



(11)

EP 3 431 630 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
23.01.2019 Bulletin 2019/04

(51) Int Cl.:
C23C 24/04 (2006.01)

(21) Application number: **18184451.5**

(22) Date of filing: **19.07.2018**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(72) Inventors:
• **BINEK, Lawrence**
Glastonbury, CT Connecticut 06033 (US)
• **NARDI, Aaron T.**
East Granby, CT Connecticut 06026 (US)

(74) Representative: **Dehns**
St. Brides House
10 Salisbury Square
London EC4Y 8JD (GB)

(30) Priority: **19.07.2017 US 201715653582**

(71) Applicant: **United Technologies Corporation**
Farmington, CT 06032 (US)

(54) **HYDROGEN BASED COLD SPRAY NOZZLE AND METHOD**

(57) A method for cold spray deposition of a material on a Substrate (100), comprising the steps of entraining a metal powder material in a stream of accelerant gas (104) comprising hydrogen; forming a flow of shield gas

(106) around the stream of accelerant gas (104); and impacting the substrate (100) with the stream of accelerant gas (104) whereby the metal powder material is deposited on the substrate (100).

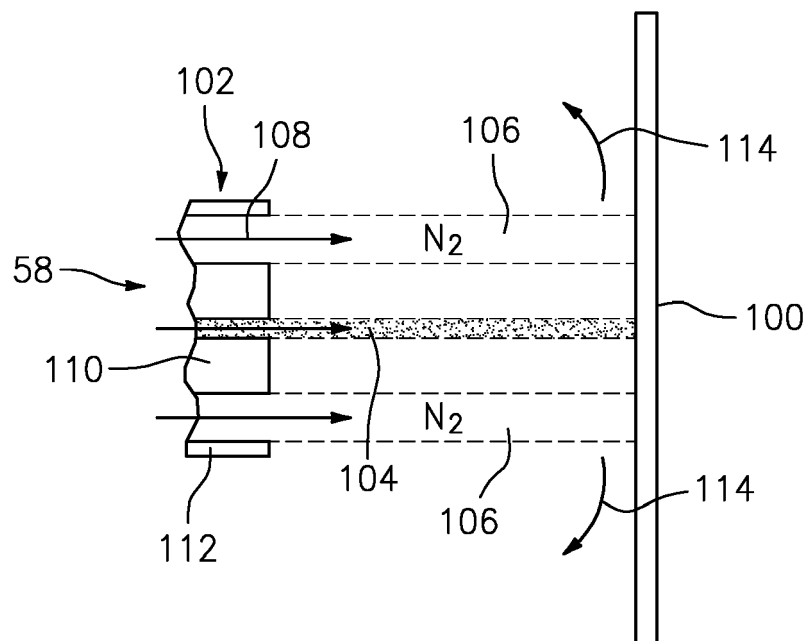


FIG. 5

Description

BACKGROUND OF THE DISCLOSURE

[0001] The present disclosure relates to a cold spray process which involves deposition of powdered materials through a supersonic nozzle using kinetic energy and plastic deformation upon impacting a target to consolidate the powdered materials. This occurs through a process similar to cold welding, where surface strains on the particle and the impacting substrate expose fresh metal surfaces which then bond.

[0002] In order to achieve superior material properties through cold spray deposition, high particle velocity is required. Known cold spray processes use a combination of helium and heat to accelerate metal particles to a predetermined velocity sufficient to obtain good bonding of the metal particles with the substrate. However, helium is an expensive consumable without a reclamation system. Further, the helium gas temperature may need to be raised, increasing the sonic velocity of the gas, in turn increasing the particle impact velocity to a level which would then be sufficient to achieve good particle bonding. This increased heat can cause fouling of the nozzle, leading to a need to replace or maintain the nozzles to bring them back into service.

[0003] Alternately, nitrogen can be used in the cold spray process for accelerating particles to sufficient velocities to achieve bonding. The sonic velocity of nitrogen at any temperature is less than half of the velocity of helium at the same spray gas temperature. As with helium, increased temperature can increase the sonic velocity of nitrogen, but very high temperatures, 600-1000°C, may be required for many materials to achieve acceptable velocity at which point many of the attractive characteristics of a cold spray deposit are lost. As in the case of higher temperature helium, it is also more likely to foul nozzles when running very high nitrogen temperatures.

SUMMARY OF THE DISCLOSURE

[0004] According to an aspect of the disclosure, there is provided a method for cold spray deposition of a material on a substrate comprising the steps of: entraining a metal powder material in a stream of accelerant gas comprising hydrogen; forming a flow of shield gas around the stream of accelerant gas; and impacting the substrate with the stream of accelerant gas whereby the metal powder material is deposited on the substrate.

[0005] In a non-limiting embodiment of the method, the stream of accelerant gas comprises a majority of hydrogen.

[0006] In a further non-limiting embodiment of the method, the stream of accelerant gas comprises at least 70% vol hydrogen.

[0007] In a further non-limiting embodiment of the method, the stream of accelerant gas comprises at least 90% vol hydrogen.

[0008] In a further non-limiting embodiment of the method, the stream of accelerant gas has a critical velocity ratio of at least one.

[0009] In a further non-limiting embodiment of the method, the stream of accelerant gas has a critical velocity ratio of between 1.5 and 2.0.

[0010] In a further non-limiting embodiment of the method, the stream of accelerant gas is at a temperature of less than about 400°C.

[0011] In a further non-limiting embodiment of the method, the stream of accelerant gas is at a temperature of less than about 200°C.

[0012] In a further non-limiting embodiment of the method, gas mixture leaving an area of impact of the stream of accelerant gas with the substrate has a hydrogen content of less than 5% vol.

[0013] In a further non-limiting embodiment of the method, the shield gas is selected from the group consisting of inert gases and gas which is substantially inert with the substrate and metal powder at temperature of the stream of accelerant gas, and mixtures thereof.

[0014] In a further non-limiting embodiment of the method, the shield gas is selected from the group consisting of nitrogen, helium, argon, carbon dioxide and mixtures thereof.

[0015] In a further non-limiting embodiment of the method, the shield gas is nitrogen.

[0016] In a further non-limiting embodiment of the method, the metal powder material comprises particles of aluminum, copper, nickel, iron, tantalum, niobium, cobalt, or mixtures or alloys thereof, where the particle sizes vary from about 5 μm to 40 μm.

[0017] In a further non-limiting embodiment of the method, the metal powder material comprises particles of aluminum, copper or mixtures thereof.

