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(71) Applicant: **COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION** [AU/AU]; Limestone Avenue, Campbell, Australian Capital Territory 2612 (AU).

(72) Inventors: **OH, Chull, Hee**; c/- CSIRO, Private Bag 10, Clayton South, Victoria 3169 (AU). **GULIZIA, Stefan**; c/- CSIRO, Private Bag 10, Clayton South, Victoria 3169 (AU).

(74) Agent: **PHILLIPS ORMONDE FITZPATRICK**; Level 16, 333 Collins Street, Melbourne, Victoria 3000 (AU).

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(54) **Title**: METHOD OF PRODUCING A POWDER PRODUCT

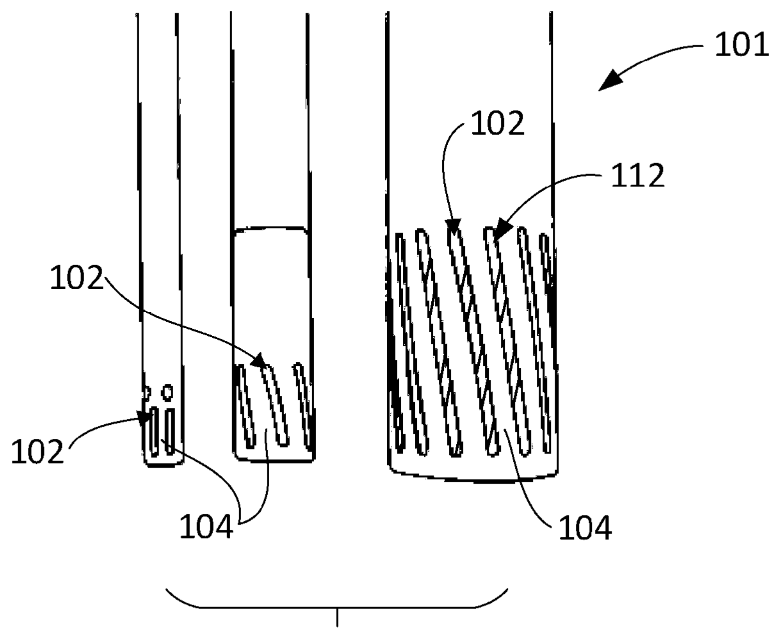

Figure 1B

(57) Abstract: A method of producing a powder suitable for additive manufacturing and/or powder metallurgy applications from a precursor particulate material comprising: subjecting the precursor particulate material to at least one high shear milling process, thereby producing a powder product having a reduced average particle size and a selected particle morphology.

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METHOD OF PRODUCING A POWDER PRODUCT

TECHNICAL FIELD

[001] The present invention generally relates to a method of producing a powder product from a precursor material. The invention is particularly applicable for producing a powder product suitable for additive manufacturing processes such as electron (laser) beam melting or cold spray deposition, or for powder metallurgy applications, and it will be convenient to hereinafter disclose the invention in relation to those exemplary applications. However, it is to be appreciated that the invention is not limited to that application and the powder product could be used in any number of applications and products in which a desired powder morphology and size is required.

BACKGROUND OF THE INVENTION

[002] The following discussion of the background to the invention is intended to facilitate an understanding of the invention. However, it should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was published, known or part of the common general knowledge as at the priority date of the application.

[003] Metal powders having a specific particle size and morphology are required for direct (additive) manufacturing processes such as cold spray, electron (laser) beam melting or continuous direct powder rolling processes. For example, titanium / titanium alloy powder used in electron (laser) beam melting preferably has a particle size of less than 250 μm with a narrow particle size distribution range. The particles are also required to have a regular morphology, such as spherically or cylindrically shaped powder particles, in order to provide high flowability.

[004] Existing commercial titanium / titanium alloy powder production processes include hydride-de-hydride (HDH), gas atomization (GA), plasma-rotating electrode and plasma atomization (PREP) processes. Each of these processes requires the production of a solid Ti or Ti alloy feedstock product,

such as a wire, bar, rod or billet, which is subsequently processed using brittle fracture, atomization, arcing or the like to produce the powder.

[005] In the hydride-de-hydride process, solid Ti or Ti alloy feedstock are processed to remove contaminants, hydrogenated to produce brittle material and then ground under argon in a vibratory ball mill. The resulting particles are angular and measure between 50 and 300 µm. This process is time consuming, can introduce contamination, and produces particles having a sharp angular shaped morphology which are not favourable for additive manufacturing processes. In contrast, fine powders produced by plasma-rotating electrode and plasma atomization or gas atomisation methods are spherically shaped, but are extremely expensive to produce compared to hydride-de-hydride processed metal or metal alloy powders due to the high temperatures used to atomize the metal in these processes. Significant metal loss can also result from such process conditions.

[006] It would therefore be desirable to provide an alternate method of producing a powder, preferably a powder having a desired morphology and size, suitable for additive manufacturing applications.

SUMMARY OF THE INVENTION

[007] The present invention provides in a first aspect a method of producing a powder from a precursor particulate material comprising:

subjecting the precursor particulate material to at least one high shear milling process,

thereby producing a powder product having a reduced average particle size and a selected particle morphology, preferably suitable for additive manufacturing and/or powder metallurgy applications.

[008] The present invention provides a novel powder manipulation method for producing a powder from a precursor particulate material. The precursor particulate material is subjected to a high shear milling process to produce a powder having selected properties. The method produces a powder, preferably a metal powder, with a desirable powder morphology, particle size and particle

size distribution (PSD) without the need for plasma-rotating electrode and plasma atomization, gas atomisation or hydride-de-hydride routes. The powder product is preferably processed to a suitable morphology and particle size for use as raw materials for the additive manufacturing (AM) processes, such as (but not limited to) Arcam & cold spray, or for other consolidation processes such as powder metallurgy (PM).

[009] The method of the present invention has been developed primarily for titanium / titanium alloys powders. However, it should be appreciated that the method of the present invention can be used for shaping and sizing other metal powders for additive manufacturing and powder metallurgy applications. Examples of other suitable particulates and powders include ductile (e.g. aluminium, magnesium, copper, zinc etc.) or porous metal /metal alloy particulates.

[010] The powder product is processed by the method of the present invention to preferably produce a powder product that has at least one of: high flowability; high apparent/tap density; and low contamination, and preferably each of these properties.

[011] With respect to flowability, it is preferred that the flowability of the powder product, and in particular Ti /Ti alloy powders, is improved from non-flowable to at most 35 seconds / 20 cm^3, preferably at most 25 seconds / 20 cm^3, more preferably at most 23 seconds / 20 cm^3, yet more preferably between 20 seconds / 20 cm^3 and 23 seconds / 20 cm^3. Similarly, in some embodiments the apparent / tap density of the powder product is improved at least by 100%, preferably by > 120%.

[012] With respect to contamination, it is preferred that the powder product is not contaminated with compounds or elements distinct/different from the desired metal or metal alloy (or combination thereof). In some embodiments, the powder product to be at least 99% pure, more preferably at least 99.5 % pure.

[013] In an exemplary application, the process is used to produce a powder product having a suitable morphology and particle size for use as raw materials for additive manufacturing (AM) processes or for other consolidation processes such as powder metallurgy (PM). In such applications, the process of the present invention mills the precursor particulate material to a powder to optimise the following powder characteristics: a high production yield of desired particle size in the produced powder; having high flowability; and having high apparent / tap density. It is also preferred for the powder product to have a low contamination. It should be appreciated that the ranges for these factors preferably fall within the values defined above.

[014] The morphology and physical properties of precursor particulate material including that material's porosity and hardness affects the morphology, reduction of particle size and yield of the powder with desired particle size product. Fine powder production yields by high shear milling of harder and denser particulates are lower than that of softer and more porous particulates. Thus, where precursor particulate material are dense and hard, the milling yield may be significantly reduced compared to porous of soft particulate material.

[015] Notwithstanding the above, the precursor particulate material can comprise any suitable starting material. In some embodiments, the precursor particulate material comprises a coarse particulate material. In some instances, the precursor material comprises, irregularly shaped particulates, which may be porous. The precursor material is preferably a metal, metal alloy or mixture thereof. Examples of precursor materials include Ti particulates produced from a Ti manufacturing process, such as Ti sponge or particulates produced from the Kroll process, or the Armstrong process. Another suitable precursor particulate material is the particulate or powder product produced from the TIRO process as detailed in international patent publication No. WO2006/042360A1 and international patent publication No. WO2011/137489A1, of which the contents of each should be taken as being incorporated into the present specification by the above references.

[016] In some embodiments, the precursor particulate material comprises a porous or soft particulate material. For example, CP grade titanium is softer than most titanium alloys (for example $TiAl_6V_4$). Therefore, high shear milling of CP grade titanium sponge will typically produce more fine and spherical shaped powder than high shear milling of most titanium alloys.

[017] The precursor particulate material typically has a particle size distribution which is unsuitable for additive manufacturing processes or for powder metallurgy applications. The process of the present invention is therefore used to reduce the average particle size of the precursor particulate material. In some embodiments, the reduced particle has a particle size distribution in which at least 80%, preferably 90% of the particles have an average particle size <500 µm. In some embodiments, the precursor particulate material has a particle size distribution in which at least 80%, preferably 90% of the particles have an average particle size <250 µm. In some embodiments, at least 90%, preferably at least 95%, more preferably at least 99% of the particles have an average particle size <300 µm, preferably <250 µm, and more preferably <150 µm. In some embodiments, the above average particle size results for application of the process of the present invention to 8 mm precursor particulates.

