



- (51) **International Patent Classification:**
B22F 1/02 (2006.01) *B22F 3/105* (2006.01)
- (21) **International Application Number:**
PCT/US2015/010836
- (22) **International Filing Date:**
9 January 2015 (09.01.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/925,466 9 January 2014 (09.01.2014) US
- (71) **Applicant:** UNITED TECHNOLOGIES CORPORATION [US/US]; 1 Financial Plaza, Hartford, Connecticut 06101 (US).
- (72) **Inventors:** SHE, Ying; 46 Shannon Road, East Hartford, Connecticut 06118 (US). NARDI, Aaron T.; 17 Concord Drive, East Granby, Connecticut 06026 (US). DARDAS, Zissis A.; 35 Fourth Street, Worcester, Massachusetts 01602 (US). KLECKA, Michael A.; 75 Hockanum Boulevard, Unit 3827, Vernon, Connecticut 06066 (US). EASTMAN, Scott A.; 41 Brookview Drive, Glastonbury, Connecticut 06033 (US).
- (74) **Agent:** O'SHEA, Patrick; O'Shea Getz P.C., 1500 Main Street, Suite 912, Springfield, Massachusetts 01115 (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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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, 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).

[Continued on next page]

(54) **Title:** MATERIAL AND PROCESSES FOR ADDITIVELY MANUFACTURING ONE OR MORE PARTS

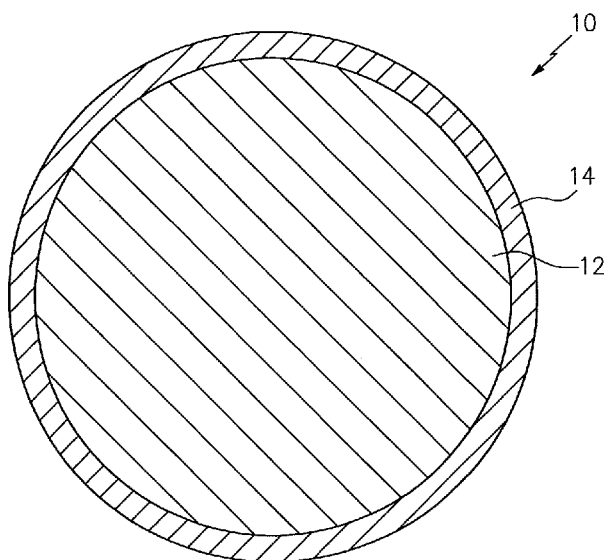


FIG. 1

(57) **Abstract:** Material is provided for forming a part using a manufacturing system. The material includes a plurality of discrete particles. Each of the particles includes a metal powder core encapsulated by a non-metal coating. At least the cores of the particles are adapted to be solidified together by the manufacturing system to form the part.

WO 2015/106113 A1



Published:

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

MATERIAL AND PROCESSES FOR ADDITIVELY MANUFACTURING
ONE OR MORE PARTS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application Serial No. 61/925,466 filed January 9, 2014, which is hereby incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

1. Technical Field

[0001] This disclosure relates to material and processes for additive manufacturing one or more parts.

2. Background Information

[0002] Various additive manufacturing processes are known in the art for forming one or more parts. The term “additive manufacturing” may describe a process where a part or parts are formed by accumulating and/or fusing material together, typically in a layer-on-layer manner. Layers of material, for example, may be cold sprayed sequentially onto one another to form the part(s). In another example, layers of material may be sintered or otherwise melted sequentially onto one another to form the part(s).

[0003] Part(s) are typically additively manufactured from metal powder. This metal powder may be degassed in order to remove entrained gasses and/or moisture therefrom, which if not removed can create various defects within the part(s). However, if the degassed metal powder is exposed to air or atmosphere containing residual moisture during storage and/or loading into an additive manufacturing system, the degassed metal powder may re-adsorb moisture. The metal powder therefore may require additional degassing, which can increase manufacturing time and cost.

[0004] There is a need in the art for improved additive manufacturing materials and processes.

SUMMARY OF THE DISCLOSURE

[0005] According to an aspect of the invention, material is provided for forming a part using a manufacturing system. This material includes a plurality of discrete particles. Each of

the particles includes a metal powder core encapsulated by a non-metal coating. At least the cores of the particles are adapted to be solidified together by the manufacturing system to form the part.