[0018] In a further non-limiting embodiment of the method, the metal powder material comprises particles of aluminum having a particle size of between 20 and 40 μm.

[0019] In a further non-limiting embodiment of the method, the metal powder material comprises particles of copper having a particle size of between 10 and 30 μm.

[0020] In a further non-limiting embodiment of the method, the stream of accelerant gas is passed through a nozzle before the impacting step.

[0021] In a further non-limiting embodiment of the method, the flow of shield gas is at a higher pressure than the stream of accelerant gas.

[0022] The disclosure also provides an apparatus for cold spray deposition of a material on a substrate comprising: a nozzle communicated with accelerant gas and metal powder to be deposited on the substrate; a sleeve surrounding the nozzle and defining an annular space around the nozzle, the annular space being communicated with a shield gas.

[0023] In a non-limiting embodiment of the apparatus, the nozzle is defined substantially concentric within the sleeve.

[0024] In a further non-limiting embodiment of the apparatus, the nozzle and the sleeve define an outlet for a centered stream of the accelerant gas and a cylinder of shield gas surrounding the centered stream.

[0025] In a further non-limiting embodiment of the apparatus, a perforated bulkhead is provided in the annular space to adjust flow characteristics of the shield gas.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] A detailed description follows, with reference to the attached drawings, wherein:

FIG. 1 is a schematic illustration of a prior art cold spray system and method;

FIG. 2 is a schematic illustration of a cold spray system and method in accordance with the present disclosure;

FIG. 3 is a schematic illustration of a system and process showing a further exemplary embodiment;

FIG. 4 shows an enlarged view of a heater for heating the accelerant gas;

FIG. 5 schematically illustrates a non-limiting embodiment of a method of cold spray deposition;

FIG. 6 illustrates an exemplary embodiment of a cold spray system mounted on a robot arm;

FIG. 7 is a side elevational view of a further exemplary embodiment of a system for cold spray deposition according to the disclosure.

FIG. 8 is a perspective view of a further exemplary embodiment of a system for cold spray deposition;

FIG. 9 is a sectional perspective view of a further exemplary embodiment; and

FIG. 10 is a side schematic illustration of a further non-limiting configuration of the present disclosure.

[0027] Like reference numbers and designations in the various drawings indicate like elements.

DETAILED DESCRIPTION

[0028] The present disclosure relates to cold spray deposition of a material such as a metal powder or particulate on a substrate.

[0029] FIG. 1 shows a prior art system 10 which uses helium as an accelerant gas. System 10 includes a gas/heater control console 12, a powder feeder 14, a gas heater 16, a cold spray nozzle 18 and a spray hood 20. The workpiece to be treated is treated in spray hood 20.

[0030] Two streams of gas are fed to cold spray nozzle 18. The first stream 22 passes through powder feeder 14 and conveys a helium with powder mixture to nozzle 18 at a relatively low flow rate. The second stream 24 passes through gas heater 16 at a significantly higher flow rate, and is mixed with the first stream in nozzle 18 to deliver the powder entrained in helium accelerant gas at an elevated temperature and velocity. As set forth above, in order to accomplish higher impacting velocity with either helium or nitrogen, the temperature can be increased but is limited to a point where the nozzle will be fouled. Further, if helium is used, the expensive gas is either lost, or must be recycled using expensive equipment.

[0031] FIG. 2 shows an illustrative embodiment of a system 50 using hydrogen. System 50 includes a gas control console 52, a hydrogen source 54, a powder feeder 56 and a coaxial cold spray nozzle assembly 58 for applying powder to a substrate in spray hood 60. Nozzle assembly 58 is also communicated with a source of shield gas, in this case nitrogen which is fed to nozzle assembly 58 through line 61. Powder feeder 56, nozzle assembly 58 and spray hood 60 can be positioned within a cold spray acoustic enclosure 62 as illustrated. Further, a hydrogen detector 64 can be positioned in proximity to spray hood 60 to monitor for escaping hydrogen.

[0032] Enclosure 62 is also communicated with a source 66 of outside makeup air, and a dust collector 68 is also communicated with spray hood 60. In operation, hydrogen is fed through one line 63 which passes through powder feeder 56 to deliver a stream of hydrogen and entrained powder particles to nozzle 58. Shield gas is fed through stream 61, also to nozzle assembly 58. Nozzle assembly 58 delivers a centered stream of hydrogen accelerant gas with entrained powder for cold spray deposition upon a workpiece, as well as a cylindrical flow of shield gas, in this case, nitrogen, surrounding the flow of hydrogen. The shield gas serves to dilute and safely remove hydrogen gas from the point of application, after impact with the workpiece. This prevents escape of hydrogen at elevated levels or concentrations and

helps ensure safety of the process. Shield gas can be fed through line 61 at a significantly higher flow rate or pressure than the hydrogen accelerant gas. With a system as illustrated in FIG. 2, high quality cold spray deposition can be accomplished at significantly lower temperatures which avoid fouling of the nozzle. Further, in this non-limiting example, costs of heating of the accelerant gas can be avoided. Finally, hydrogen is available at a reduced cost as compared to helium. Thus, a system as shown in FIG. 2 can be used to produce high quality cold spray deposition using a cheaper accelerant gas and at conditions which produce higher quality deposition with less chance of fouling of the nozzle.

[0033] FIG. 3 shows a further illustrative embodiment according to the disclosure. Similar elements with respect to FIG. 2 carry similar reference numerals. In this regard, however, system 50' of FIG. 3 can be provided with a heater 70 to heat the stream of hydrogen, accelerant gas and powder, if desired. Due to the high velocity which can be accomplished using hydrogen as accelerant gas, any heating which will be necessary would be a low level of heating. Thus, the heater 70 as shown in FIG. 3 could be a heating coil positioned within a box or tube-type furnace. Such a configuration is shown in FIG. 4.

[0034] FIG. 4 shows heater 70 having a hydrogen gas tube 72 which passes through a box or tube furnace 74. The tube 72 can be in the form of a coil within box 74, and can be surrounded by a conduit 76 for carrying shield or inert gas such as nitrogen. In this regard, pressure of shield gas in line 76 should be greater than pressure of hydrogen gas in line 72 so that any leaks do not result in loss of hydrogen into the work area or atmosphere.