[018] It should be appreciated that the size of precursor particulate material which can be subjected to a high shear milling process is dependent a number of factors. The maximum size of particulates is related to the size of rotor used in the high shear mill process and also the morphology and the physical properties of particulates, including porosity, hardness and ductility. For example, the maximum particle size processable in a high shear milling process having a high shear milling device with a 15 mm diameter rotor would be about 10 mm diameter, where that precursor particulate material was a relatively porous particulate material. However, where that material has a suitably high porosity, it may be possible to process >10 mm particulates. Exemplary porosities of the precursor particulate which assist high shear milling would be preferably > 10%.

[019] If the size of particulates is too large for high shear milling, then the particulates can be broken into smaller pieces by another comminution process prior to the high shear milling process. In such embodiments, the precursor particulate material may be subject to one or more pre-processing stage prior to undergoing the high shear milling process. These pre-processing stages include one or more comminution processes including crushing, grinding, milling or the like. In some embodiments, the pre-processing stages include the use of at least one of jaw crusher, cone crusher, hammer crusher, ball mill, vertical ring mill, roller mill, hammer mill, roller press, vibration mill, jet mill, press, or the like.

[020] The high shear milling process of the present invention preferably modifies the particle morphology of the precursor particulate material from an irregular shape to powder product having a substantially uniform shaped particle such as (but not limited to) angular, platelet, spherical, rod or cylindrical shaped particles. In some embodiments, the particle morphology of the powder product comprises a substantially regular shaped particle, such as (but not limited to) spherical, rod or cylindrical shaped particles.

[021] It should be appreciated that the morphology of the powder product is dependent on and can be controlled by changing the shear milling process conditions including at least one of shear milling rotor speed; shear milling time; or amount of precursor powder. For example, a precursor particulate material which is subject to a high shear milling process with higher milling speeds and/or longer milling times compared to another high shear mill process would typically include a higher proportion of spherical shape morphology.

[022] Furthermore, the critical mass of powder also contributes to a change of powder morphology to spherical shape during high shear milling, because the collisions between powder particles and/or between powder particles and stator during the milling process contribute to morphology change of the processed powder.

[023] The reduced average particle size of the powder product is a result of comminution of the precursor particulate material by the high shear milling

process. The particle size range which is produced by the high shear milling depends on milling conditions and the properties of particulates. The fine powder produced by the high shear milling process preferably has a particle size range in which has a particle size range in which at least 90%, preferably at least 95%, more preferably at least 99% of the particles have an average particle size <250 μm. In some embodiments, the fine powder produced by the high shear milling process has a particle size range in which has a particle size range in which at least 90%, preferably at least 95%, more preferably at least 99% of the particles have an average particle size <250 μm, and preferably <150 μm. In some embodiments, the particle size range of <250 μm is preferably >90%, and more preferably >95%. In some embodiments, the particle size ranges between 45 and 106 μm would be >40%, and preferably >80%. Milling yield of metal powder depends on physical property of the precursor particulates. For example, high shear milling of a highly porous titanium sponge produced from the Kroll, Armstrong and TIRO processes can in some embodiments result in a >95 % production yield of sub-30 micron powder.

[024] The high shear milling process of the present invention preferably includes at least one high shear milling device. A high shear milling device typically includes milling head which includes a rotatable rotor or impeller housed within a stator. The stator comprises a stationary cover or cage, preferably having a series of diagonal slots, which surrounds and encloses the rotor. The slots are preferably angled between 5 and 30 degrees to/ from the central longitudinal axis of the stator, more preferably between 5 and 20 degrees, yet more preferably between 7 and 12 degrees, and in some embodiments about 10 degrees to the central longitudinal axis of the stator. The slots can have any suitable dimension. In one embodiment, the slots have are 3 mm wide and 50 mm long. In operation, the milling head is brought into contact with the precursor particulates and the rotor (in combination with the stator) contacts and comminutes the precursor particulate material through shear and other mechanical forces. In some embodiments, the precursor particulate material is immersed in a liquid during the high shear milling process. This reduces the dust produced during the high shear milling process,

improves the safety and reduces the risk of dust related explosion. The liquid preferably comprises at least one of water, alcohol kerosene or other liquids.

[025] Many high shear milling conditions were examined by the inventors to optimise the desired powder characteristics. Whilst not wishing to be limited to any one parameter, it was found that some important parameters affecting high shear milling processes include:

- Milling speed, i.e. circumferential speed of a rotor (m/min, circumference of the rotor × rotational speed (RPM)). Higher milling speeds produce more fine particles. In some embodiments, the milling speed (circumferential speed of the rotor) is at least at least 700 m/min, preferably at least 1200 m/min, and more preferably at least 2500 m/min.

- Duration of milling: Longer milling times produce more fine particles. In some embodiments, the duration of high shear milling of precursors which are produced by the Kroll, the Armstrong or TIRO processes (to produce maximum amount of 45 – 150 μm milled powder) is at least 5 minutes, more preferably at least 20 mins, and yet more preferably at least 30 mins. In order to produce maximum amount of <45 μm milled powder, it would need more preferably longer than 30 mins.

- Batch amount: Milling smaller batch masses result in more fine particles.

- Rotor size: Larger rotor size produce more fine particles due to higher circumferential speed for a given milling speed (RPM). In some embodiments, the rotor has a rotor diameter, and the precursor particulate material comprise particles having an average particle size of less than the rotor diameter, preferably less than 80% the rotor diameter, preferably less than 75% the rotor diameter, and yet more preferably less than 50% of the rotor diameter.

- Number of high shear mills in a milling: a larger number of high shear mills produce more fine powder (e.g. high shear milling of titanium powder with two or more high shear mills produces more fine powder than when milling with one high shear mill). In some embodiments, the high shear milling process includes at least two high shear mills so as to produce more fine powder.

- Gap distance between rotor and inside wall of stator: Smaller gap distance between a rotor and milling stator casing produce more fine particles. In some embodiments the shear mill includes a stator which extend substantially around the rotor, the stator being configured to have less than 5.0 mm gap between the rotor (preferably the distal end of the rotor blade) and the inner surface of the stator casing, preferably less than 2.0 mm gap, more preferably less than 1.0 mm gap, and yet more preferably less than 0.8 mm gap. In some embodiments, the gap is between 0.2 and 0.8 mm, preferably between 0.4 and 0.6 mm, more preferably about 0.4 mm.

- Morphology and physical properties of particulates, as discussed above.

[026] In a second aspect, the present invention provides a method of producing a powder for additive manufacturing and/or powder metallurgy applications from a precursor particulate material comprising:

subjecting the precursor particulate material to at least one high shear milling process,

thereby producing a powder product having a reduced average particle size and a particle morphology suitable for additive manufacturing and/or powder metallurgy applications comprising a substantially uniform shaped particle selected from at least one of angular, platelet, spherical, rod or cylindrical shaped particles.

[027] It is to be understood that this second aspect of the present invention can include the above defined features of the first aspect of the present invention.

[028] In a third aspect, the present invention provides a powder of particulate material produced from a method according to the first aspect of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[029] The present invention will now be described with reference to the figures of the accompanying drawings, which illustrate particular preferred embodiments of the present invention, wherein:

[030] Figures 1A and 1B illustrates two shear milling devices used in the shear milling process according to an embodiment of the present invention in which the devices comprise (A) 7.4 mm diameter rotor and 10 mm diameter stator; (B) 15 mm diameter rotor and 20 mm diameter stator and (C) 35.2mm diameter rotor and 40 mm diameter stator.

[031] Figure 1C illustrates the rotor configurations of the shear milling devices shown in Figures 1A and 1B comprising (A) 7.4 mm diameter rotor and 10 mm diameter stator; (B) 15 mm diameter rotor and 20 mm diameter stator and (C) 35.2mm diameter rotor and 40 mm diameter stator.

[032] Figures 1D and 1E illustrates two alternate rotor configurations that can be used in the shear milling devices shown in Figures 1A and 1B.

[033] Figures 1F provides isometric views of rotor configurations that can be used in the shear milling devices shown in Figures 1A and 1B, comprising (A) 35.2 mm diameter rotor and 40 mm diameter stator, and B) 95.2 mm diameter rotor and 100 mm diameter stator.

[034] Figure 1G provides cross-sectional view of two shear milling devices used in the shear milling process according to an embodiment of the present invention, comprising (A) 35.2 mm diameter rotor and 40 mm diameter stator, and B) 95.2 mm diameter rotor and 100 mm diameter stator.

[035] Figure 1H provides a front view of the stators of the two shear milling devices shown in Figure 1G, comprising (A) 40 mm diameter stator, and B) 100 mm diameter stator.

[036] Figure 2 illustrates the experimental set up of one shear milling process according to an embodiment of the present invention incorporating at least one of the shear milling devices shown in Figures 1A and 1B.

[037] Figure 3 illustrates the particle size distribution of high shear milled Ti-5 titanium powder as a function of gap distance between rotor and casing.

[038] Figure 4 provides an optical micrograph of Ti precursor particulates (Ti-6a) used in one embodiment of the process of the present invention.

[039] Figure 5 provides an optical micrograph of one product Ti powder particle produced after high shear milling the precursor Ti particles as shown in Figure 4, in accordance with one embodiment of the process of the present invention.

DETAILED DESCRIPTION

[040] The present invention relates to powder manipulation method for producing a powder from a precursor particulate material. The present invention is preferably used to produce cost effective, fine and highly flowable metal powders with minimum contamination by manipulating a coarse particulate precursor material which has a large particle size and irregularly shaped particles.

[041] In the process of the present invention, a precursor particulate material is subjected to a high shear milling process to produce a powder having selected properties. In one exemplary application, the powder product is processed to a suitable morphology and particle size for use as raw materials for the additive manufacturing (AM) processes or for other consolidation processes such as powder metallurgy (PM).

