de 500 °C à 800 °C, plus préférablement encore de 600 °C à 750 °C, et plus préférablement encore de 600 °C à 700 °C,
dans lequel la pression dans le réacteur peut se situer dans la plage allant de 0,11 à 0,12 MPa, plus préférablement de 0,11 MPa à 0,115 MPa,
dans lequel les particules de poudre métallique (46) sont mises en contact avec le premier gaz dans le réacteur à lit fluidisé (12) pendant au moins 1 minute, plus préférablement de 1 minute à 30 minutes, plus préférablement de 1 minute à 10 minutes, et plus préférablement encore de 1 minute à 5 minutes, et
dans lequel les particules de poudre métallique (46) après nitruration présentent un rapport azote: oxygène en % en poids en surface situé dans la plage allant de 5,96:26,2 à 12,26:16,75, tel que déterminé par spectroscopie de photoélectrons induite par rayons X.

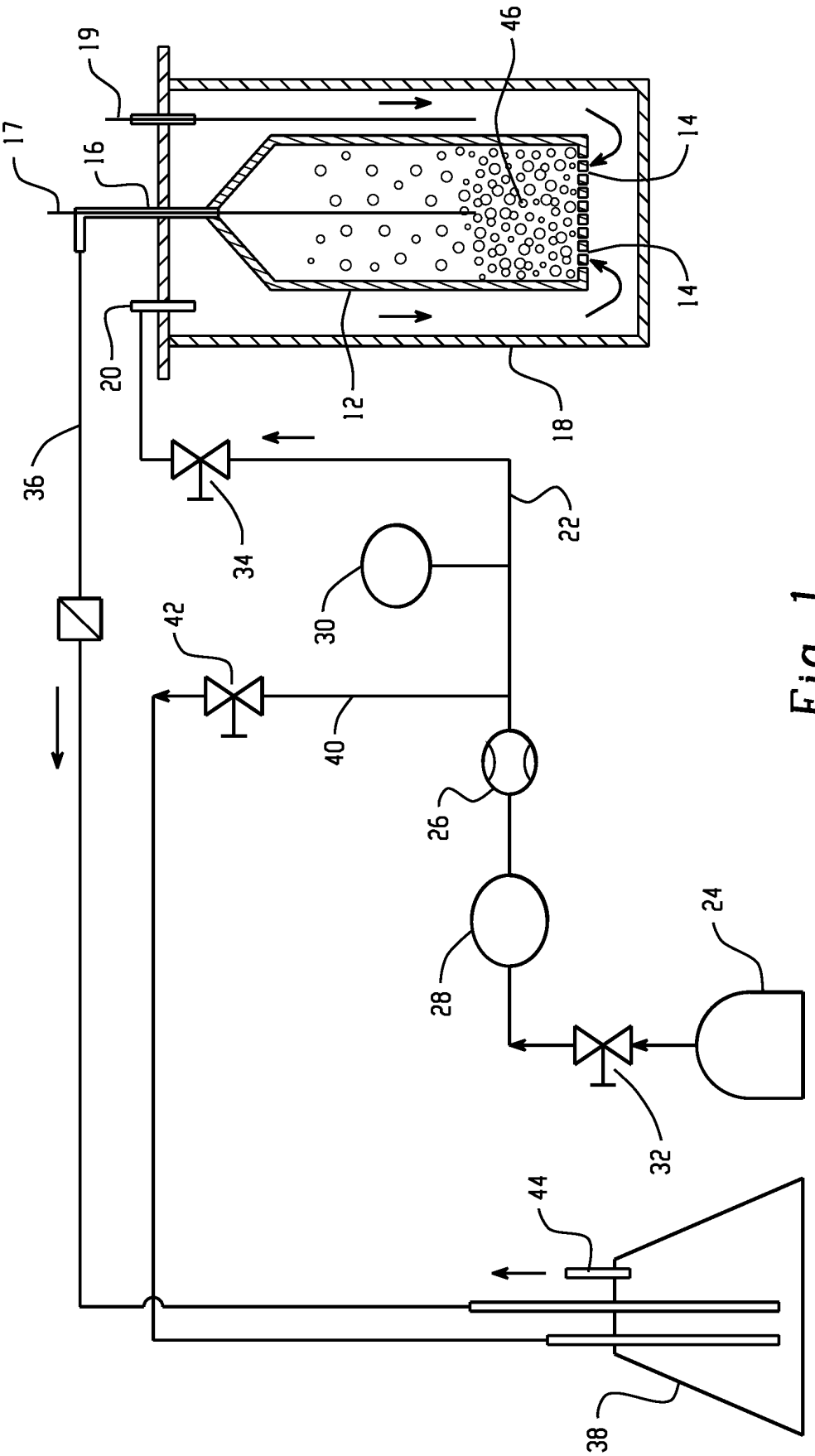
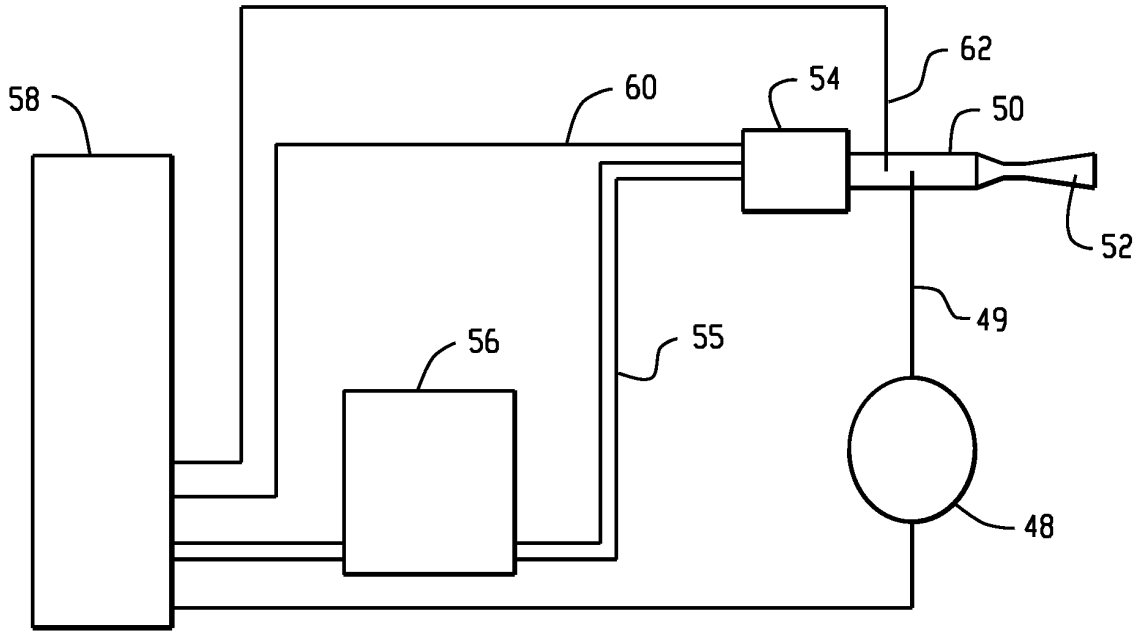