[0006] According to another aspect of the invention, another material is provided for forming a part using an additive manufacturing system. This material includes a plurality of discrete particles. Each of the particles includes a coating on a degassed metal powder core. The coating is adapted to prevent the core from adsorbing moisture. The coating is also adapted to decompose and/or volatilize to expose the core. The cores of the particles are adapted to be solidified together by the additive manufacturing system to form the part.

[0007] According to another aspect of the invention, a process is provided for forming a part using an additive manufacturing system. A plurality of discrete particles are provided. Each of these particles includes a metal powder core encapsulated by a non-metal coating. At least some of the cores are solidified together using the additive manufacturing system to form at least a portion of the part.

[0008] The manufacturing system may be an additive manufacturing system.

[0009] The metal powder core of at least one of the particles may be a degassed metal powder core.

[0010] The coating of at least one of the particles may be adapted to prevent the core from adsorbing moisture.

[0011] The coating of at least one of the particles may be adapted to decompose and/or volatilize to expose the core.

[0012] The coating of at least one of the particles may be configured from or otherwise include polymer. The coating of at least one of the particles may also or alternatively be configured from or otherwise include ceramic.

[0013] The coating of at least one of the particles may be configured from or otherwise include at least one of the following materials: alkoxysilane, aminosilane, organic phosphoric acid, nitride, fluoride, epoxy, thiol, disulphide, thiolate, triazol, alkylphosphonic acids, fluoropolymers, silicones, polypyrrol, polyaniline, and other polymeric assembled monolayers.

[0014] The core of at least one of the particles may include a single metal particle. In addition or alternatively, the core of at least one of the particles may include a plurality of metal particles.

[0015] The core of at least one of the particles may be configured from or otherwise include at least one of the following materials: aluminum, copper, titanium, nickel and steel.

[0016] The coating of at least some of the particles may be removed to expose the cores of the respective particles. The coating may be removed through decomposition and/or volatilization.

[0017] The additive manufacturing system may include a cold spray device.

[0018] The additive manufacturing system may include a laser and/or an electron beam energy source.

[0019] The foregoing features and the operation of the invention will become more apparent in light of the following description and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 is cross-sectional illustration of an additive manufacturing particle;

[0021] FIG. 2 is a block diagram of a system for additively manufacturing one or more parts; and

[0022] FIG. 3 is a flow diagram of a process for forming one or more parts using the additive manufacturing system of FIG. 2 and material including the additive manufacturing particle of FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

[0023] Material is described below for additively manufacturing one or more parts. This additive manufacturing material includes a plurality of discrete particles that collectively form powder. An exemplary of one of these additive manufacturing particles 10 is illustrated in FIG. 1 and described below. It is worth noting, however, that one or more of the additive manufacturing particles included in the additive manufacturing material may alternatively have different configurations and/or compositions than that described below and illustrated in FIG. 1.

[0024] The additive manufacturing particle 10 of FIG. 1 includes a metal powder core 12 covered and/or encapsulated by a coating 14. The core 12 may include one or more metal particles. Each of these metal particles may be composed from one or more of the following core materials: aluminum (Al), copper (Cu), titanium (Ti), nickel (Ni), steel, and/or alloys

thereof. One or more of the metal particles, of course, may also or alternatively be composed from one or more core materials other than those described above.

[0025] The core 12 may be a degassed metal powder core. For example, before being encapsulated within the coating 14, the core 12 may be degassed to remove entrained gas, adsorbates and/or moisture therefrom. Various degassing processes are known in the art and therefore are not described in further detail.

[0026] The core 12 may have a size (e.g., an average diameter) of between about five micrometers (5 μ m) and about five-hundred micrometers (500 μ m); e.g., between about twenty micrometers (20 μ m) and about sixty micrometers (60 μ m). The present invention, however, is not limited to the foregoing exemplary core sizes.

[0027] The coating 14 is adapted to substantially reduce or prevent the core 12 from adsorbing moisture. The coating 14 therefore may enable the additive manufacturing particle 10 to be stored outside of a controlled additive manufacturing environment (e.g., a vacuum or noble gas environment) without compromising the core material for subsequent additive manufacturing. In contrast, a metal particle without such a coating may adsorb moisture during the storage and/or transportation thereof. This moisture may subsequently cause surface defects and/or porosity defects in a part formed from the now non-degassed metal particle.