[0035] FIG. 5 schematically illustrates flow in accordance with the present disclosure. FIG. 5 shows workpiece 100 and schematically illustrates the outlet end 102 of a cold spray nozzle assembly 58. As shown, a centrally located stream of accelerant gas 104 is impinged upon workpiece 100 from the nozzle of cold spray assembly 58, while a cylindrical shield of gas 106 is formed around the centered stream through shield gas flowing along an annular space 108 between nozzle 110 and outer sleeve 112. Stream 104 engaging workpiece 100 remains substantially entirely hydrogen with entrained particles. Thus, shield gas 106, which prevents the escape of undiluted hydrogen defines a cylindrical shield or shroud around the stream of accelerant gas. After impacting workpiece 100, arrows 114 schematically illustrate gases leaving the impact area, and these gases are diluted to the point where they contain hydrogen in an amount of up to about 5% vol.

[0036] As set forth above, exit velocity (m/s) is a key parameter in obtaining good results with a cold spray deposition. Table 1 below sets forth pressure temperature and exit velocity for several different types of accelerant gas. As shown, helium can generate an exit velocity of 674 m/s at a pressure of 30 bar (3 MPa) and a temperature of 20°C. At the same pressure and temperature, nitrogen as an accelerant gas produces an exit velocity of only 397 m/s. This velocity can be increased if either the temperature or pressure are somewhat significantly increased, as shown in Table 1 (where 1 bar = 0.1 MPa).

Table 1: Velocity performance of copper under various process conditions

Gas Type	Pressure (bar)	Temperature (°C)	Exit Velocity (m/s)
He	30	20	674
N2	30	20	397
N2	30	1000	683
N2	60	600	666
H2	30	20	802

[0037] Finally, the last line of Table 1 compares exit velocity for a stream of hydrogen as accelerant gas, and shows that exit velocity is significantly higher than it is for helium or nitrogen at the same conditions.

[0038] The flow of hydrogen accelerant gas can advantageously comprise a majority of hydrogen. More ideally, the accelerant gas can comprise at least 70% volume of hydrogen, more preferably at least 90% of volume hydrogen.

[0039] The stream of accelerant gas can advantageously be fed to the workpiece at a critical velocity ratio, or CVR (the ratio of particle velocity to the critical velocity for particle bonding), of at least one, and more desirably at a critical velocity ratio of between 1.5 and 2.0. Further, such CVRs can be achieved at a temperature of the stream of accelerant gas of about 20°C when spraying copper particles with an average particle size of 20 μm and a gas pressure of 20 bar (2 MPa). Similarly, relatively high strength aluminum alloy powder such as aluminum alloy 6061, with an average particle size of about 30 μm, can achieve this same CVR range with a hydrogen gas temperature of only 100°C and a pressure of 20 bar (2 MPa). Even high strength super-alloy powders such as Inconel 625 with average particle sizes of 20 μm can achieve this same CVR range with a hydrogen gas temperature of only 200°C and a pressure of 35 bar (3.5 MPa). Generally, temperatures higher than 200°C are not needed for most metals or alloys of the particle size ranges discussed. However some metals may experience benefits due to higher temperature accelerating gases. Gas temperatures as

high as 400°C or even higher are possible with the heating arrangement described, but increases in temperature will add to the system complexity with higher temperature capable hardware, hose flexibility, and even hydrogen absorption into some metals and alloys.

[0040] The shield gas can advantageously be any gas which remains substantially inert at conditions likely to be encountered during the process. More specifically, the shield gas can be selected from the group consisting of inert gases and gases which are substantially inert with the substrate and metal powder at temperatures of the stream of accelerant gas and mixtures thereof. In a further non-limiting aspect of the disclosure, the shield gas can be selected from the group of nitrogen, argon, carbon dioxide, and mixtures thereof, most preferably nitrogen.

[0041] The substrate and powder materials can be any metals or ceramic-metal composites including aluminum, copper, nickel, iron, tantalum, niobium, cobalt or mixtures or alloys thereof. In one aspect of the present disclosure, when the particles are aluminum, the particles desirably have a particle size of between 20 and 40 μm . When the metal powder material is particles of copper, these particles can be provided at a particle size of between 10 and 30 μm . Other desirable particle size ranges would be applicable to other metals and alloys where generally higher density and higher strength materials require lower particle size ranges.

[0042] FIG. 6 shows a cold spray nozzle assembly 58 according to the present disclosure mounted to a robot arm 200 which can be utilized and controlled to position nozzle 58 relative to 100.

[0043] FIG. 7 is an enlarged view of the nozzle portion of FIG. 6, and shows nozzle assembly 58 with a split clamp 202 for mounting nozzle assembly 58 to arm 200. Inlets 204, 206 lead through split clamp 202 and can be used to feed accelerant gas and powder to nozzle assembly 58 described above. This leads to a stream of accelerant gas and powder which exits nozzle assembly 58 at an outlet end 208 to impact workpiece 100. An inlet 210 is shown which can be used to feed shield gas into a space between an outer sleeve 212 and the inner nozzle structure 214. FIG. 8 is a perspective view similar to that shown in FIG. 7, and further illustrates an annular space 216 through which shield gas flows during operation of the device.

[0044] Turning to FIG. 9, a sectional view of the nozzle assembly 58 as shown in FIG. 8 is presented, and further illustrates internal structure and gas flow of the apparatus according to this structure. Inlets 204, 206 are shown through which powder feed and hydrogen gas feed can be conducted into a central flow area 218 which leads into the nozzle jet of nozzle 214 to produce a stream 104 of hydrogen accelerant gas with entrained powder particles for impacting workpiece 100 as desired.

[0045] The embodiment of FIG. 9 shows two inlets 210 through which shield gas are introduced into an annular space 216 between sleeve 212 and nozzle 214. The cylindrical flow 106 of shield gas, around the stream 104 of hydrogen accelerant gas, which serves to sufficiently dilute hydrogen concentration after impacting workpiece 100 such that gases leaving the area of impact with workpiece 100 are at sufficiently reduced levels of hydrogen, particularly before they encounter air or oxygen.

[0046] In this configuration, a bulkhead 217 can be positioned within annular space and have through-passages or perforations to allow shield gas to pass through bulkhead 217. Such a configuration can help to produce a smooth and uniform flow of shield gas in a cylindrical pattern as desired.

[0047] FIG. 10 shows a side view of a further configuration of a hydrogen cold spray nozzle assembly. In this configuration, like numerals have again been used to depict like elements. One particular aspect of FIG. 10, however, is that a single inlet 205 is utilized for both hydrogen gas and powder. Since hydrogen can be used at relatively low or cool temperatures, the entire flow of hydrogen gas can be used to entrain the metal powders, and the entire flow can be substantially straight and aligned along the longitudinal access of stream 218 through nozzle 214. This simplifies construction of the device by removing one inlet, and is also advantageous in that the flow path of hydrogen is maintained in a straight line, therefore avoiding impact areas which could lead to fouling of the nozzle.