[042] It should be appreciated that the inventors of the present invention considered a large number of comminution processes for comminuting a coarse particular precursor material into a powder product having the desired particle size and morphology suitable for additive manufacture and other powder metallurgy application. The properties of high shear milled titanium powder were:

- a high production yield of <150 μm size powder;
- high flowability of 23 to 35 seconds / 20 cm^3 (from non flowable precursor particulates);
- apparent / tap density of high shear milled powder are improved at least by more than 100%; and
- low contamination of less than 1%, resulting in a product powder purity of at least 99%.

[043] A number of crushing, grinding and pressing processes were considered by the inventors to provide the above desired powder properties from a precursor particulate material. None of these processes were found to provide the required powder product properties. Despite the shortcomings of these and other similar comminuting processes, the inventors found that the application of a high shear milling process to the same precursor particulate material provided a powder product having the desired processes. High shear milling processes and conditions were then investigated in order to optimise the process to produce the powder product and morphology and average particle size characteristics required for additive manufacturing (AM) processes and other powder consolidation processes such as powder metallurgy (PM).

[044] One type of high shear milling device used in the process of the present invention is shown in Figures 1A, to 1H. Three different sized shear milling devices are illustrated in Figures 1A to 1C comprising (A) 7.4 mm diameter rotor and 10 mm diameter stator (or milling shaft); (B) 15 mm diameter rotor and 20 mm diameter stator and (C) 35.2 mm diameter rotor and 40 mm diameter stator. The high shear milling device used in the present invention can be sourced from a variety of manufacturers. However, in the particular illustrated embodiments, three devises are shown in Figures 1A and 1B, namely (A) Small device (10mm diameter stator) and (B) medium device (20 mm diameter stator) High Shear Mill are high shear mixing/milling devices from Ystral GmbH, 1020 type (220V, 1.25A, 50Hz, 260W, Max: 25000 rpm). Furthermore, (C) the large device (40mm diameter) is a high shear mixing/milling device from from Ystral GmBH, comprising 40/38E3 type (230V, 8.2A, 50-60W, 1800W, Max: 23500 rpm).

[045] The illustrated high-shear mill devices 100 comprise a milling shaft 100A and a milling head 101 having a stator 104 and a rotatably driven rotor or impeller 102 enclosed within the stator 104. As best illustrated in Figures 1A and 1B, each stator 104 comprises a cage with a series of diagonal thin slots which is seated around the rotating rotor, through which material is drawn and engages through contact and rotation forces of the rotor 102. For the illustrated embodiment shown in Figure 1A(C) and 1B(C), the stator 104 has a diameter of 40 mm, internal diameter of about 36 mm and includes 16 equispaced slots 112 which are 3 mm wide and 50 long comprising apertures which penetrate through the wall of the stator 104. Each slot 112 is angled about 10 degrees from the axial axis running through the length of the stator 104. The 36 mm internal diameter of the stator 104 provides around 0.4 mm gap between the outer edge of the rotor 104 and inner wall of the stator 104. The stator 104 is preferably constructed from high tensile steel, for example 4340 high tensile steel. The rotor 102 is driven by a motor 106, in the illustrated case the motor is an electric motor, though it should be appreciated that any suitable driver or motor could be used. The high-shear mill device 100 is typically immersed in a tank or other receptacle 210 containing the material to be milled, as shown in Figure 2.

[046] The rotor 102 can have a large variety of suitable configurations. Figure 1C and 1G shows the rotor 102 configuration in detail. In this Figure, each of these rotors 102 has two or four spaced apart rotor blades 102A set on a drive disc 102B. With reference to the high shear milling devices shown in Figures 1A and 1B, the rotor 102 has two blades 102A for each of these embodiments (rotor 102 having diameters 7.4 mm, 15 mm, 35.2 mm). A four blade rotor 102 is preferably used on larger diameter rotors, for example a rotor having a 95.2 mm diameter, such as shown in Figure 1G(B). It should be appreciated that the rotor blades 102A rotate through rotation of drive disc 102B, impacting material which is drawn into the stator 104.

[047] Two alternate configurations used in the milling heads 101 of the high shear milling device shown in Figures 1A and 1B are shown in Figures 1C and

1D. Each of these rotors 102 has four spaced apart rotor blades 102A set on a drive disc 102B. Again, it should be appreciated that the rotor blades 102A rotate through rotation of drive disc 102B, impacting material which is drawn into the stator 104. It should be appreciated that other rotor configurations can be used having a different number of rotor blades, blade configurations and the like.

[048] Figure 1G and 1H provides a cross-sectional view of two embodiments of the shear milling devices used in the shear milling process according to an embodiment of the present invention. As shown in Figure 1F these embodiments have (A) 35.2 mm diameter rotor 102 and 40 mm diameter stator 104, and B) 95.2mm diameter rotor 102 and 100 mm diameter stator 104. The particular rotors 102 of these devices are illustrated in Figure 1G. As described above, the rotor 102 comprises two or four spaced apart rotor blades 102A set on a drive disc 102B. The rotor 102 in Figure 1F(A) comprises a two blade rotor 102 where the blades 102A are position 180 degrees apart. Each blade 102A extends relative to the central axis between R8 mm and R17.6 mm (i.e. the out radius of the rotor 102). Each blade 102A is 10 mm wide and 60 mm long (measured from the base side of drive disc 102B). However, it should be appreciated that any suitable dimensions could be used for a specific application, and the invention should not be restricted to this particular exemplified configuration. The rotor 102 in Figure 1F(B) comprises a four blade rotor 102 where the blades 102A are position 90 degrees apart. Each blade 102A extends relative to the central axis between R26 mm and R47.6 mm (i.e. the out radius of the rotor 102). Each blade 102A is 20 mm wide and 60 mm long (measured from the base side of drive disc 102B. However, it should be appreciated that any suitable dimensions could be used for a specific application, and the invention should not be restricted to this particular exemplified configuration. Each rotor 102 is operatively connected to drive shaft 110, which in turn is connected to shaft coupler 112, which (whilst not illustrated) is operatively connected to a motor. Operation of the motor drives rotation of drive shaft 110, which in turn rotates the rotor 102 within the stator 104.

[049] Moreover, as shown in Figure 1H, the stators 104 of each of these embodiments comprise cylindrical cages have the following configurations:

(A) Figure 1H(A) shows a stator 104 having a diameter of 100 mm having 16 equispaced slots 112 which are 3 mm wide and 50 long comprising apertures which penetrate the wall. Each slot 112 is angled about 10 degrees from the axial axis running through the length of the stator. This stator 104 has a 36 mm internal diameter which provides around 0.4 mm gap between the outer edge of the rotor 104 and inner wall of the stator 104. The illustrated stator 104 is 130 mm long (along axial length). Though it should be appreciated that this length could be any length as long as the rotor 102 is enclosed within the stator 104.

(B) Figure 1H(B) shows a stator 104 having a diameter of 100 mm having 36 equispaced slots 112 which are 3 mm wide and 50 long comprising apertures which penetrate the wall. Each slot 112 is angled about 10 degrees from the axial axis running through the length of the stator. This stator 104 has a 96 mm internal diameter which provides around 0.4 mm gap between the outer edge of the rotor 104 and inner wall of the stator 104. The illustrated stator 104 is 96 mm long (along axial length). Again, it should be appreciated that this length could be any length as long as the rotor 102 is enclosed within the stator 104.

[050] Again, each stator 104 is preferably constructed from high tensile steel, for example 4340 high tensile steel.

[051] Without wishing to be limited to any one theory, a fluid (in this case with the precursor particles) flows into the bottom opening of the stator 104 and flows out through the slots 112 and undergo shear when one area of that fluid travels with a different velocity relative to an adjacent area. A high-shear mill device 100 therefore uses the high-speed rotor 102 to create flow and shear, resulting in comminution and deformation of the particles flowing through and around the rotor 102 and stator 104. The tip velocity, or speed of the fluid at the outside diameter of the rotor 102 is higher than the velocity at the center of the rotor 102, and it is this velocity difference that creates shear. The stator 104

creates a close-clearance gap between the rotor 102 and itself and forms an extremely high-shear zone for the material as it exits the rotor 102.

[052] As shown in Figure 2, a high shear milling apparatus 200 (in this case an experimental, laboratory apparatus) comprises the high shear mill device 100 installed and clamped in place on a stable stand 120 with the mixing head 101 inserted into a mixing container, in the illustrated case, jar 210. The jar 210 includes a cover 212 to seal the precursor particulates and powder product within the jar 210. As the process of the present invention concerns milling a particulate material into a powder, the precursor particulates are immersed in a fluid, typically one of water, an alcohol, or kerosene, when milled within the jar 210, to reduce the production of fine dust during milling. This reduces the dust produced during the high shear milling process, improves the safety and reduces the risk of dust related explosion.

[053] In operation, the milling head 101 is brought into contact with the precursor particulates and the rotor 102 in combination with the stator 104 of the milling head 101 contacts and comminutes the precursor particulate material through shear and other mechanical forces as described above.

[054] It should be appreciated that persons skilled in the art would understand that the laboratory scale device 100 and apparatus 200 shown in Figures 1A, 1B and 2 could be scaled up to an industrial scale using for example larger high shear milling devices, and a number of parallel or series arranged devices.

[055] As can be appreciated, a number of design factors can affect the high shear milling process include the diameter of the rotor and its rotational speed, the distance between the rotor and the stator, the duration of milling, and the number of high shear milling devices used. These factors and other properties of the process of the present invention will be demonstrated in the following examples:

EXAMPLES

[056] The method of the present invention has been developed primarily for titanium / titanium alloys powders, and as such the following examples

demonstrate that particular application. However, it should be appreciated that the method of the present invention should not be limited to that application can be used for shaping and sizing other metal powders for additive manufacturing and powder metallurgy applications.

Example 1 - High shear milling results as a function of milling speed (rpm)

[057] High shear milling yields were examined as a function of mixing speed (mixer rpm) to determine the effect of mixing speed on particle size reduction and particle size distribution.