[0028] Referring again to FIG. 1, the coating 14 may also be adapted to partially or substantially completely decompose and/or volatilize in order to partially or substantially completely expose the core 12 for subsequent additive manufacturing. In this manner, the coating 14 may be removed from the core 12 prior to formation of the part(s), which reduces the likelihood of or substantially prevents the coating material from altering the mechanical properties and/or the intended chemical composition of the part(s).

[0029] The coating 14 may be a non-metal coating such as, for example, a polymer coating, a ceramic coating, a polymer-ceramic coating, or any other type of coating that does not include a metal component and is adapted as described above. The coating 14, for example, may be composed from one or more of the coating materials listed below in Table I. The coating 14, however, may also or alternatively be composed of one or more coating materials other than those described above and listed in Table I.

Table I		
Core	Coating	
Representative Metal Core Material	Chemical Class(es)	Representative Non-Metal Coating Material(s)
Aluminum	Alkoxysilane	Triethoxy silane
	Aminosilane	Aminopropyldimethylethoxysilane
	Organic phosphonic acid	Pentane phosphonic acid
	Nitride	Nitrogen (e.g., N ₂)
	Fluoride	Fluorocarbon
	Epoxy	
	Organic vapor coating	Paralene, cyanoacrylate
Copper	Thiol, disulphide, thiolate	Organic thiol
	Triazol	Benzenetriazole (BTA)
	Organic vapor coating	Paralene, cyanoacrylate
	Inorganic vapor coating	Silane
Titanium	Inorganic vapor coating	Titanium nitride
	Chemisorption	Fluorinated polymers
Nickel	Chemisorption	Alkylphosphonic acids
Steel	Electropolymerization	Polypyrrol/polyaniline

[0030] The coating material may be deposited on the core 12 to form the coating 14 through one or more of the following processes: chemical adsorption, physical adsorption and/or covalent bonding. Various chemical adsorption, physical adsorption and covalent bonding processes are known in the art and therefore are not described in further detail. The coating material, of course, may also or alternatively be deposited on the core 12 using one or more processes other than those described above.

[0031] FIG. 2 illustrates a system 16 for additively manufacturing a part 18 (or parts) from the additive manufacturing material (e.g., powder) describe above. This additive manufacturing system 16 includes a support 20, an additive manufacturing device 22 and a controller 24. The additive manufacturing system 16 also includes a housing 26, such as a sealed enclosure or pressure vessel, in which the support 20 and at least a portion of the additive manufacturing device 22 are located.

[0032] The support 20 includes a support surface 28. This support surface 28 is configured to support the additive manufacturing material and/or at least a portion of the part 18 (or parts) during the formation of the part 18 (or parts). The support surface 28, for example, may be substantially horizontal relative to gravity. The support surface 28 may also have a generally planar geometry.

[0033] The additive manufacturing device 22 may be configured as a cold spray device, a laser sintering device, or an electron beam melting device. Various cold spray devices, laser sintering devices and electron beam melting devices are known in the art and therefore are not described in further detail. In addition, various other types and configurations of additive manufacturing devices are known in the art and the present invention is not limited to any particular ones thereof.

[0034] The controller 24 is in signal communication (e.g., hardwired and/or wirelessly coupled) with the additive manufacturing device 22. The controller 24 is adapted to signal the additive manufacturing device 22 to perform at least a portion of the process described below. The controller 24 is implemented with a combination of hardware and software. The hardware includes memory and a processing device (or system), which includes one or more single-core and/or multi-core processors. The memory may be a non-transitory computer readable medium, and configured to store software (e.g., program instructions) for execution by the processing device. The hardware may also or alternatively include analog and/or digital circuitry other than that described above.

[0035] FIG. 3 is a flow diagram of a process for forming a part 18 (or parts) using the additive manufacturing material and the additive manufacturing system 16. An example of a part that may be formed with the additive manufacturing system 16 is a rotor blade for a turbine engine; e.g., a turbine blade, a compressor blade or a fan blade. Other examples of a part that may be formed with the additive manufacturing system 16 include a stator blade for a turbine engine, a guide vane for a turbine engine, a gas path wall for a turbine engine as well as various other components included in a turbine engine. The process of FIG. 3 and the additive manufacturing system 16, of course, may also or alternatively form parts other than those included in a turbine engine.