[0048] It should be appreciated that the various configurations described and illustrated herein provide for use of hydrogen as an accelerant in a cold spray process to overcome cost and fouling issues in helium-based systems and methods, and to improve quality of results of the cold spray deposition, while maintaining a safe shield of nitrogen or other effectively inert and/or diluting gas around the stream of hydrogen such that the hydrogen is diluted and removed from the impact area with the workpiece after impact is conducted.

[0049] One or more embodiments of the present invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

Claims

1. A method for cold spray deposition of a material on a substrate (100), comprising the steps of:

entraining a metal powder material in a stream of accelerant gas (104) comprising hydrogen;

forming a flow of shield gas (106) around the stream of accelerant gas (104); and impacting the substrate (100) with the stream of accelerant gas (104) whereby the metal powder material is deposited on the substrate (100).

2. The method of claim 1, wherein the stream of accelerant gas (104) comprises a majority of hydrogen, optionally at least 70% vol hydrogen, or at least 90% vol hydrogen.
3. The method of claim 1 or 2, wherein the stream of accelerant gas (104) has a critical velocity ratio of at least one, and optionally between 1.5 and 2.0.
4. The method of any of claims 1 to 3, wherein the stream of accelerant gas (104) is at a temperature of less than about 400°C, and optionally less than about 200°C.
5. The method of any preceding claim, wherein gas mixture (114) leaving an area of impact of the stream of accelerant gas (104) with the substrate (100) has a hydrogen content of less than 5% vol.
6. The method of any preceding claim, wherein the shield gas (106) is selected from the group consisting of inert gases and gas which is substantially inert with the substrate (100) and metal powder at temperature of the stream of accelerant gas (104), and mixtures thereof.
7. The method of any preceding claim, wherein the shield gas (106) is selected from the group consisting of nitrogen, helium, argon, carbon dioxide and mixtures thereof.
8. The method of any preceding claim, wherein the metal powder material comprises particles of aluminum, copper, nickel, iron, tantalum, niobium, cobalt, or mixtures or alloys thereof, where the particle sizes vary from about 5 μm to 40 μm.
9. The method of any preceding claim, wherein the metal powder material comprises:
particles of aluminum having a particle size of between 20 and 40 μm; or
particles of copper having a particle size of between 10 and 30 μm.
10. The method of any preceding claim, wherein the stream of accelerant gas (104) is passed through a nozzle (110; 214) before the impacting step.
11. The method of any preceding claim, wherein the flow of shield gas (106) is at a higher pressure than the stream of accelerant gas (104).
12. An apparatus for cold spray deposition of a material on a substrate (100), comprising:
a nozzle (110; 214) communicated with accelerant gas (104) and metal powder to be deposited on a substrate (100); and
a sleeve (112; 212) surrounding the nozzle (110; 214) and defining an annular space (108; 216) around the nozzle (110; 214), the annular space (108; 216) being communicated with a shield gas (106).
13. The apparatus of claim 12, wherein the nozzle (110; 214) is defined substantially concentric within the sleeve (112; 212).
14. The apparatus of claim 12 or 13, wherein the nozzle (110; 214) and the sleeve (112; 212) define an outlet for a centered stream of the accelerant gas (104) and a cylinder of shield gas (106) surrounding the centered stream (104).
15. The apparatus of any of claims 12 to 14, further comprising a perforated bulkhead (217) in the annular space (108; 216) to adjust flow characteristics of the shield gas (106).