Method

[058] A laboratory scale, bench top high shear milling apparatus 200 (as shown in Figure 2) was used to mill 30 g batches of Ti particulates. The details of the specimens for the Ti-1 titanium powder experimental runs are provided in Table 1.

[059] Table 1: Details of the batches

Milling conditions	Milling speed (rpm)	Milling time (minutes)	Sample designation
Batch: 30 g Ti particulates (< 8 mm) Milling liq: Water, 300 g Milling time:15 minutes	As-received (before milling)	0	Ti-1
	24,000	15	Ti-1a
	16,000	15	Ti-1b
	12,000	15	Ti-1c

[060] As shown in Figure 2, the high shear mill 200 apparatus contains high shear milling device 100, having a milling head 101 comprising a stator 104 and enclosed rotor 102. Rotation of the rotor is driven by an electric motor 106 via driver a drive shaft (not shown in Figure 2). The high shear milling device 100 is installed on a stable stand 120. The milling head is designed to be received within a container, in this case milling jar 210. The jar 210 includes a cover 212 to seal the precursor particulates and powder product within the jar 210. In use, a specified amount of a milling liquid (as specified in the respective example run), and the precursor particulates to be milled are placed in a jar. The total

amount of the mixture is ideally less than half of the jar height to prevent over spilling during milling. The milling head 101 of the high shear mill device 100 is lowered to the milling jar 210, with the end of the rotor 102 being spaced 10 mm apart from the bottom of the milling jar 210. The high shear milling device 100 is then operated for a designated period, after which the device 100 is turned off and the the resulting slurry of milled particulates and milling liquid is removed from the jar 210 and dried for at least 10 hours in a vacuum oven at 110 °C.

[061] After being dried, the resulting powder is placed in a stack of sizing sieves (of a particle sizing sieve arrangement) which was mounted and vibrated on a vibrating table for 0.5 hour to separate the powder into the respective size fractions.

<u>Results</u>

[062] The resulting particle size distribution of high shear milled powder is shown in Table 2.

[063] Table 2: Particle size distributions of high shear milled Ti-1 powders at different milling speed

Particle size (μm)	(Wt%)			
	As received Ti-1 (before milling)	Ti-1a (24000rpm/15mins)	Ti-1b (16000rpm/15mins)	Ti-1c (12000rpm/15mins)
> 250	37	0	0.1	0.1
150 - 250	21	0.1	0.1	1.0
106 - 150	16	0.1	0.6	4.8
75 - 106	16	1.1	5.7	16.5
45 - 75	7	16.5	32.5	38.1
25 - 45	3	53.3	36.1	25.1
< 25	0	28.9	24.9	14.5

[064] A comparison of the above resultant particle size distributions indicates that more fine powder is produced using higher milling speeds.

Example 2 - High shear milling results as a function of milling time

[065] High shear milling yields were examined as a function of milling time to determine the effect of mixing speed on particle size reduction and particle size distribution.

Method

[066] A laboratory scale, bench top high shear milling apparatus 200 (as shown in Figure 2) was used to mill 30 g batches of Ti particulates. The high shear milling conditions for the Ti-2 titanium powder experimental runs are provided below:

- Batch: 30 g Ti particulates (<8 mm)
- Milling liquid: Water, 360 g;
- Milling speed: 25,000 rpm;
- Milling time: for 15 (Ti-2a), 30 (Ti-2b) and 45 minutes (Ti-2c).

[067] The same high shear milling device was used as described and operated in Example 1. After high shear milling, the resulting slurry of particles and milling liquid was dried for at least 10 hours in a vacuum oven at 110ºC.

Results

[068] The particle size distributions of Ti-2a, Ti-2b and Ti-2c experimental runs are shown in Table 3.

[069] Table 3: Particle size distribution in wt% of high shear milled Ti-2 titanium powder for different milling time

Specimen	>250 µm	250-150	150-106	106-75	75-45	45-25	<25 µm
Ti-2 (as-received)	64.39	31.27	4.06	0.28	0.00	0.00	0.00
Ti-2a	0.74	33.86	29.14	15.70	9.14	3.74	7.69
Ti-2b	0.08	0.11	2.78	21.84	37.12	17.3	20.77
Ti-2c	0.29	0.33	0.45	5.72	30.58	27.77	34.87

[070] It was identified from analysis of the particle size distribution of Ti-2 after high shear milling that the longer period of high shear milling was, the higher portion of fine particles was produced.

[071] After 45 minutes of high shear milling, ~36 wt% of 106 to 45 µm and ~63 wt% of <45 µm powder were produced (total ~99 wt% of <106 µm).

Example 3 - High shear milling results as a function of circumferential speed (rotor size)

[072] High shear milling of titanium particulates was undertake at two different circumferential speeds (7.4 mm and 15 mm diameter rotors, 10 mm and 20 mm diameter stators respectively at 21,000 rpm, see Figure 1A and 1B and corresponding description above) to determine the effect of rotor and stator size on particle size reduction and particle size distribution.

Method

[073] A laboratory scale, bench top high shear milling apparatus 200 (as shown in Figure 2) was used to mill 50 g batches of Ti particulates. The high shear milling conditions for the Ti-3 titanium powder experimental runs are provided below:

- Batch: 50 g Ti particulates (<8 mm)
- Milling liquid: Isopropanol, 700 g;
- Milling speed: 25000 rpm;
- Rotor size :
  - Ti-3a and Ti-3b: 7.5 mm diameter;
  - Ti-3c and Ti-3d: 15 mm diameter;
- Milling time:
  - Ti-3a and Ti-3c: 1 hour;
  - Ti-3b and Ti-3d: 2 hours.

[074] The same high shear milling device was used as described and operated in Example 1. In this case, the mixture of Ti powder and isopropanol was placed in a plastic milling jar. Milling was undertaken in a fume cupboard with compress air blown over the top of the container to disperse the alcohol fume. The mixer was also earthed.

[075] After operating the high shear mill for the designated time (1 and 2 hours), the resulting slurry of particles and milling liquid was dried in a vacuum oven at 80℃ for at least 10 hours. The resulting dried powder was then placed

in a sieve sizing apparatus, which was placed in a vibrating table for 0.5 hour to separate the powder into the respective size fractions.

Results

[076] The results after sieving are shown in Table 4:

[077] Table 4: Particle size distribution of high shear milled Ti-3 titanium particulates with different circumferential speeds (7.4 and 15 mm diameter rotors)

	Wt%				
	>300 µm	300>>100	100>>32	<32 µm	total
Ti-3a	0.05	42.73	42.07	15.19	100.00
Ti-3b	0.08	11.05	68.31	20.64	100.00
Ti-3c	0.03	0.65	69.44	29.87	100.00
Ti-3d	0.01	0.36	51.74	47.89	100.00

[078] The yield of the production of < 32 µm Ti powder from coarse titanium particulates after high shear milling with a 7.5 mm diameter rotor was a half of that with 15 mm diameter rotor. This indicated that the high shear milling experimental run with higher circumferential speed produced more fine powder.

Example 4 - High shear milling results as a function of batch amount

[079] High shear milling yields were examined as a function of batch amount to determine the effect of mixing speed on particle size reduction and particle size distribution.

Method

[080] A laboratory scale, bench top high shear milling apparatus 200 (as shown in Figure 2) was used to mill two different batch sizes of Ti particulates. The milling conditions for the Ti-4 titanium powder experimental runs are provided below:

- Batch:
  - Ti-4a: 50 g Ti particulates (< 8 mm);
  - Ti-4b: 130 g Ti particulates (< 8 mm);

- Milling liquid: Isopropanol, 800 g;
- Milling speed: 25,000 rpm;
- Rotor size (cm): 15 mm diameter;
- Number of high shear mixers used in a high shear milling: 2 each;
- Milling time: 2 hours.

[081] The milling process was same described in Example 3.

Results

[082] The results after sieving are shown in Table 5:

[083] Table 5: Particle size distribution of high shear milled Ti-4 titanium particulates.

	Wt%				
	>300 µm	300>>100	100>>32	<32 µm	Total
Ti-4a	0.04	0.30	33.81	65.86	100.00
Ti-4b	0.03	0.42	50.16	49.39	100.00

[084] The production yield of <32 µm Ti powder from milling a larger amount of Ti powder (130 g, Ti-4b) under the same milling conditions was significantly lower than that of Ti-4a. This indicates that milling batch size can affect the particle size distribution, and in particular smaller batches are preferred to larger batches for a desired production yield of specified particle size powder.

Example 5 - Gap distance between rotor and inside wall of the stator

[085] High shear milling yields were examined as a function of the gap distance between rotor and inside wall of the stator to determine the effect of the gap distance on particle size reduction and particle size distribution.

[086] It was identified from various high shear milling of titanium particulates that the gap distance between the rotor and a stator is an important parameter to obtain high yields of fine powder. Therefore two different gap distances were examined, L1 and L2 (detailed below) where L1 <L2.

<u>Method</u>

[087] A laboratory scale, bench top high shear milling apparatus 200 (as shown in Figure 2) was used to mill 30 g batches of Ti particulates. The milling conditions the Ti-5 titanium powder experimental runs are provided below:

- Batch: 30 g Ti particulates (<8 mm)
- Milling liquid: Water, 300 g;
- Milling speed: 21000 rpm;
- Rotor size (cm): 15.0 mm diameter;
- Gap distance:
    - Ti-5a: L1 (<1 mm);
    - Ti-5b: L2 (<2 mm), L2> L1;
- Milling time: 30 minutes.

[088] The same high shear milling device was used as described and operated in Example 1. After milling, the resulting slurry of particles and milling liquid was dried and sieved as described in Example 1.