[0036] Prior to the formation of the part 18 (or parts), the additive manufacturing material may be stored in an ambient environment outside of the additively manufacturing

system 16. Alternatively, the additive manufacturing material may be stored in a controlled environment (e.g., a vacuum or noble gas environment) and/or in a reservoir 30 (e.g., a hopper) of the additive manufacturing system 16.

[0037] In step 300, the additive manufacturing material is loaded into the additive manufacturing system 16. The additive manufacturing material, for example, may be poured out or otherwise directed from its storage container into the reservoir 30, which may selectively feed the material to the additive manufacturing device 22.

[0038] In step 302, the coating 14 is removed from at least some of the additive manufacturing particles (e.g., particle 10) to expose the core material; e.g., the degassed metal powder cores. For example, a conduit and/or a chamber 32 configured with the additive manufacturing device 22 may be heated with a heater to or above an elevated (e.g., above ambient) temperature at which the coating material decomposes and/or volatilizes. This conduit and/or chamber 32 may be connected upstream of a material applicator 34 (e.g., a powder bed nozzle or a cold spray nozzle) of the additive manufacturing device 22. The material applicator 34 therefore may receive the exposed core material (e.g., the degassed metal powder cores) from the conduit and/or chamber 32.

[0039] In step 304, at least some of the exposed core material is formed into at least a portion of the part 18 (or parts). The material applicator 34, for example, may cold spray the exposed core material onto the support surface 28 to build up a base layer. The material applicator 34 may subsequently cold spray one or more additional layers of the exposed core material onto the base layer to accumulatively form the part 18 (or parts). As each layer of material is cold sprayed, it may fuse to a previously sprayed layer thereby solidifying at least some of the metal powder cores 12 together to form the part 18 (or parts).

[0040] In another example, the material applicator 34 may deposit a uniform and compacted layer of the exposed core material onto the support surface 28. A laser or electron beam energy source 36 may subsequently solidify (e.g., sinter or otherwise melt) some or all of the metal powder cores 12 in the layer together to form a base layer of the part 18 (or parts). The material applicator 34 may subsequently deposit one or more additional uniform and compacted layers of the exposed core material onto the base layer, and the laser or electron beam energy source 36 may respectively solidify some or all of the metal powder cores 12 in the additional

layer(s) to form additional layers of the part 18 (or parts). Of course, the process of FIG. 3 is not limited to the foregoing exemplary material buildup techniques or devices.

[0041] One or more of the process steps of FIG. 3 may be omitted, re-arranged and/or combined. For example, in some embodiments, the additive manufacturing material may be stored with the additive manufacturing system 16. In some embodiments, the coating 14 may be removed within the material applicator 34 and/or as the additive manufacturing particles (e.g., particle 10) are directed from the material applicator 34 towards the support surface 28. In some embodiments, the coating material may not be removed from the particles (e.g., particle 10) where, for example, the coating material does not substantially affect the chemical composition and/or mechanical properties of the part 18 (or parts) formed therefrom.

[0042] The process of FIG. 3 may include one or more additional steps other than those described above. For example, in some embodiments, the part 18 (or parts) may undergo additional manufacturing processes during and/or after the material buildup step 304. Examples of such additional manufacturing processes may include, but are not limited to, machining, surface finishing, coating, etc. In some embodiments, the part 18 (or parts) may also or alternatively undergo additional manufacturing processes before the material buildup step 304 where, for example, the additive manufacturing material is built up upon an existing part or portion of a part (or parts); e.g., to repair a part, etc.

[0043] While the material disclosed herein is described above with reference to additive manufacturing, this material may also or alternatively be used for other manufacturing processes. The material, for example, may be solidified together by a manufacturing system during casting, hot pressing, extruding, etc. The present invention therefore is not limited to any particular manufacturing processes or systems.

[0044] While various embodiments of the present invention have been disclosed, it will be apparent to those of ordinary skill in the art that many more embodiments and implementations are possible within the scope of the invention. For example, the present invention as described herein includes several aspects and embodiments that include particular features. Although these features may be described individually, it is within the scope of the present invention that some or all of these features may be combined within any one of the aspects and remain within the scope of the invention. Accordingly, the present invention is not to be restricted except in light of the attached claims and their equivalents.

