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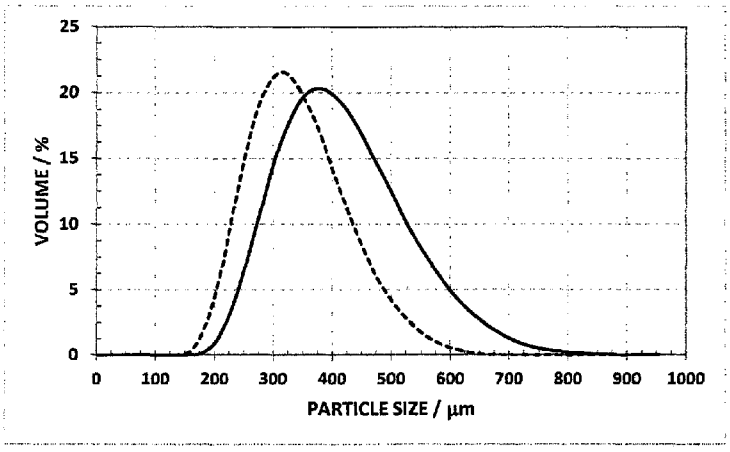


FIGURE 3

(57) Abstract: A method is provided for producing a metal powder suitable for a powder metallurgy process. The method involves steps of identifying a first set of powder size characteristics that define a metal powder suitable for use in a powder metallurgy process, obtaining a non-metallic powder comprising a plurality of non-metallic particles, selecting a fraction of the non-metallic particles having a second set of powder size characteristics, and reducing the selected fraction of non-metallic particles to a metal powder. The metal powder formed by the reduction has powder size characteristics approximating the first set of powder size characteristics and is suitable for use in the powder metallurgy process. The method preferably allows the reduction of a non-metallic feedstock directly to a powder having desired powder size characteristics, such as a desired particle size distribution, for use in a powder metallurgy process without need for any further processing.

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Production of powder for powder metallurgy

The invention relates to a method for producing metal powder suitable for use in a selected powder metallurgy process.

Background

The present invention concerns a method for the production of metal powder by reduction of a feedstock comprising a plurality of non-metallic particles, such as oxide particles. As is known from the prior art, electrolytic processes may be used, for example, to reduce metal compounds or semi-metal compounds to metals, semi-metals, or partially reduced compounds, or to reduce mixtures of metal compounds to form alloys. In order to avoid repetition, unless otherwise indicated the term metal will be used in this document to encompass all such products, such as metals, semi-metals, alloys, intermetallics. The skilled person will appreciate that the term metal may, where appropriate, also include partially reduced products.

In recent years, there has been great interest in the direct production of metal by direct reduction of a solid feedstock, for example, a metal-oxide feedstock. One such direct reduction process is the Cambridge FFC® electro-decomposition process (as described in WO 99/64638). In the FFC process, a solid compound, for example a metal oxide, is arranged in contact with a cathode in an electrolysis cell comprising a fused salt. A potential is applied between the cathode and an anode of the cell such that the compound is reduced. In the FFC process, the potential that produces the solid compound is lower than a deposition potential for a cation from the fused salt.

Other reduction processes for reducing feedstock in the form of a cathodically connected solid metal compound have been proposed, such as the Polar® process described in WO 03/076690 and the process described in WO 03/048399.

Conventional implementations of the FFC process and other solid-state electrolytic reduction processes typically involve the production of a feedstock in the form of a porous preform or precursor, fabricated from a sintered powder of the solid compound to be reduced. This porous preform is then painstakingly coupled to a cathode to enable the reduction to take place. Once a number of preforms have been coupled to the cathode, then the cathode can be lowered into the molten salt and the preforms can be reduced. During reduction of many metal oxides, for example titanium dioxide, the individual particles making up the preform undergo further sintering forming a solid mass of metal, which may have entrapped salt.

It may sometimes be desirable to produce metallic powder, for example metal powder for subsequent processing using various known powder metallurgy techniques. Metal powder has

previously been produced by a processing route involving direct reduction of solid preforms, such as pellets, to form solid pellets of reduced metal. After reduction, these reduced pellets may be crushed or ground to form metal powder of a desired particle size. Alternatively, metal powders can be produced by melting and atomisation, thereby producing spherical powders. In addition, some metals such as titanium can be converted to powder by a hydride de-hydride process.

Different powder metallurgy processes require different metal powder size characteristics, and metal powders need to be processed in order to produce the desired characteristics. Waste powder may need to be re-melted if it has size characteristics unsuitable for powder metallurgy, and this is extremely inefficient.

Summary of the Invention

The invention provides a method for producing metal powder as defined in the appended independent claims, to which reference should now be made. Preferred or advantageous features of the invention are set out in various dependent sub-claims.