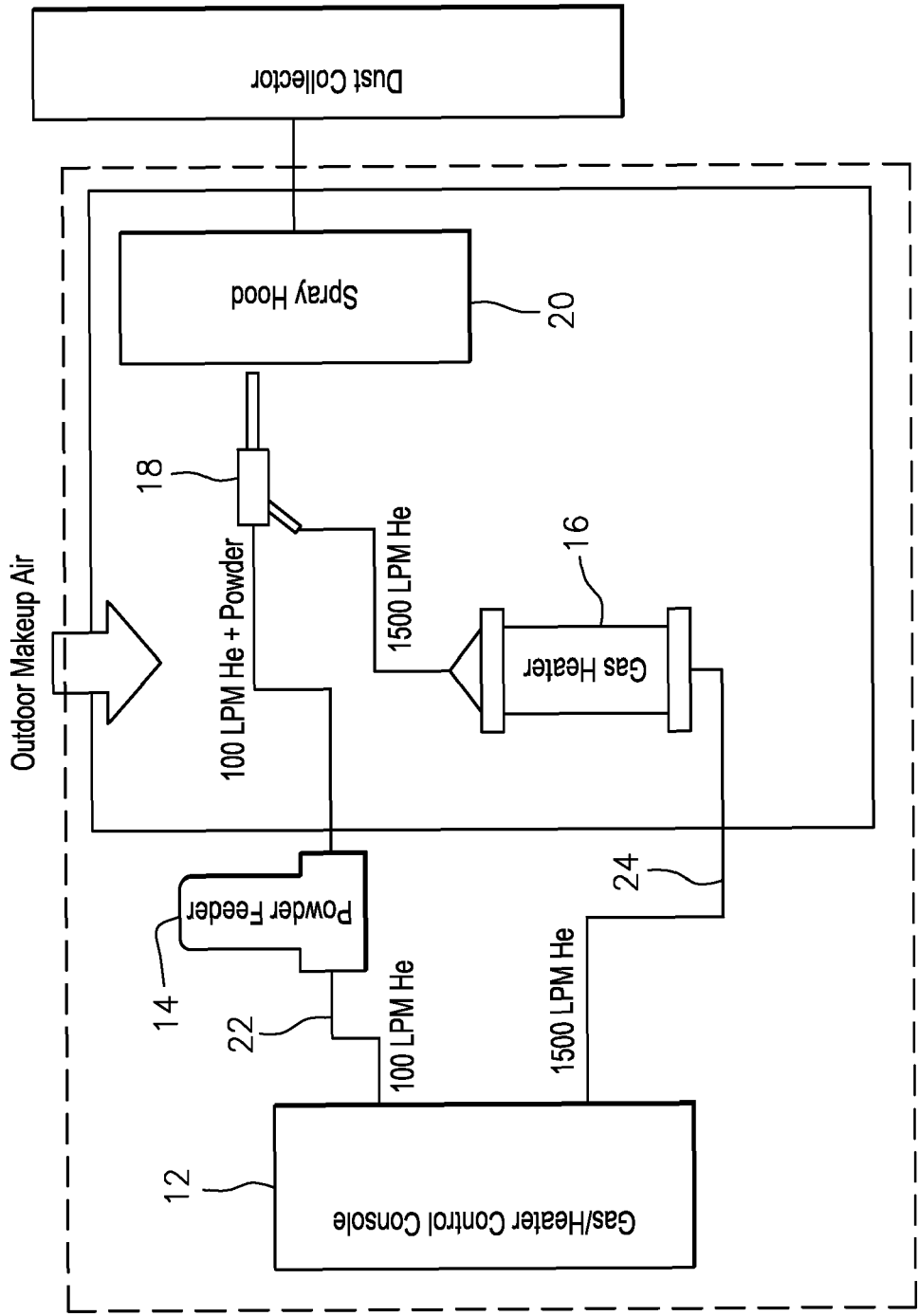


FIG. 1
(PRIOR ART)