What is claimed is:

1. Material for forming a part using a manufacturing system, the material comprising:
a plurality of discrete particles, each of the particles including a metal powder core encapsulated by a non-metal coating;
wherein at least the cores of the particles are adapted to be solidified together by the manufacturing system to form the part.
2. The material of claim 1, wherein the metal powder core of one of the particles comprises a degassed metal powder core.
3. The material of claim 1, wherein the coating of one of the particles is adapted to prevent the core from adsorbing moisture.
4. The material of claim 1, wherein the coating of one of the particles is adapted to decompose to expose the core.
5. The material of claim 1, wherein the coating of one of the particles is adapted to volatilize to expose the core.
6. The material of claim 1, wherein the coating of one of the particles comprises polymer.
7. The material of claim 1, wherein the coating of one of the particles comprises ceramic.
8. The material of claim 1, wherein the coating of one of the particles comprises at least one of the following materials: alkoxysilane, aminosilane, organic phosphoric acid, nitride, fluoride, epoxy, thiol, disulphide, thiolate, triazol, alkylphosphonic acids, fluoropolymers, silicones, polypyrrol, polyaniline, and polymeric assembled monolayers.
9. The material of claim 1, wherein the core of one of the particles includes one or more metal particles.

10. The material of claim 1, wherein the core of one of the particles comprises at least one of the following materials: aluminum, copper, titanium, nickel and steel.
11. Material for forming a part using an additive manufacturing system, the material comprising:
 - a plurality of discrete particles, each of the particles including a coating on a degassed metal powder core;
 - the coating adapted to prevent the core from adsorbing moisture, and further adapted to decompose and/or volatilize to expose the core;
 - wherein the cores of the particles are adapted to be solidified together by the additive manufacturing system to form the part.
12. A process for forming a part using an additive manufacturing system, the process comprising:
 - providing a plurality of discrete particles, each of the particles including a metal powder core encapsulated by a non-metal coating; and
 - solidifying at least some of the cores together using the additive manufacturing system to form at least a portion of the part.
13. The process of claim 12, wherein the metal powder core of one of the particles comprises a degassed metal powder core.
14. The process of claim 12, wherein the coating of one of the particles is adapted to prevent the core from adsorbing moisture.
15. The process of claim 12, further comprising removing the coatings from at least some of the particles to expose the cores of the respective particles.
16. The process of claim 12, wherein the coating of one of the particles comprises at least one of the following materials: polymer and ceramic.

17. The process of claim 12, wherein the core of one of the particles includes one or more metal particles.
18. The process of claim 12, wherein the core of one of the particles comprises at least one of the following materials: aluminum, copper, titanium, nickel and steel.
19. The process of claim 12, wherein the additive manufacturing system comprises a cold spray device.
20. The process of claim 12, wherein the additive manufacturing system comprises one of a laser and an electron beam energy source.