Thus, a method of producing metal powder for a powder metallurgy process may comprise the steps of, identifying a first set of powder size characteristics defining a metal powder suitable for use in a particular powder metallurgy process, obtaining a non-metallic powder comprising a plurality of non-metallic particles, selecting a fraction of the non-metallic particles having a second set of powder size characteristics, and reducing the selected fraction of non-metallic particles to a metal powder, the metal powder having powder size characteristics that are approximately equivalent to the first set of powder size characteristics suitable for use in the powder metallurgy process. Preferably the resulting metal powder has the first set of powder size characteristics.

A method of producing a metallic powder may comprise steps of selecting particle size characteristics of a non-metallic feedstock such that metal powder particles resulting from reduction of the feedstock have predetermined particle size characteristics.

Particle size characteristics of a powder may include one or more parameters selected from the list consisting of average particle diameter, median (D50) particle diameter, D10 particle diameter, D90 particle diameter, particle diameter distribution, average particle volume, median particle volume, and particle volume distribution.

The method for producing metallic powder may further comprise the steps of arranging a cathode and an anode in contact with a molten salt within an electrolysis cell, arranging a

volume of feedstock comprising the selected fraction of non-metallic particles within the electrolysis cell, causing a molten salt to flow through the volume of feedstock, and applying a potential between the cathode and the anode such that the feedstock is reduced to metal.

The method for producing metallic powder may further comprise the steps of arranging a cathode and an anode in contact with a molten salt within an electrolysis cell, an upper surface of the cathode supporting a feedstock comprising the selected fraction of non-metallic particles, and a lower surface of the anode being vertically spaced from the feedstock and the cathode, and applying a potential between the cathode and the anode such that the feedstock is reduced to metal.

The method for producing metallic powder may further comprise the steps of arranging a cathode and an anode in contact with a molten salt within an electrolysis cell, an upper surface of the cathode supporting a free-flowing feedstock comprising the selected fraction of discrete non-metallic particles, and a lower surface of the anode being vertically spaced from the feedstock and the cathode, and applying a potential between the cathode and the anode such that the feedstock is reduced to a plurality of discrete metal particles.

The following preferred or advantageous features may be used in conjunction with any aspect described above. Preferred and advantageous features may be combined in any permutation or combination.

It is preferred that the feedstock formed from the selected fraction of non-metallic particles is a free-flowing powder comprising a plurality of separate discrete particles of feedstock material. The use of free-flowing particles, for example free-flowing powder particles, as a feedstock may provide considerable advantage over prior art electro-decomposition methods that have required a powdered non-metallic feedstock to be formed into a porous perform or precursor prior to reduction. Preferably, individual particles in the feedstock are reduced to individual particles of metal. Preferably, there is substantially no alloying between separate particles during reduction of the feedstock to metal. Preferably, there is substantially no sintering between adjacent feedstock particles during reduction.

In the prior art, powder has been formed by reducing pellets of oxide material (each pellet formed by consolidation of thousands of individual oxide particles) into pellets of metal. These metal pellets have then been crushed to form metal powder. The metal powder is then further processed to produce a metal powder of desired characteristics for a particular end use, for example by sieving to select a particular size distribution and/or a particular average particle size of the metallic powder. The inventors have determined that, contrary to previous understanding, it is possible to reduce a non-metallic feedstock, comprising discrete particles of

feedstock material, directly into a powder comprising discrete particles of metal material. Not only is the step of preparing feedstock preforms eliminated (which was previously understood to be essential), but there is no need to crush reduced pellets to form a commercially usable metallic powder. Furthermore, by processing the non-metallic powder to select a specific powder size characteristic, no energy is wasted in reducing material that will not be used in the desired powder metallurgy process.

Advantageously, the feedstock may be naturally occurring sand or fine gravel or may comprise free-flowing particles derived from a naturally occurring sand or very fine gravel. The sand or gravel may be a beneficiated sand or gravel. Sands and gravels may contain one or more metallic ore minerals, either as whole particles or as crystallites within particles. Such minerals may be reduced using a process according to the invention to extract the metallic component. For example, the feedstock may derive from a naturally occurring rutile sand. Rutile is the most common naturally occurring titanium dioxide polymorph.

The feedstock may comprise particles derived from crushed rock, for example a crushed ore. The feedstock may comprise particles derived from a crushed slag, for example a slag formed by heating a mineral sand or ore.

Advantageously, the feedstock may comprise a naturally occurring mineral. For example, the feedstock may comprise a naturally occurring sand such as rutile or ilmenite. Such natural sands comprise many particles, each of which may have a different composition. Such sands may also comprise multiple grains of different mineral types.

Particles of material, and particularly particles of sand, are rarely perfect spheres. In practice individual particles may have different lengths, widths, and breadths. For convenience, however, particle sizes are usually stated as a single diameter, which is approximately correct providing the particles do not have an excessively high aspect ratio. Sands and gravels may be described by a single average particle size for the purposes of this invention.