10 ↗

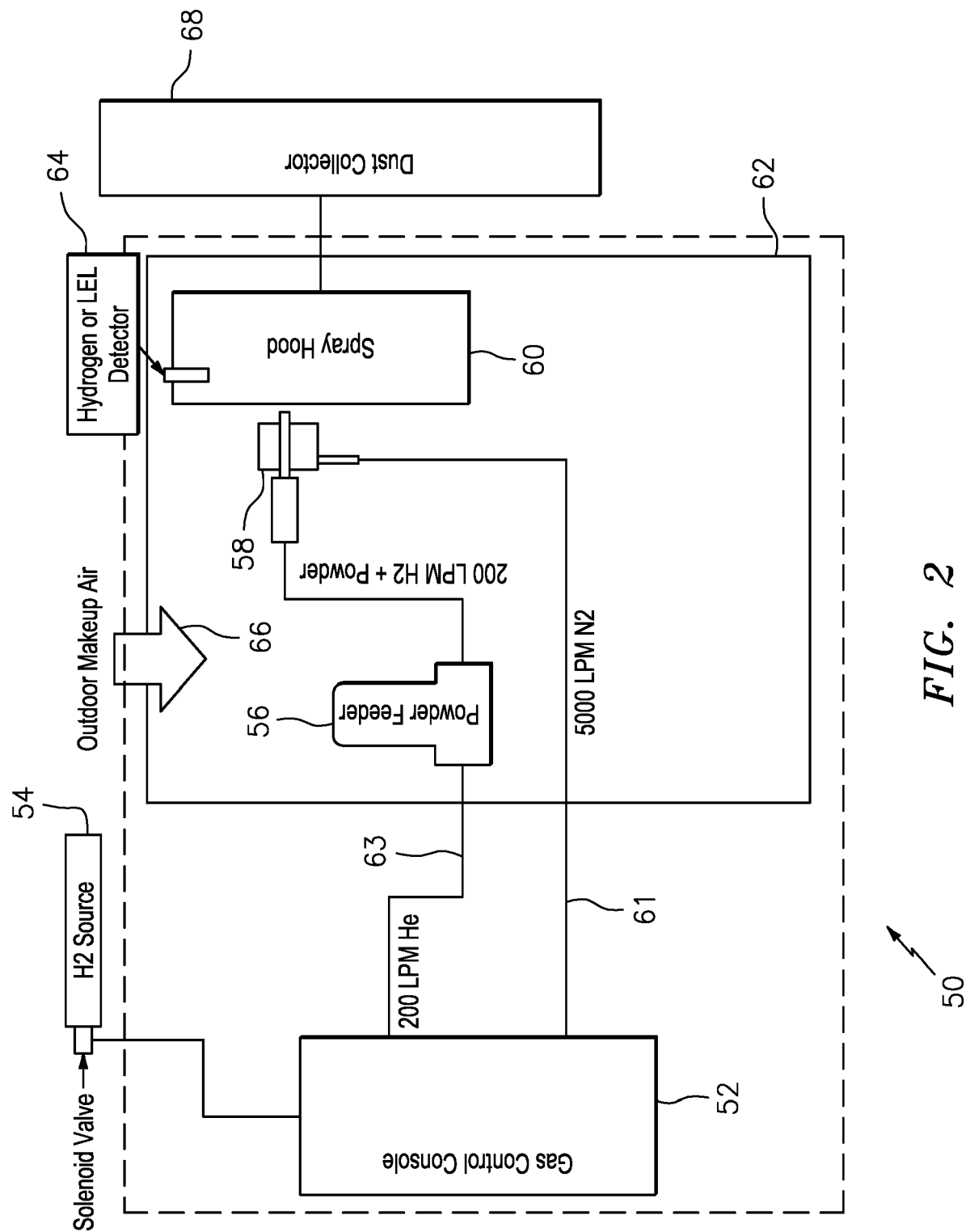


FIG. 2

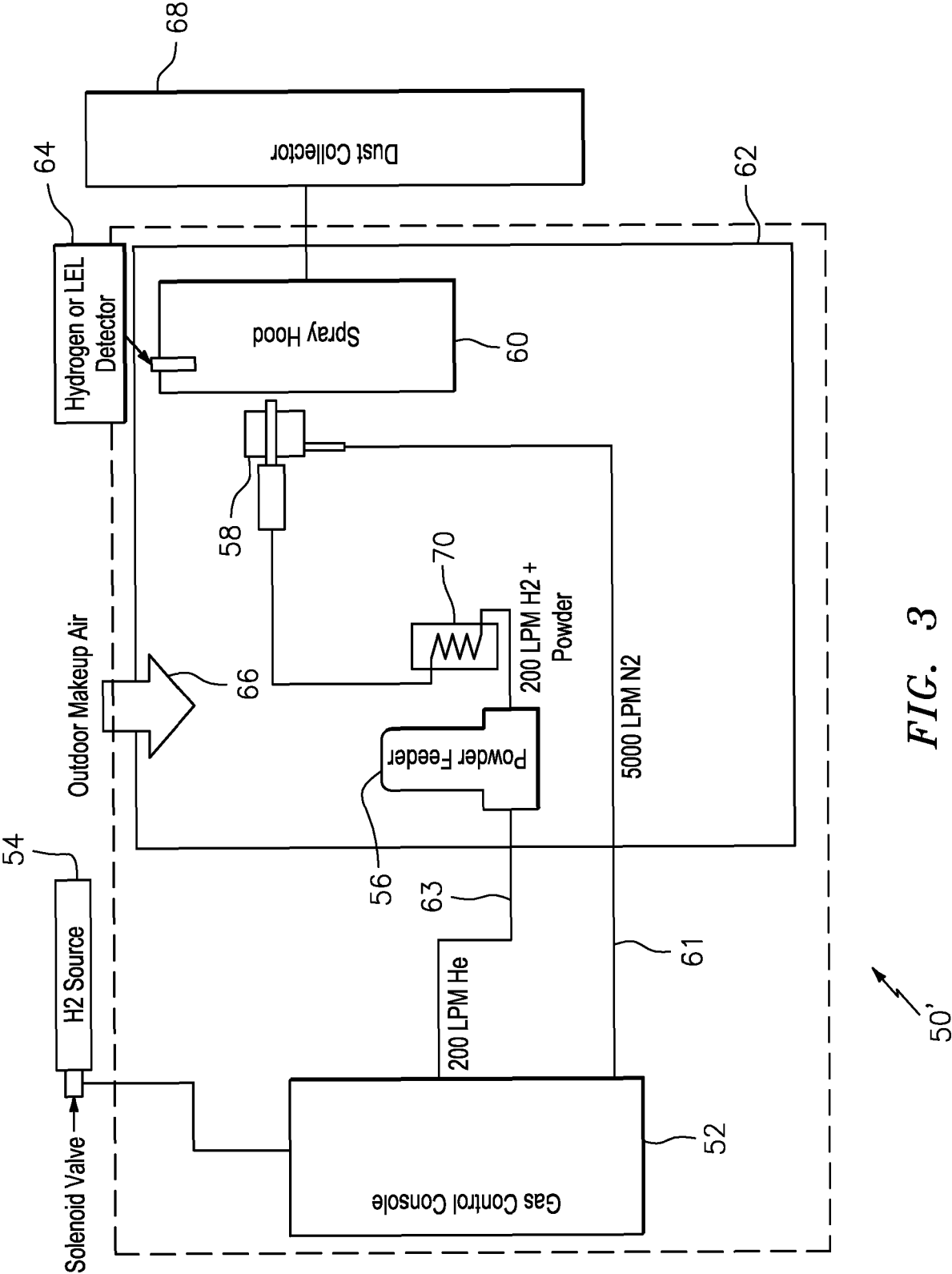


FIG. 3

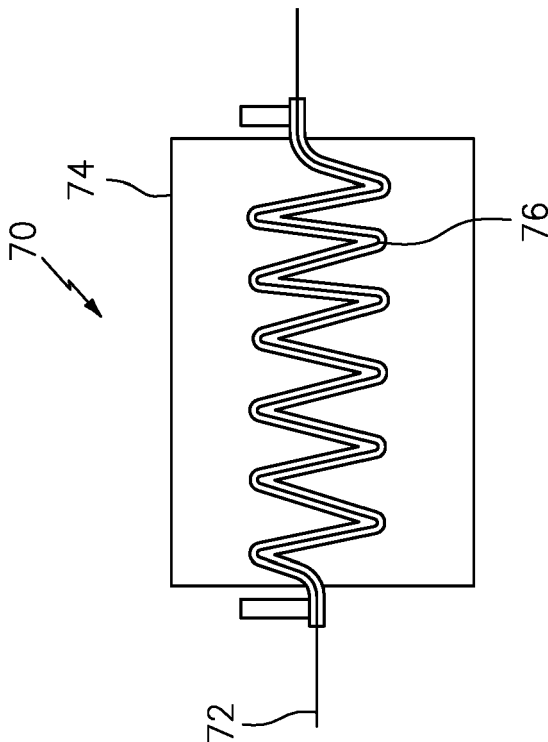


FIG. 4