<u>Results</u>

[089] The result is shown in Table 6 and Figure 3 which shows the particle size distribution of high shear milled Ti-5 titanium powder as a function of gap distance between rotor and casing

[090] As seen in Table 6 and Figure 3, a small gap (Ti-5a) produced a lot more fine powder.

[091] Table 6 Particle size distribution of HS milled Ti-5 powder with different gap distance

Sample	> 250μm	250-150	150-106	106-75	75-45	45-25	<25μm
Ti-5a	0.5 wt%	5.4	18.0	27.9	27.2	10.9	10.1
Ti-5b	6.2 wt%	42.7	19.0	9.4	12.5	4.6	5.5

Example 6 - Changes in particle morphology during high shear milling

[092] The particle morphology of the powder product from the high shear milling process was examined to determine the effect of the high shear milling process on particle morphology.

Method

[093] A laboratory scale, bench top high shear milling apparatus 200 (as shown in Figure 2) was used to mill 30 g batches of Ti particulates. The high shear milling conditions for the Ti-6 titanium powder experimental runs are provided below:

- Batch: 30 g of Ti /Ti alloy sponge particulates (< 8mm)
- Milling liquid: Water, 360 g;
- Milling speed: 25,000 rpm;
- Milling time: 20 mins (Ti-6).

[094] The same high shear milling device was used as described and operated in Example 1. After high shear milling, the resulting slurry of particles and milling liquid was dried for at least 10 hours in a vacuum oven at 110 ºC.

[095] The morphology of the particulate before (T-6a) and after (T-6b) high shear milling was investigated using an optical microscope. The flowability, apparent density and tap density of the powder before and after high shear milling were also investigated using ASTM B8555-06, ASTM B703 and ASTM B527.

Results

[096] Figures 4 and 5 show a comparison of the particle morphology before (T-6a) and after (T-6b) the high shear milling. As can be observed, the high shear milling process modified the morphology of the powder from an irregular shape to a spherical shape.

[097] Powder morphology changes from irregular to spherical shapes after high shear milling are noticed in up to 45 micron size powder. Smaller than 45

micron powder which was high shear milled had angular shape morphology. This indicated that the critical mass of powder (to have enough impact energy to modify the surface of the particles) would an important factor to change their morphology to spherical shape during high shear milling in liquid, because morphology change of the powder would be caused by the collisions between powder particles, and the collisions between particle and rotor / stator during the milling process. Titanium powder which was high shear milled with higher milling speeds and longer milling times contain a higher proportion of spherical shape morphology.

[098] Flowability measurements of two similar particle size range of titanium powders (before (as received) and after high shear milling) found that the flowability of the high shear milled titanium powder was increased from not flowable (as-received powders) to up to 23 seconds / 20 cm^3. As a comparison, the flowability of commercial spherical shape Ti /Ti alloy powders (produced by gas atomisation method) for EBM was 21 seconds / 20 cm^3). The apparent density and also tap density after high shear milling were also improved by more than 100% (e.g. apparent density: from 0.3 g/cm^3 to >0.6 g/cm^3, tap density : from 0.4 g/cm^3 to >0.9 g/cm^3).

[099] Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is understood that the invention includes all such variations and modifications which fall within the spirit and scope of the present invention.

[100] Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification (including the claims) they are to be interpreted as specifying the presence of the stated features, integers, steps or components, but not precluding the presence of one or more other feature, integer, step, component or group thereof.

CLAIMS

1. A method of producing a powder from a precursor particulate material comprising:

subjecting the precursor particulate material to at least one high shear milling process,

thereby producing a powder product having a reduced average particle size and a selected particle morphology.

2. A method according to claim 1, wherein the powder product has a particle size range in which at least 90%, preferably at least 95%, more preferably at least 99% of the particles have an average particle size < 300 μm, preferably < 250 μm, and more preferably < 150 μm.

3. A method according to claim 1 or 2, wherein the particle morphology of the powder product comprises a substantially uniform shaped particle, preferable angular, platelet, spherical, rod or cylindrical shaped particles.

4. A method according to any preceding claim, wherein the particle morphology of the powder product comprises a substantially regular shaped particle.

5. A method according to any preceding claim, wherein the morphology of the powder product can be controlled by changing the shear milling process conditions including at least one of shear milling rotor speed; shear milling time; or amount of precursor powder.

6. A method according to any preceding claim, wherein the powder product has at least one of: high flowability; high apparent / tap density; and low contamination.

7. A method according to any preceding claim, wherein the flowability of the powder product is at most 35 seconds / 20 cm^3, preferably at most 25 seconds / 20 cm^3, more preferably at most 23 seconds / 20 cm^3, yet more preferably between 20 and 23 seconds / 20 cm^3.

8. A method according to any preceding claim, wherein the apparent / tap density of the powder product is improved at least by 100% after HS milling preferably 120%.

9. A method according to any preceding claim, wherein the precursor particulate material comprises a coarse particulate material.

10. A method according to any preceding claim, wherein the precursor particulate material comprises irregularly shaped particulate material.

11. A method according to any preceding claim, wherein the precursor particulate material comprises a metal or a metal alloy.

12. A method according to any preceding claim, wherein the precursor particulate material comprises Ti particulates produced from a Ti manufacturing process, preferably a Ti sponge or particulates produced from the Kroll process, Armstrong process or Ti particulates or powder produced from TIRO process.

13. A method according to any preceding claim, wherein the precursor particulate material may be subject to at least one pre-processing step comprising at least one comminution processes.

14. A method according to any preceding claim, wherein in the high shear milling process, the precursor particulate material is immersed in a liquid.

15. A method according to claim 14, wherein the liquid comprises at least one of water, alcohol or kerosene.

16. A method according to any preceding claim, wherein the high shear milling process includes at least one high shear mill which includes a rotor for contacting and comminuting the precursor particulate material.

17. A method according to claim 16, wherein the rotor has a rotor diameter, and wherein the precursor particulate material comprise particles having an average particle size of less than the rotor diameter, preferably less than 80%

the rotor diameter, preferably less than 75% the rotor diameter, and yet more preferably less than 50% the rotor diameter.

18. A method according to claim 16 or 17, wherein the circumferential milling speed is at least at least 700 m/min, preferably at least 1200 m/min, and more preferably at least 2500 m/min.

19. A method according to any preceding claim, wherein the duration of high shear milling of porous titanium / titanium alloy particulates to produce maximum amount of 45 – 106 μm particle size range is at least 15 minutes, more preferably at least 20 mins, and yet more preferably at least 30 mins.

20. A method according to any one of claims 16 to 19, when dependent through claim 16, wherein the shear mill includes a stator which extend substantially around the rotor, the stator being configured to have less than 5 mm gap between the rotor and the inner surface of the casing, preferably less than 2 mm gap, more preferably less than 1 mm gap, and yet more preferably less than 0.8 mm gap.

21. A method according to any preceding claim, wherein the precursor particulate material is subjected to milling with at least two high shear mills.

22. A method of producing a powder for additive manufacturing and/or powder metallurgy applications from a precursor particulate material comprising:

subjecting the precursor particulate material to at least one high shear milling process,

thereby producing a powder product having a reduced average particle size and a particle morphology suitable for additive manufacturing and/or powder metallurgy applications comprising a substantially uniform shaped particle selected from at least one of angular, platelet, spherical, rod or cylindrical shaped particles.

23. A method according to claim 1, wherein the powder product has a particle size range in which at least 90%, preferably at least 95%, more preferably at least 99% of the particles have an average particle size < 300 µm, preferably < 250 µm, and more preferably < 150 µm.

24. A method according to any preceding claim, wherein the particle morphology of the powder product comprises a substantially regular shaped particle.