Preferably, a feedstock suitable for use in an embodiment of the invention substantially comprises free-flowing particles of between about 5 microns and 4000 microns. For example, for some applications a feedstock may be selected having a range of particles of with particles sizes of between 62.5 microns and 4 mm in diameter.

Average particle size may be determined by a number of different techniques, for example by sieve analysis, laser diffraction, dynamic light scattering, disc centrifuge, or image analysis. While the exact value of the average particle size of a sample of sand may differ slightly depending on the measurement technique used to determine the average value, in practice the values will be of the same order providing the particles do not have an excessively high aspect

ratio. For example, the skilled person will appreciate that the same sand may be found to have an average particle diameter of perhaps 1.9 mm if analysed by sieving, but 2.1 mm if analysed by a different technique, such as image analysis. The present invention involves powder size characteristics of a selected fraction of non-metallic particles and the metal powder that results from reduction of the non-metallic particles. It does not matter what measurement method is used to measure the powder size characteristics of the non-metallic and metal particles as long as the measurement methods are comparable.

The optimum average particle size, or optimum median particle size, of a feedstock will depend on the desired end use of the resulting metal powder. Different powder metallurgy processes have different powder requirements in terms of parameters such as average particle size and particle size distribution. A preferred metal powder for use in powder metallurgy may have an average particle size of between 5 microns and 250 microns, for example between 10 microns and 200 microns, or between 30 microns and 150 microns, or between 50 microns and 100 microns.

Sometimes a larger particle diameter is desired for a particular process. Thus, a preferred feedstock may have an average particle diameter of between 60 microns and 2 mm, preferably between 100 microns and 1.75 mm, for example between 250 microns and 1.5 mm. It is preferred that the average particle diameter is determined by laser diffraction. For example, the average particle size could be determined by an analyser such as the Malvern Mastersizer Hydro 2000MU.

It may be desirable to specify the range of particle size in a feedstock. A feedstock containing particles that vary in diameter over a wide range may pack more densely than a feedstock in which the majority of the particles are of substantially the same particle size. This may be due to smaller particles filling interstices between adjacent larger particles. It may be desirable that a volume of a feedstock has sufficient open space or voidage for a molten salt to flow freely through a bed formed by the feedstock. If the feedstock packs too densely, then the molten salt flow-path through the feedstock may be inhibited.

Particle size range may be determined by laser diffraction. For example, the particle size range could be determined by an analyser such as the Malvern Mastersizer Hydro 2000MU.

It may be convenient to select a feedstock size range by a process of sieving. The selection of size ranges or size fractions of particles by sieving is well known. One standard way of defining the particle size distribution in a sample of particles is to refer to D10, D50 and D90 values. D10 is the particle diameter value that 10% of the population of particles lies below. D50 is the particle diameter value that 50 % of the population lies below and 50% of the population lies

above. D50 is also known as the median particle size value. D90 is the particle diameter value that 90 % of the population lies below. A feedstock sample that has a wide particle size distribution will have a large difference between D10 and D90 values. Likewise, a feedstock sample that has a narrow particle size distribution will have a small difference between D10 and D90.

Particle size distribution may be determined by laser diffraction. For example, the particle size distribution, including D10, D50 and D90 values, could be determined by an analyser such as the Malvern Mastersizer Hydro 2000MU.

Preferred metallic powder size ranges may vary depending on the desired end use of the metallic powder. For example, the following provides an indication of the ranges that are typically preferred for different powder metallurgy processes. In each case, the lower value of the range indicated the D10 particle size and the upper value of the range represents the D90 particle size.

Metal injection moulding (MIM) – particle size range between 5 and 30 microns.
Gas dynamic cold spray (GDCS) – particle size range between 15 and 45 microns.
Selective laser melting (SLM) – particle size range between 20 and 50 microns.
Electron beam melting (EBM) – particle size range between 50 and 100 microns.
Laser metal deposition (LMD) – particle size range between 50 and 125 microns.
Cold isostatic pressing (CIP) – particle size range between 45 and 150 microns.
Hot isostatic pressing (HIP) – particle size range between 45 and 200 microns.

The actual particle size range of a powder for use in any of the identified processes above may vary outside the stated ranges. These figures are provided as a guideline indicating the preferred or ideal particle size ranges for metal powders used in these processes.

The method may provide a step of identifying a preferred metal particle size range suitable for a specific powder metallurgy process as indicated above, selecting a non-metallic feedstock having a different particle size range, i.e. having D10 and D90 values greater than the preferred D10 and D90 values, and reducing the feedstock particles to provide a metal powder having approximately the preferred metal particle size range.