Fig. 1


58
60
54
62
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52
49
56
55
48

Fig. 2

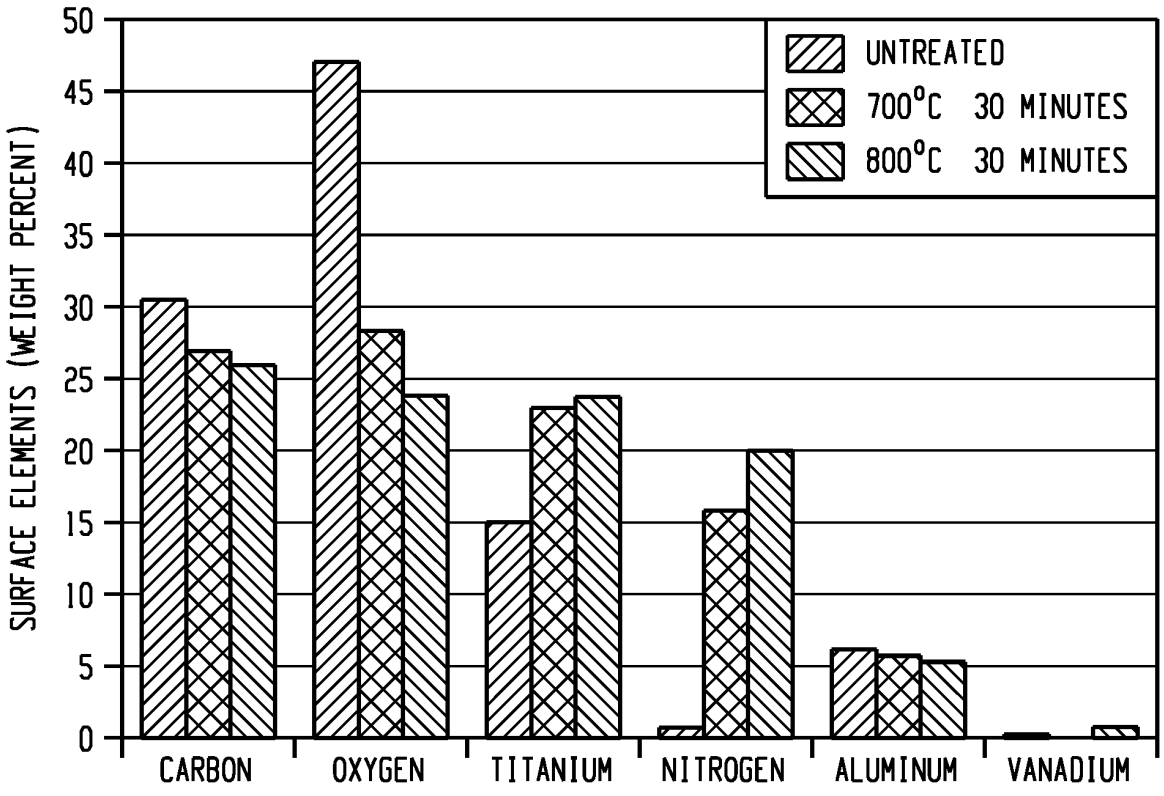
SURFACE ELEMENTS (WEIGHT PERCENT)
50
45
40
35
30
25
20
15
10
5
0
UNTREATED
700°C 30 MINUTES
800°C 30 MINUTES
CARBON
OXYGEN
TITANIUM
NITROGEN
ALUMINUM
VANADIUM

Fig. 3

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2011132874 A2 **[0003]**
- US 7232556 B **[0004]**
- US 5149514 A **[0005]**
- US 5320686 A **[0006]**