25. A powder of particulate material produced from a method according to any one of the preceding claims.

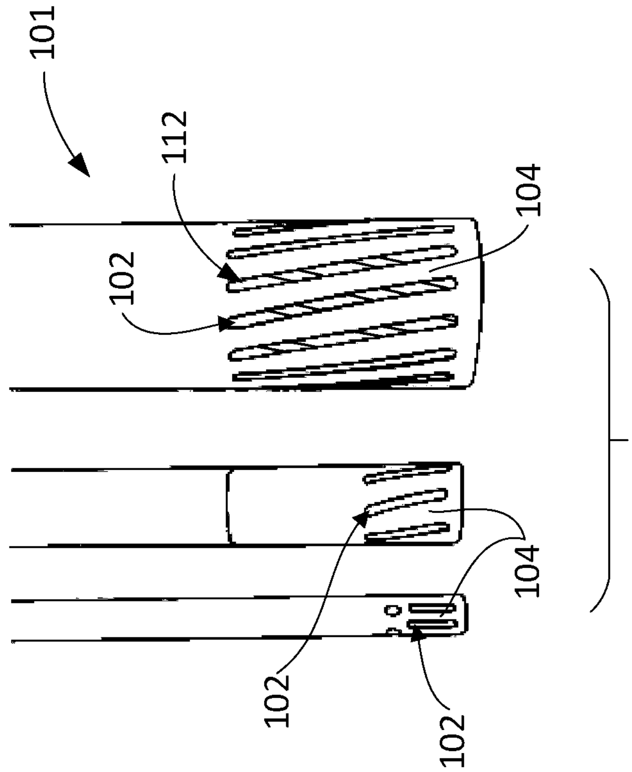

Figure 1B

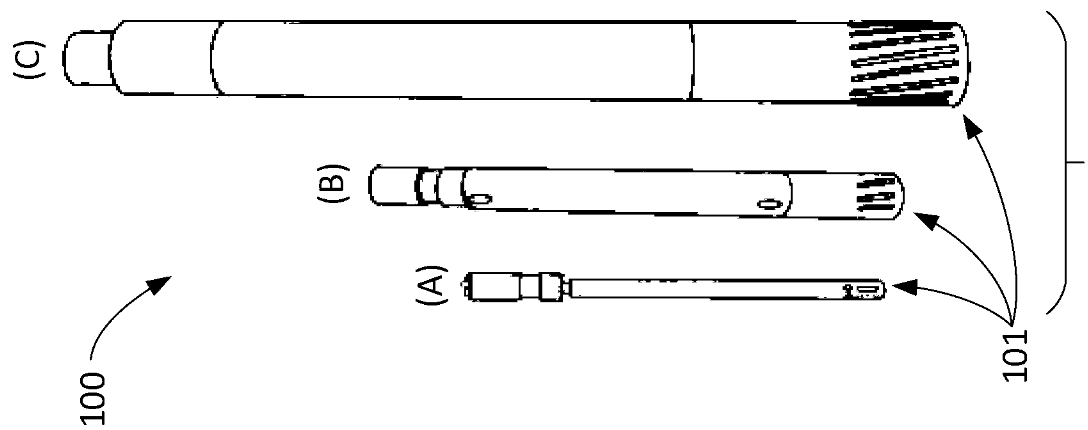

Figure 1A

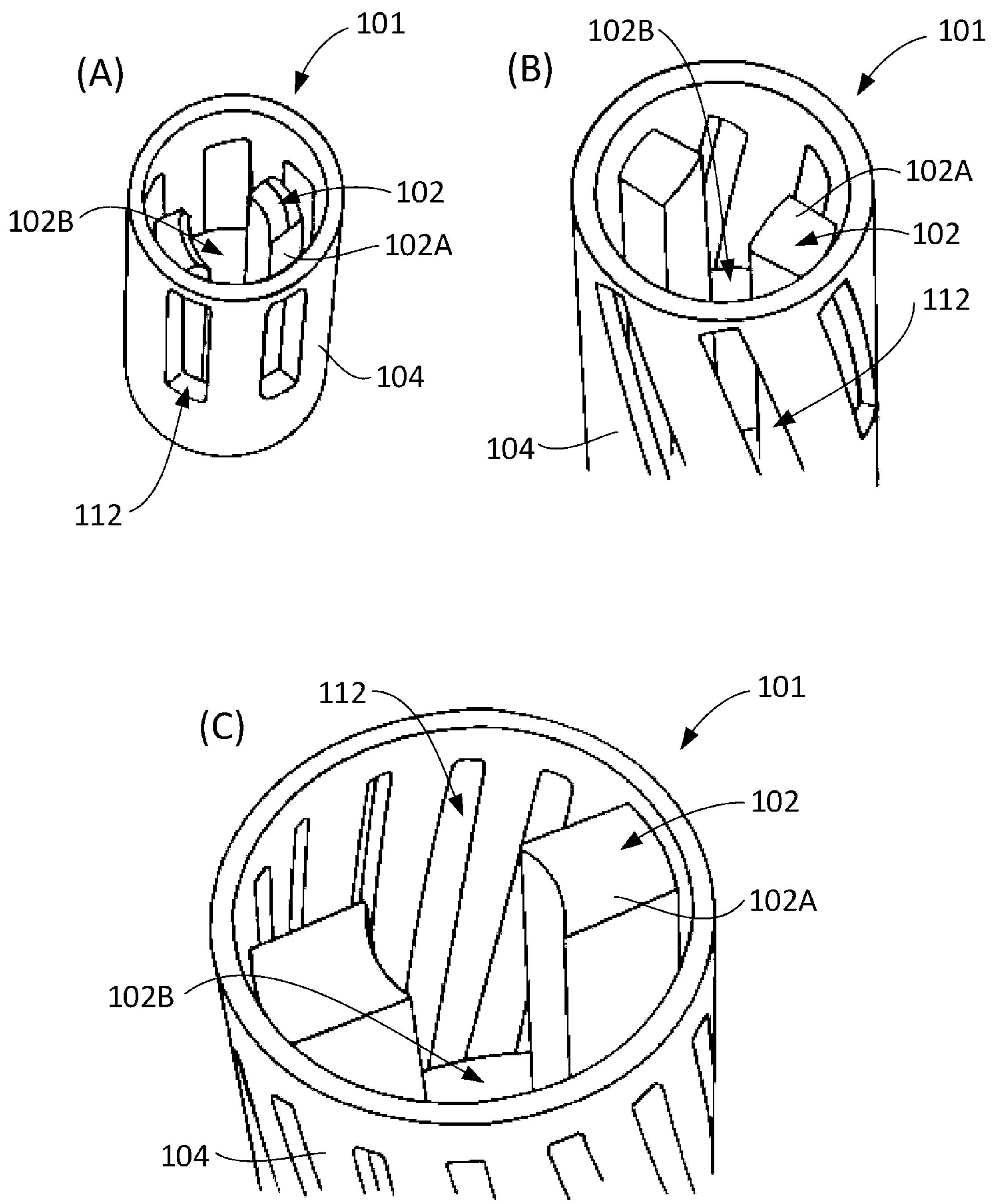
(A)
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Figure 1C