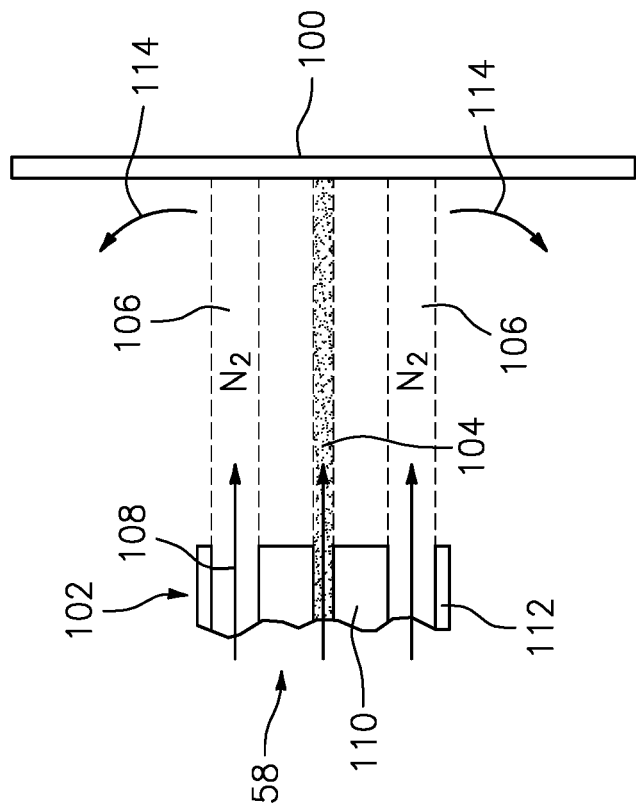
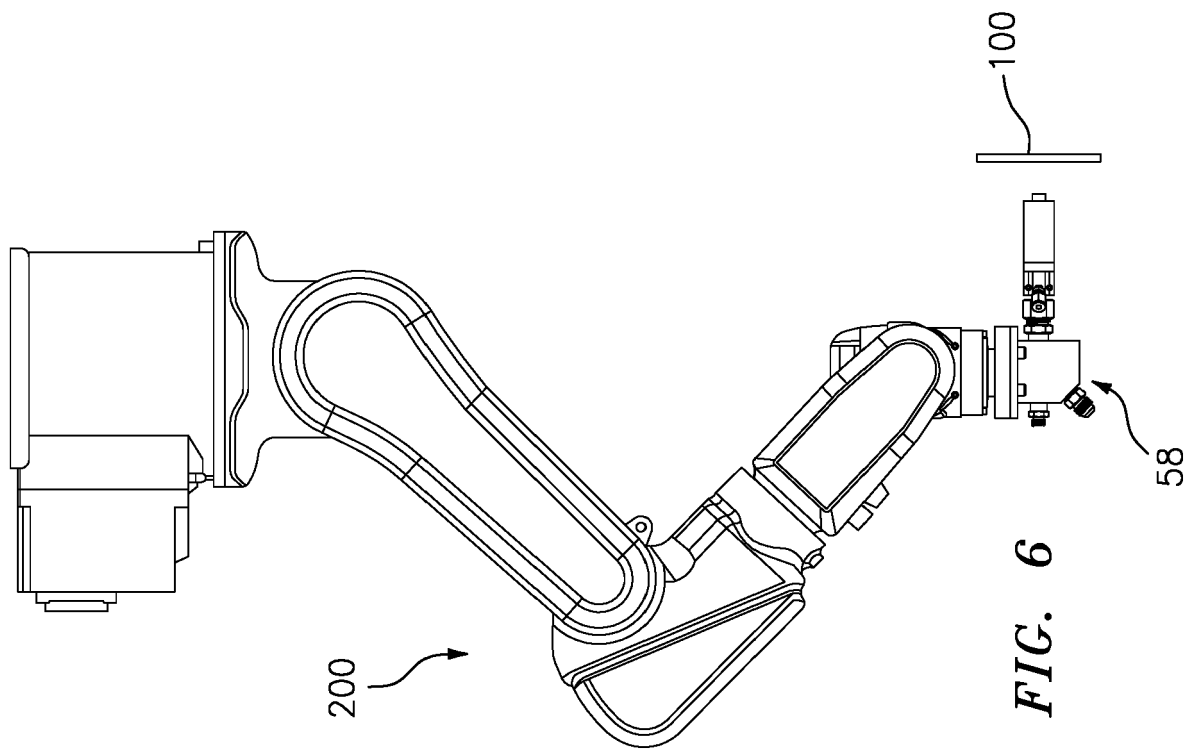
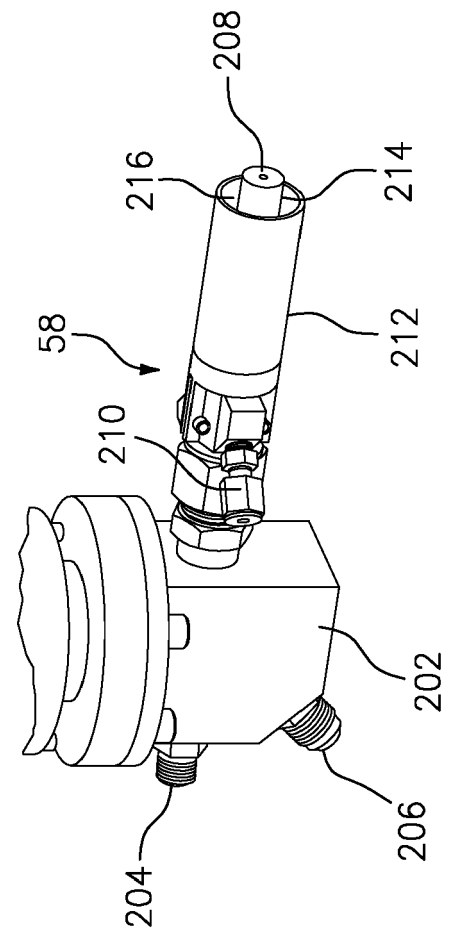
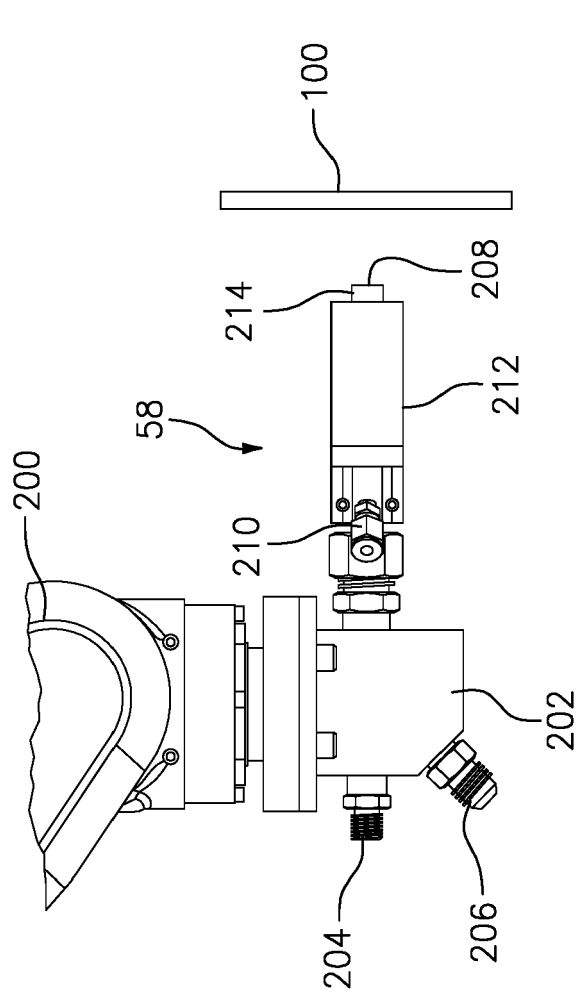