1/3

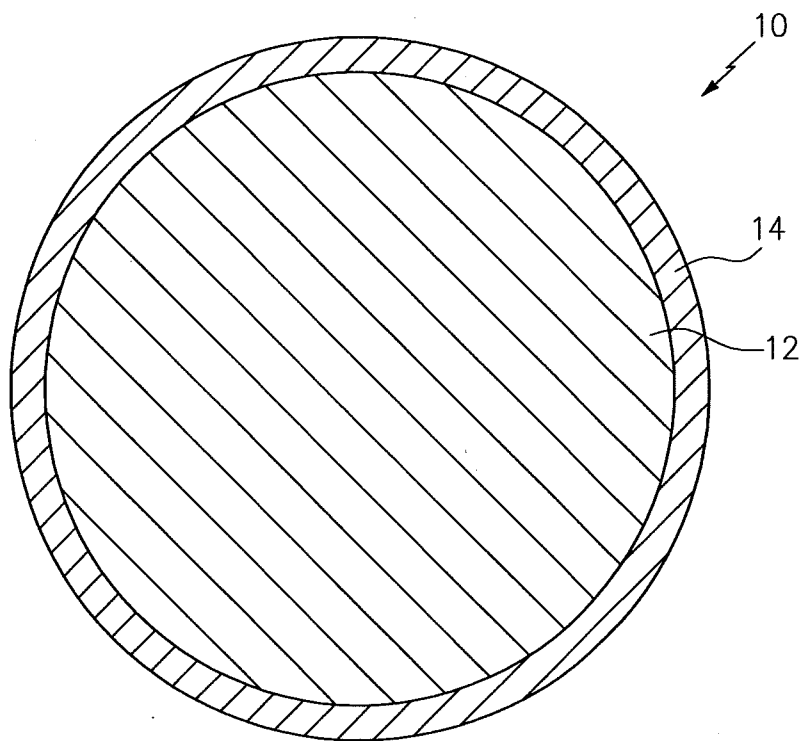


FIG. 1

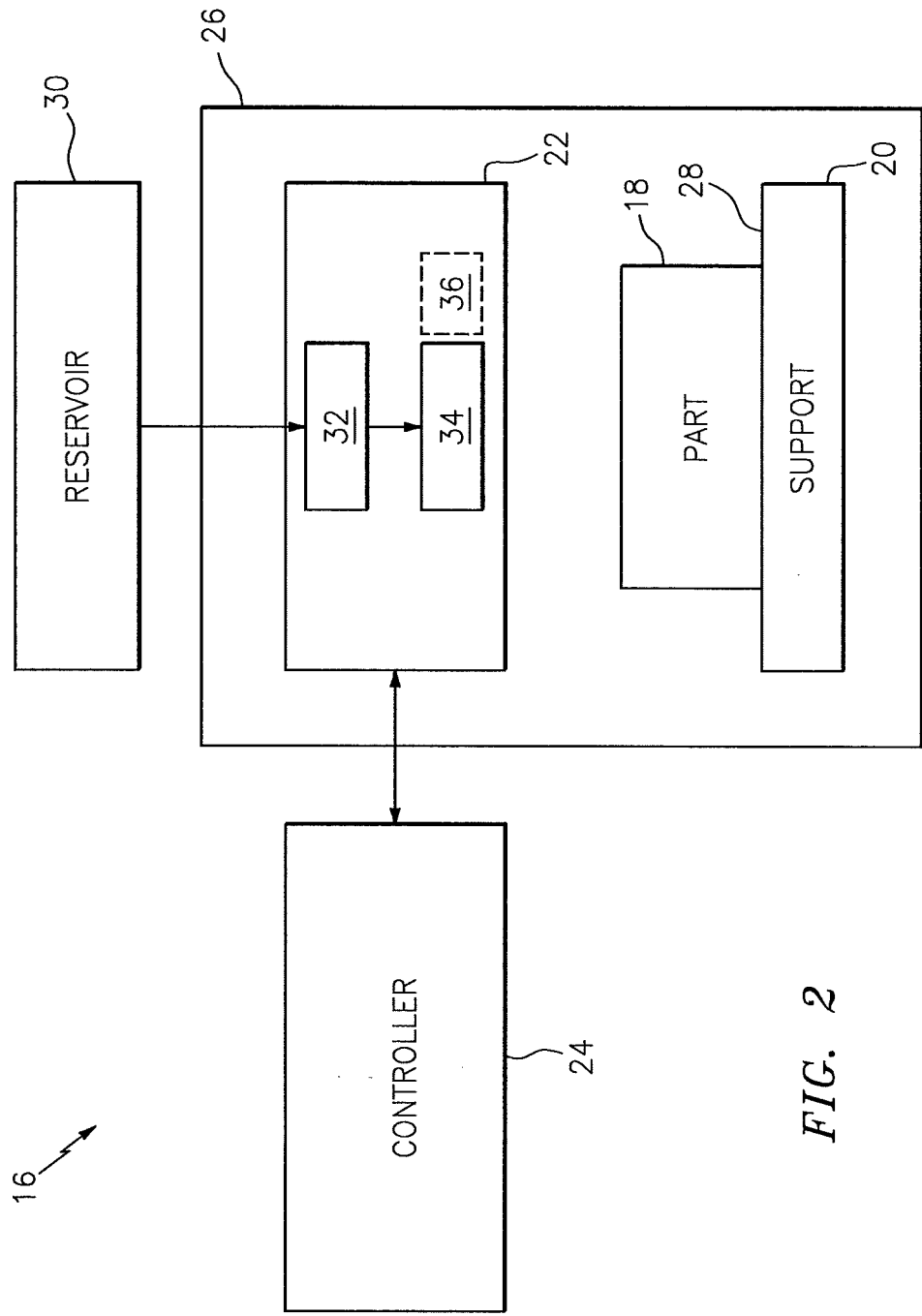
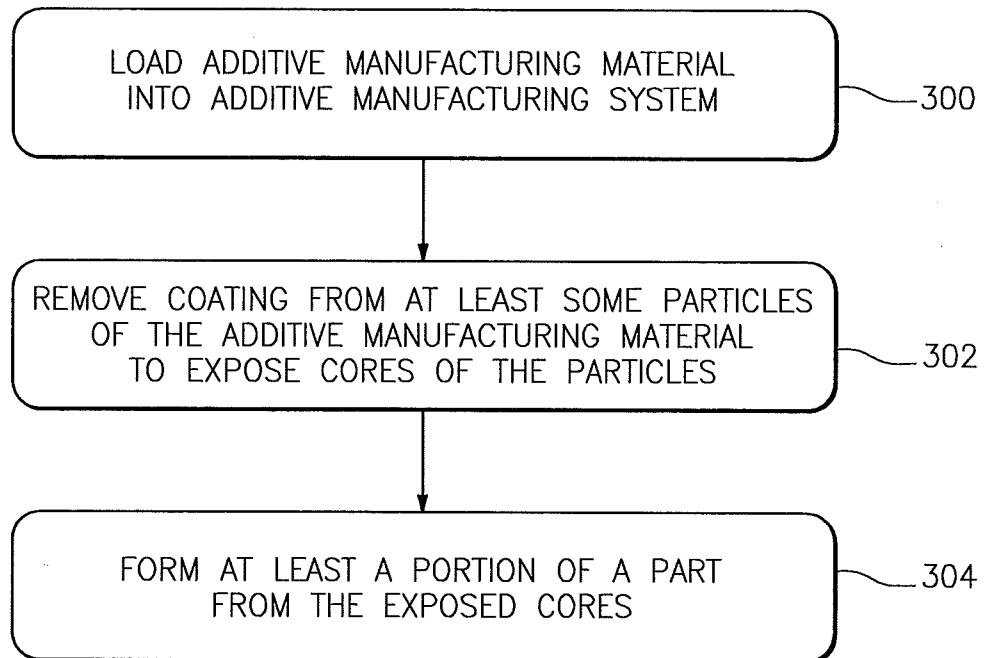