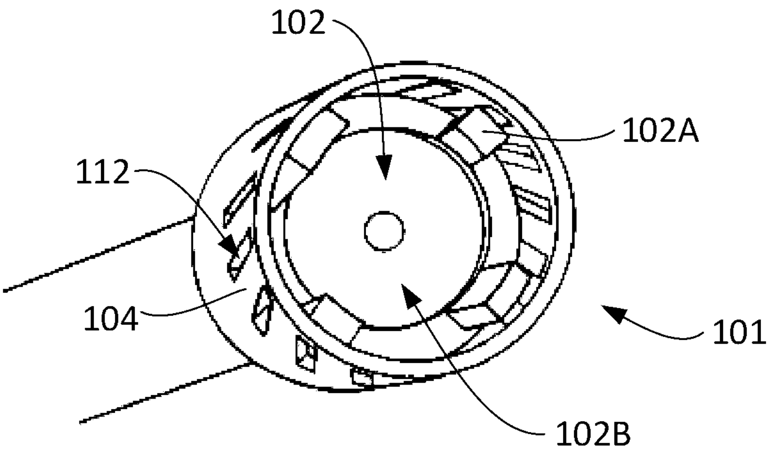


Figure 1D

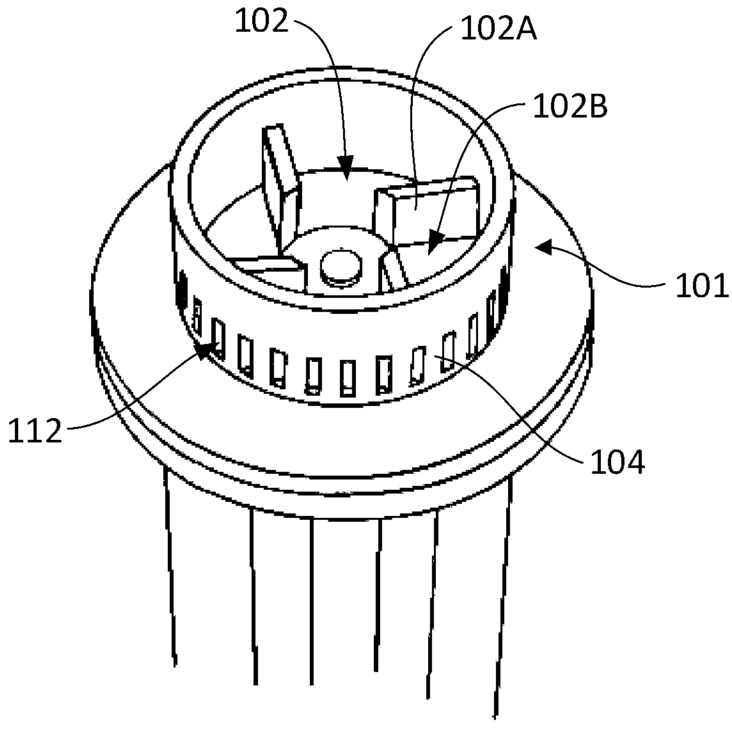


Figure 1E

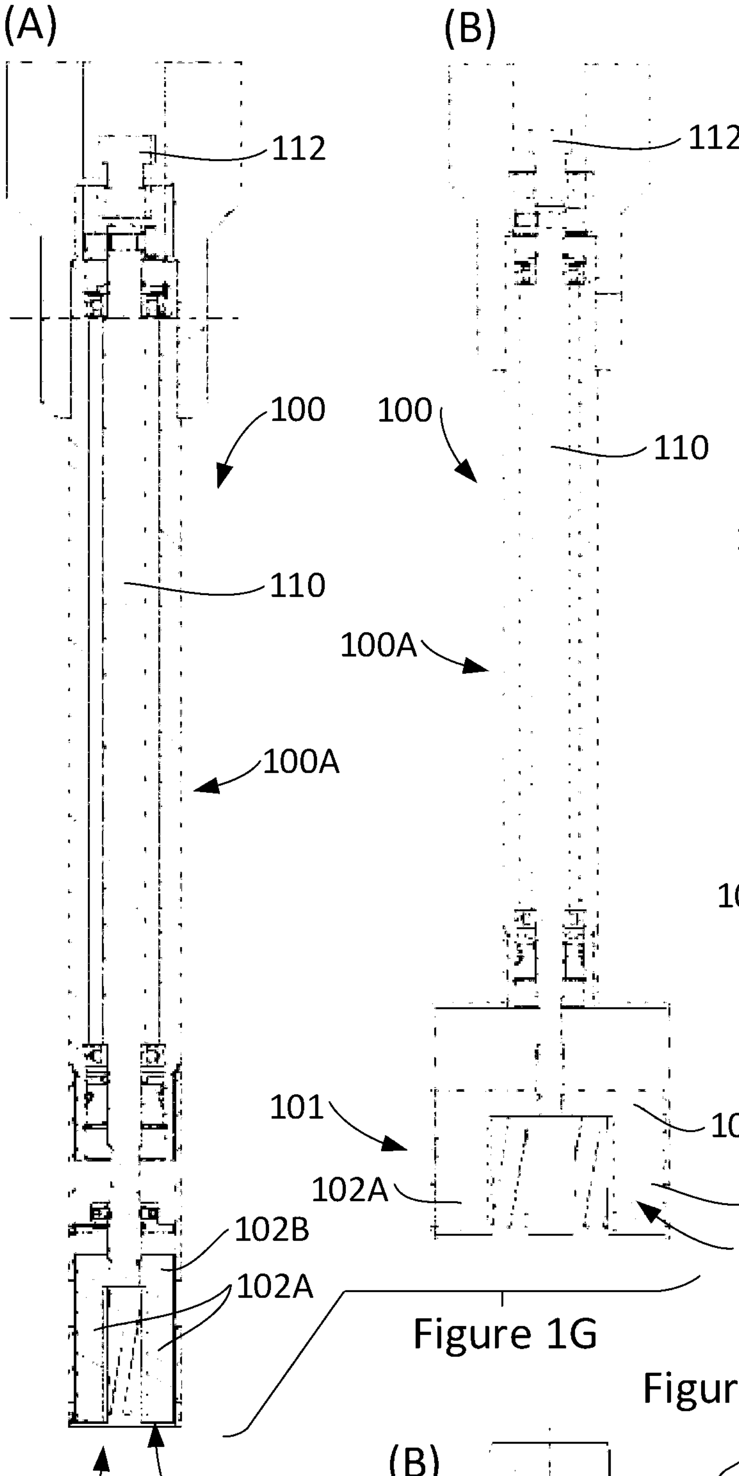


Figure 1G

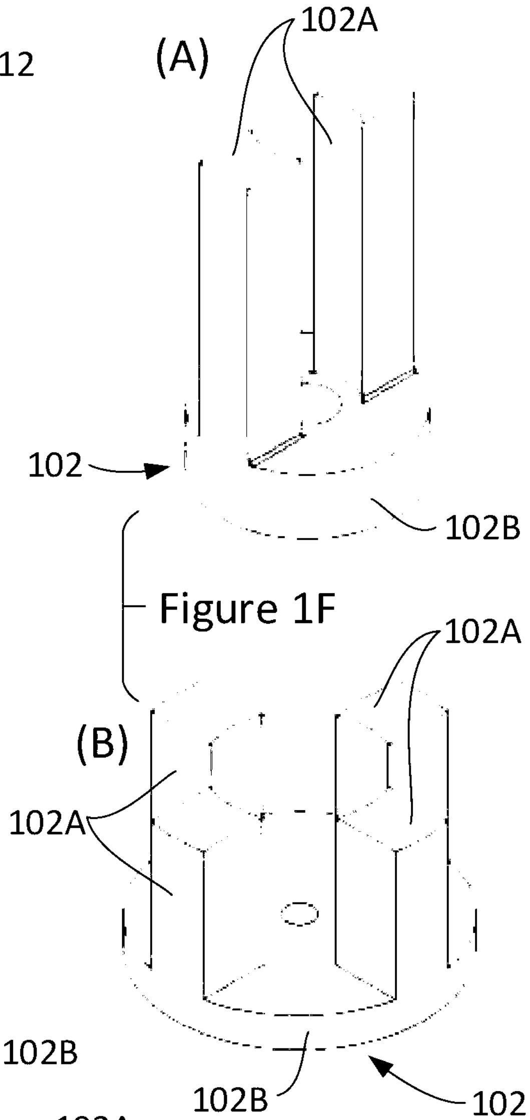


Figure 1F

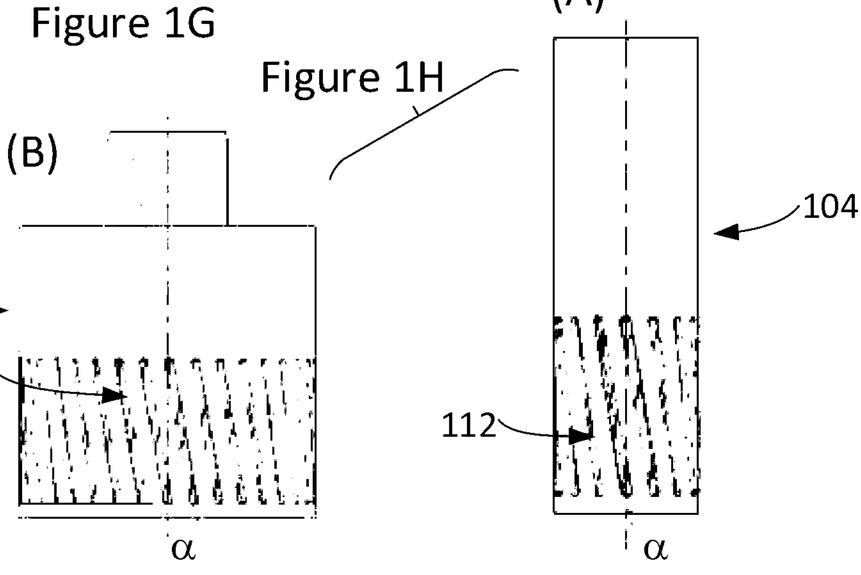


Figure 1H

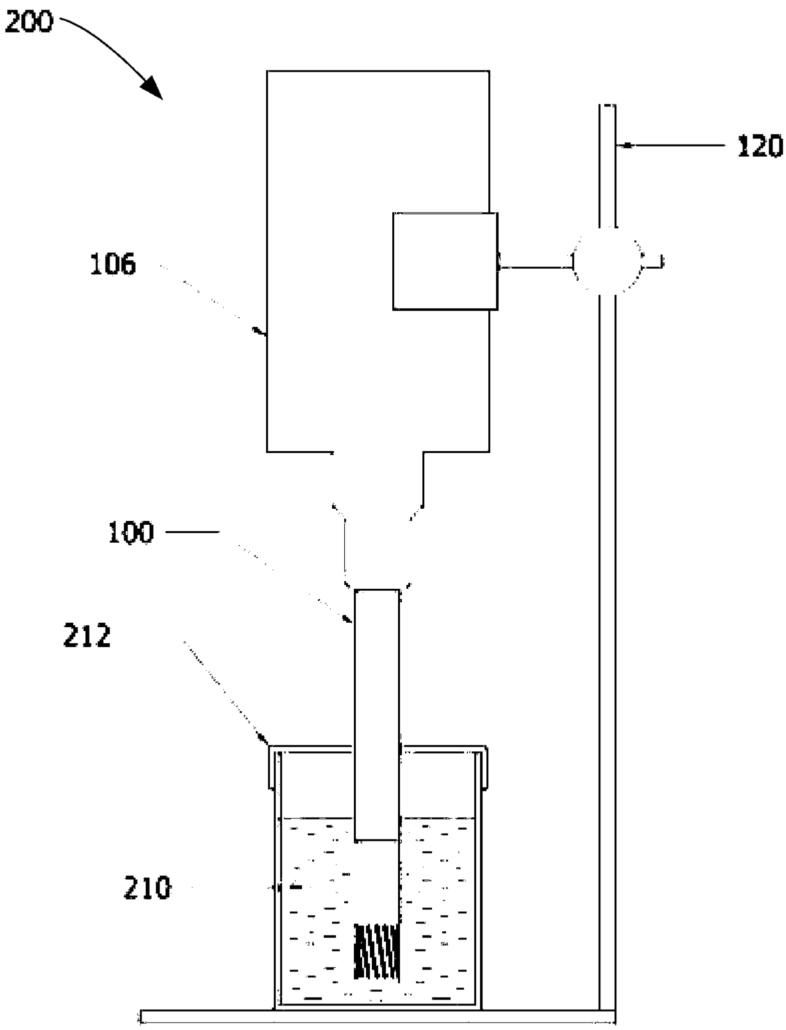
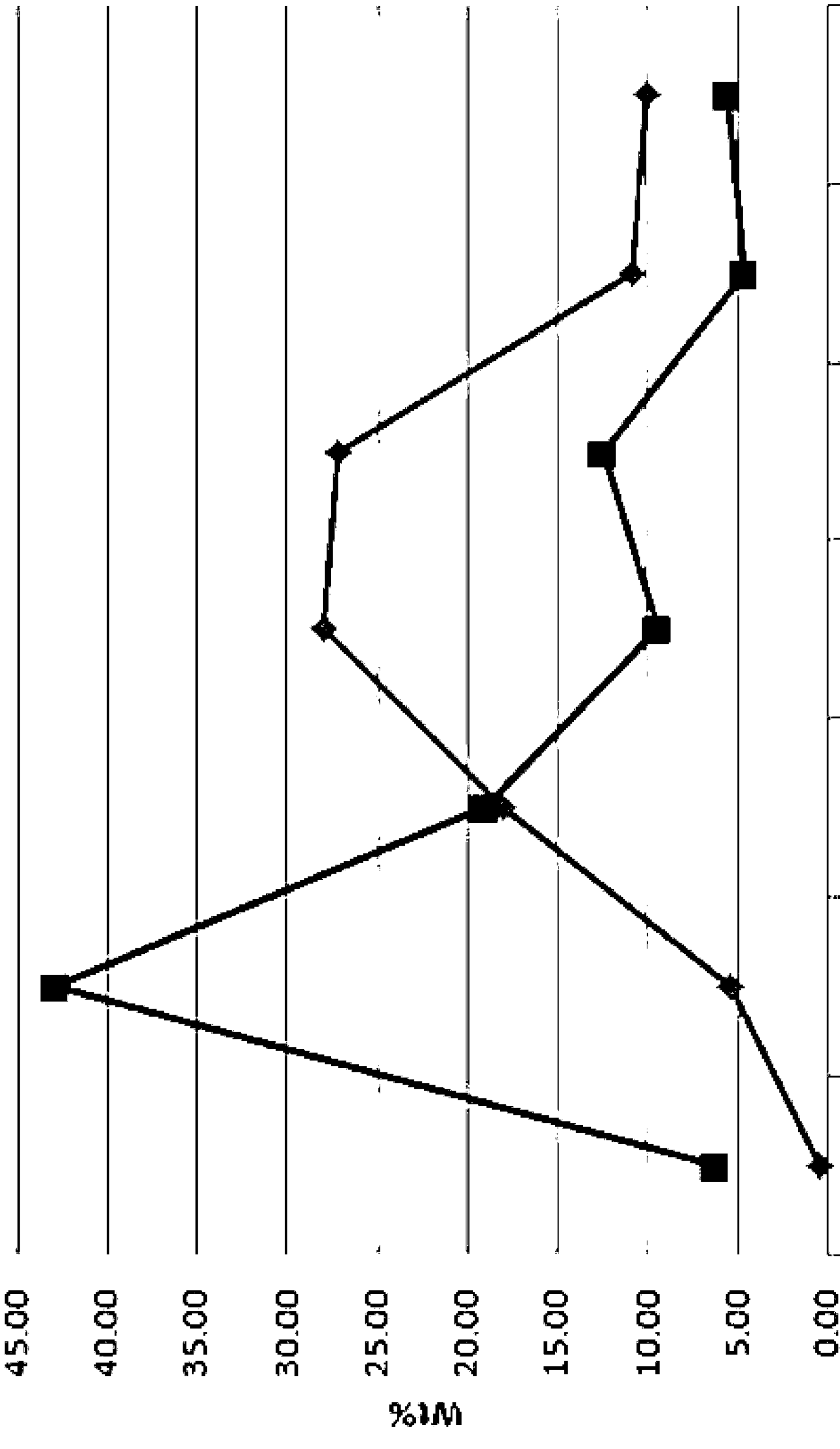