FIG. 5



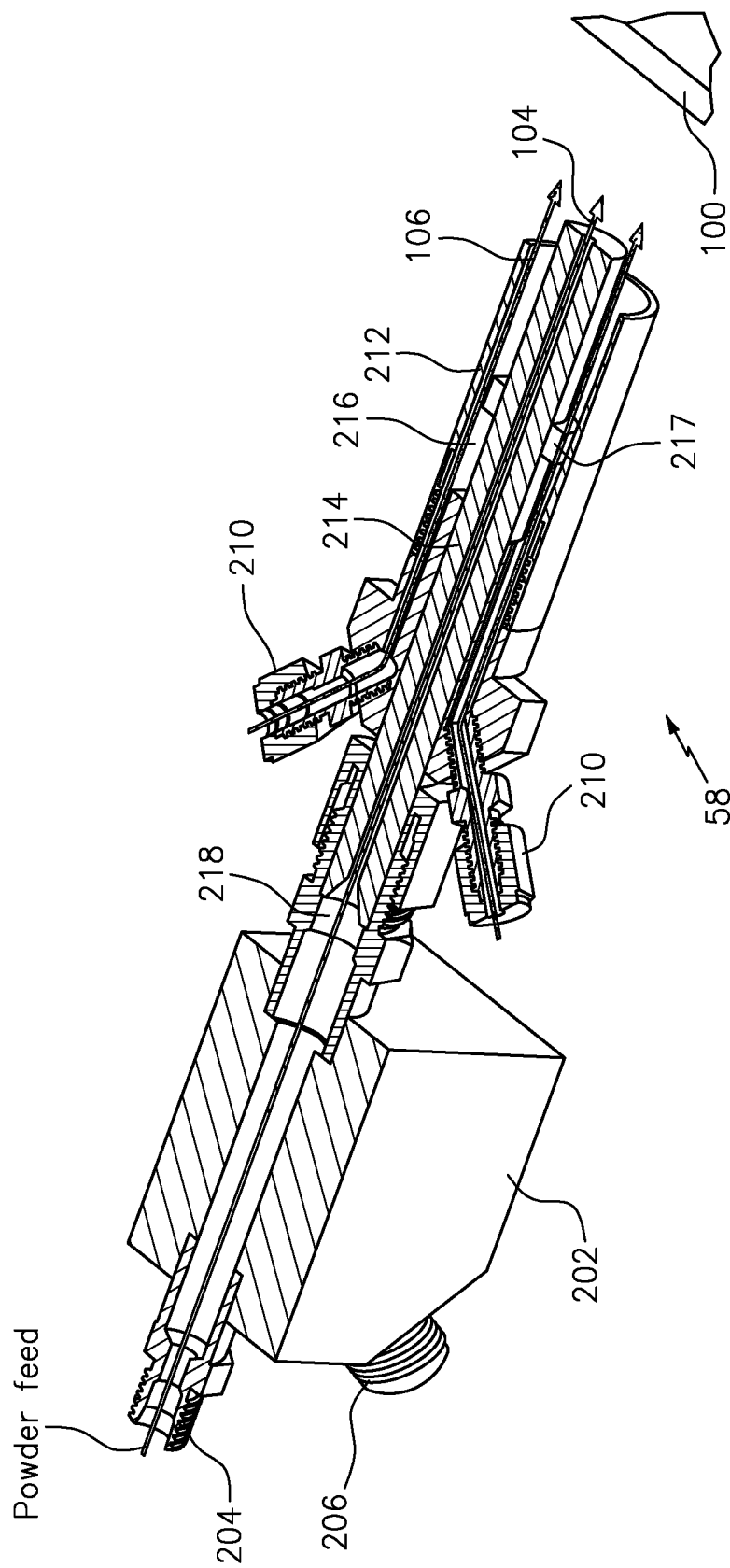


FIG. 9

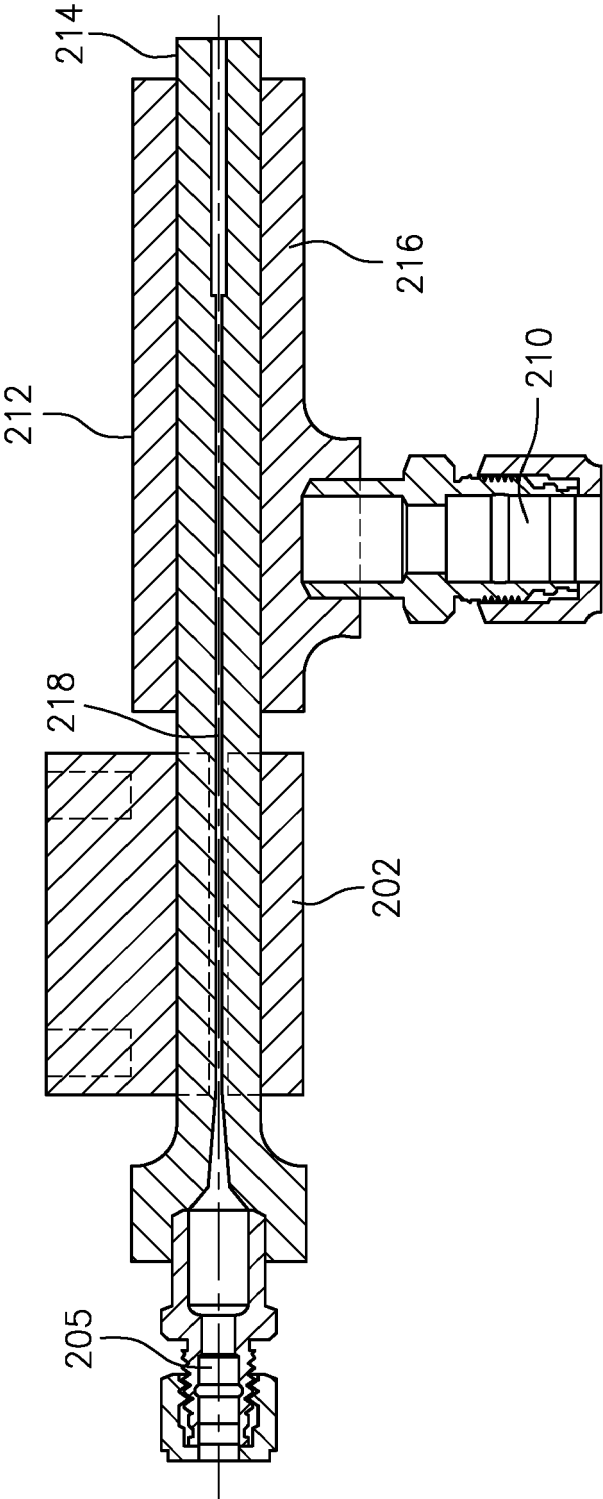


FIG. 10

Application Number
EP 18 18 4451

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 02/085532 A1 (INNOVATIVE TECHNOLOGY INC [US]) 31 October 2002 (2002-10-31) * page 11, lines 24-26 * * page 15, lines 30-32 * * page 26, line 29 - page 27, line 18 * * page 32, line 29 - page 33, line 3 * * claims * * figures 1, 2-3, 7 * -----	1-15	INV. C23C24/04
			TECHNICAL FIELDS SEARCHED (IPC) C23C
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
Munich	21 November 2018	Brisson, Olivier	
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 18 18 4451

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-11-2018

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 02085532 A1	31-10-2002	AT 321612 T	15-04-2006
		CA 2482287 A1	31-10-2002
		DE 60210267 T2	24-08-2006
		EP 1383610 A1	28-01-2004
		KR 20040031700 A	13-04-2004
		MX PA03009813 A	07-03-2005
		US 2002168466 A1	14-11-2002
		US 2005153069 A1	14-07-2005
		WO 02085532 A1	31-10-2002

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82