FIG. 2

3/3

*FIG. 3*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/010836**A. CLASSIFICATION OF SUBJECT MATTER****B22F 1/02(2006.01)i, B22F 3/105(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B22F 1/02; B22F 7/02; C08K 3/08; B23K 26/08; B27N 3/00; B22F 3/00; H01F 1/06; C23C 16/00; B22F 3/105

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & keywords: moisture, adsorb, defect, powder, degas, additive manufacture, core, coating, non-metal, and decompose

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 02-046703 A (SHIN ETSU CHEM CO., LTD.) 16 February 1990	1,3-5,7-9
Y	See claims 1 and 2.	2,6,10-20
Y	US 2002-0015654 A1 (DAS et al.) 07 February 2002 See paragraphs [0008]-[0032] and claims 1, 9.	2,11-20
Y	KR 10-0889256 B1 (LION CHEMTECH CO., LTD.) 19 March 2009 See abstract, paragraphs [0002]-[0012], and claims 1-4.	6,10,18
A	CN 102581274 A (INST. OF CHEMICAL MATERIAL, CHINA ACADEMY OF ENGINEERING PHY SICS) 18 July 2012 See abstract and paragraph [0006].	1-20
A	US 5639402 A (BARLOW et al.) 17 June 1997 See column 1, lines 20-33, column 13, line 18 - column 14, line 20.	1-20



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

27 April 2015 (27.04.2015)

Date of mailing of the international search report

28 April 2015 (28.04.2015)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. ++82 42 472 7140

Authorized officer

PARK, Tae Wook

Telephone No. +82-42-481-3405



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/010836

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 02-046703 A	16/02/1990	None	
US 2002-0015654 A1	07/02/2002	AU 7516401 A EP 1296776 A1 EP 1296776 A4 US 6676892 B2 WO 01-91924 A1	11/12/2001 02/04/2003 08/12/2004 13/01/2004 06/12/2001
KR 10-0889256 B1	19/03/2009	None	
CN102581274 A	18/07/2012	CN 102581274 B	11/06/2014
US 5639402 A	17/06/1997	AU 1995-33614 B2 EP 0775046 A1 JP 10-508324 A US 2001-0005797 A1 US 2003-0069638 A1 US 6183515 B2 US 6540784 B2 WO 96-05038 A1	18/02/1999 24/09/2003 18/08/1998 28/06/2001 10/04/2003 06/02/2001 01/04/2003 22/02/1996