Figure 2

Figure 3



	>250 µm	250>>150	150>>106	106>>75	75>>45	45>>25	<25 µm
Ti-5a (smaller gap)	0.53	5.39	18.01	27.92	27.15	10.92	10.08
Ti-5b (larger gap)	6.15	42.82	18.97	9.42	12.47	4.59	5.57

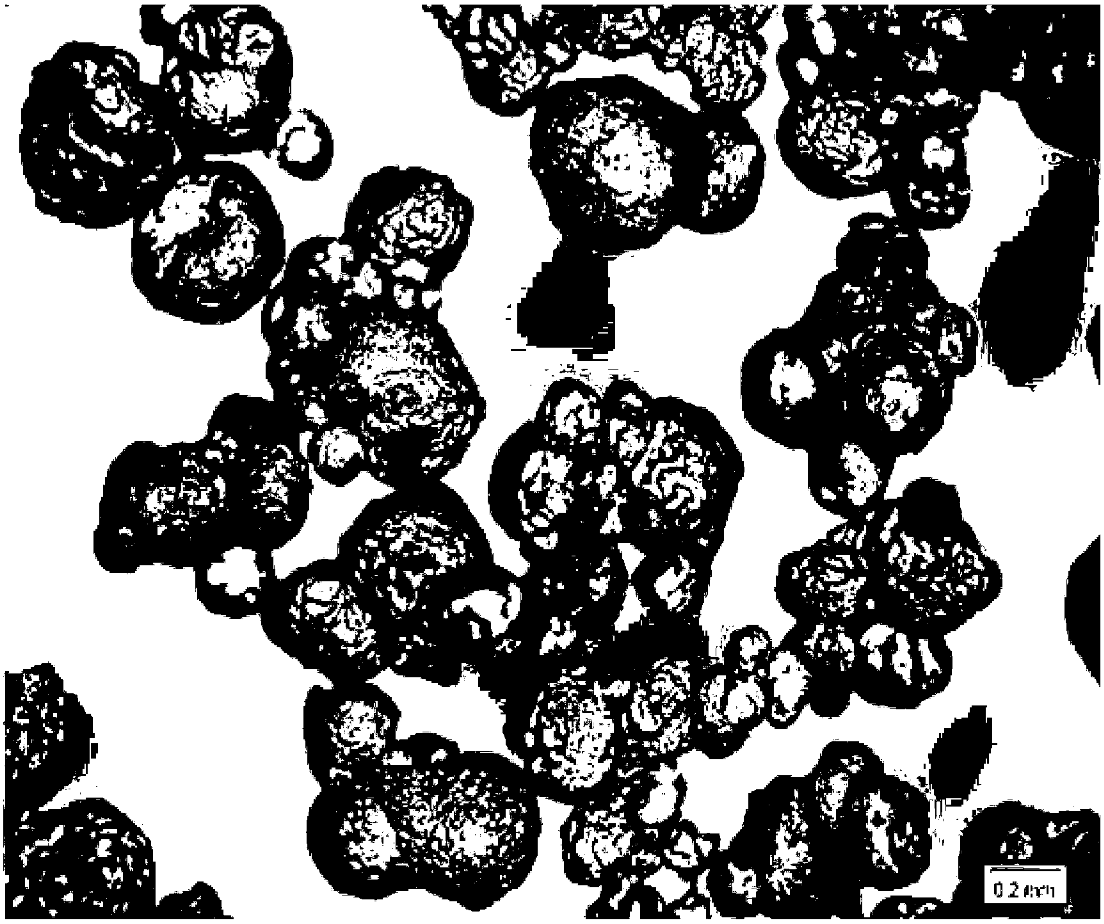
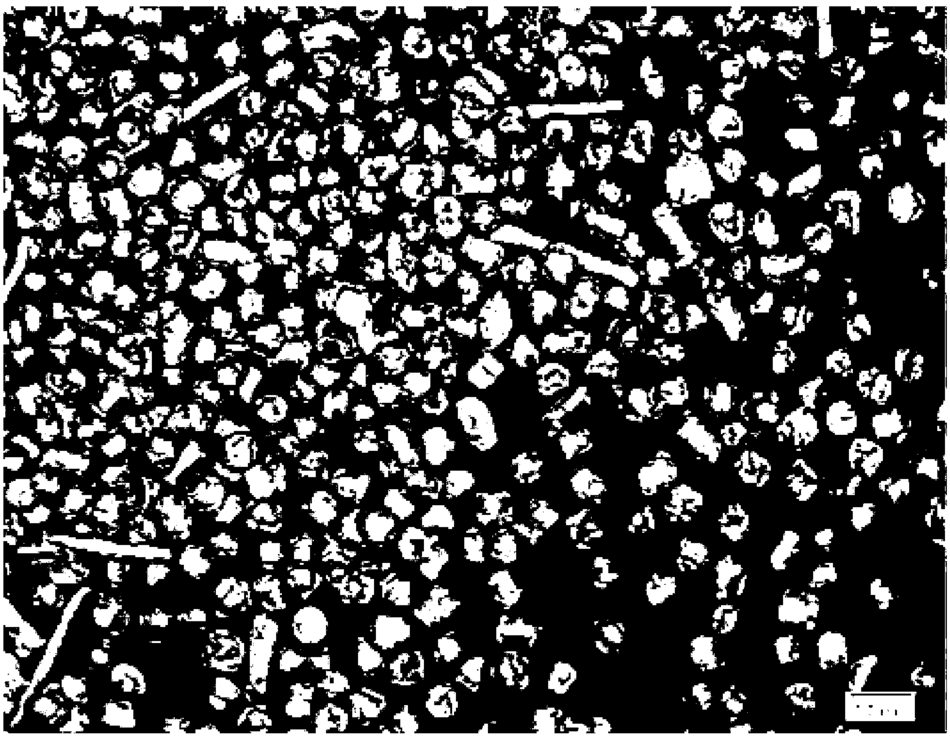


Figure 4

Figure 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2015/000353

A. CLASSIFICATION OF SUBJECT MATTER

B22F 9/04 (2006.01) B02C 7/00 (2006.01) C22C 14/00 (2006.01)

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)

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

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

WPI, EPODOC: /IC/CC (B22F 9/04, B02C, C22C 14/00) using keywords (PRODUCE, POWDER, PARTICULATES, SHEAR, MILLING, SIZE, MORPHOLOGY) and like terms

ESPACENET, AUSPAT: Applicant(s) and Inventor(s) name searched

ESPACENET; GOOGLE PATENTS: using keywords (PRODUCE, POWDER, PARTICULATES, SHEAR, MILLING, SIZE, MORPHOLOGY) and like terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C   [X] See patent family annex

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 August 2015	12 August 2015

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
Email address: pct@ipaustralia.gov.au

Authorised officer

Vijaya Mathe
AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No. 0262256162

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 5986877 A (PATHARE et al.) 16 November 1999	
X	column 2, lines 12 – 26; column 5, lines 24 – 29; column 6, lines 1 – 63; column 8, lines 1 – 6; column 13, lines 22 – 36, 52 – 54; table 6	1 - 15, 22 - 25
Y	column 2, lines 12 – 26; column 5, lines 24 – 29; column 6, lines 1 – 63; column 8, lines 1 – 6; column 13, lines 22 – 36, 52 – 54; table 6	16 - 21
	WO 2000/071256 A1 (APV NORTH AMERICA, INC.) 30 November 2000	
Y	column 2, lines 12 – 26; column 5, lines 24 – 29; column 6, lines 1 – 63; column 8, lines 1 – 6; column 13, lines 22 – 36, 52 – 54; table 6	16 - 21
	US 2012/0006922 A1 (WILSON et al.) 12 January 2012	
A	abstract; claims 1 - 16; figures 1 - 19	1 - 25
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A	page 1, lines 40 - 76; page 2, line 102 - page 3, line 12; claims 1 - 7; figures 1 - 3	1 - 25

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.