The method may provide a step of identifying a preferred median metal particle size (in other words the D50 particle size of the metal powder) suitable for a specific powder metallurgy process as indicated above, selecting a non-metallic feedstock having a different median particle size, greater than the desired D50 value of the metal product, and reducing the feedstock particles to provide a metal powder having approximately the preferred median metal particle size.

The method may provide a step of identifying a preferred average metal particle size suitable for a specific powder metallurgy process as indicated above, selecting a non-metallic feedstock having a different average particle size, greater than the desired value of the metal product, and reducing the feedstock particles to provide a metal powder having approximately the preferred average metal particle size.

The second set of powder size characteristics are preferably between 7.5 percent and 40 percent larger in magnitude than the first set of powder size characteristics, when the first and second sets of powder characteristics are measured by the same measuring technique. The second set of powder size characteristics may be between 10 percent and 30 percent larger in magnitude than the first set of powder size characteristics, for example between 15 percent and 25 percent larger in magnitude, preferably between 17 percent and 23 percent larger in magnitude.

Thus, the average particle diameter of the non-metallic feedstock may be between 7.5 percent and 40 percent larger than the preferred or idealised average metal particle diameter. The average particle diameter of the non-metallic feedstock may be between 10 percent and 30 percent larger in magnitude than the preferred average metal particle diameter, for example between 15 percent and 25 percent larger in magnitude, preferably between 17 percent and 23 percent larger in magnitude.

Likewise, the D10, D50, or D90 particle diameter of the non-metallic feedstock may be between 7.5 percent and 40 percent larger than the respective D10, D50, or D90 particle diameter of the preferred metal powder. The D10, D50 or D90 diameter of the non-metallic feedstock may be between 10 percent and 30 percent larger in magnitude than the respective D10, D50, or D90 particle diameter of the preferred metal powder, for example between 15 percent and 25 percent larger in magnitude, preferably between 17 percent and 23 percent larger in magnitude.

It may be desired to produce a metal powder for use in metal injection moulding (MIM). As stated above, an ideal powder for MIM processing may have a powder size range having D10 diameter of 5 microns and D90 diameter of 30 microns. In order to produce a metal powder with approximately this powder size range by reduction of a non-metallic feedstock it is preferred that a fraction of non-metallic powder is selected having a D10 particle diameter between 5.375 and 7 microns and a D90 particle diameter between 32.25 and 42 microns, for example D10 between 5.75 and 6.25 microns and D90 between 34.5 microns and 37.5 microns.

It may be desired to produce a metal powder for use in gas dynamic cold spray (GDCS). As stated above, an ideal powder for GDCS processing may have a powder size range having D10 diameter of 15 microns and D90 diameter of 45 microns. In order to produce a metal powder

with approximately this powder size range by reduction of a non-metallic feedstock it is preferred that a fraction of non-metallic powder is selected having a D10 particle diameter between 16 and 21 microns and a D90 particle diameter between 48 and 63 microns, for example D10 between 17.25 and 18.75 microns and D90 between 51.75 microns and 56.25 microns.

It may be desired to produce a metal powder for use in selective laser melting (SLM). As stated above, an ideal powder for SLM processing may have a powder size range having D10 diameter of 20 microns and D90 diameter of 50 microns. In order to produce a metal powder with approximately this powder size range by reduction of a non-metallic feedstock it is preferred that a fraction of non-metallic powder is selected having a D10 particle diameter between 21.5 and 28 microns and a D90 particle diameter between 53.75 and 70 microns, for example D10 between 23 and 25 microns and D90 between 57.5 microns and 62.5 microns.

It may be desired to produce a metal powder for use in electron beam melting (EBM). As stated above, an ideal powder for EBM processing may have a powder size range having D10 diameter of 50 microns and D90 diameter of 100 microns. In order to produce a metal powder with approximately this powder size range by reduction of a non-metallic feedstock it is preferred that a fraction of non-metallic powder is selected having a D10 particle diameter between 54 and 70 microns and a D90 particle diameter between 108 and 140 microns, for example D10 between 57 and 63 microns and D90 between 115 microns and 125 microns.

It may be desired to produce a metal powder for use in laser metal deposition (LMD). As stated above, an ideal powder for LMD processing may have a powder size range having D10 diameter of 50 microns and D90 diameter of 125 microns. In order to produce a metal powder with approximately this powder size range by reduction of a non-metallic feedstock it is preferred that a fraction of non-metallic powder is selected having a D10 particle diameter between 54 and 70 microns and a D90 particle diameter between 134 and 175 microns, for example D10 between 57 and 63 microns and D90 between 144 microns and 156 microns.

It may be desired to produce a metal powder for use in cold isostatic pressing (CIP). As stated above, an ideal powder for CIP processing may have a powder size range having D10 diameter of 45 microns and D90 diameter of 150 microns. In order to produce a metal powder with approximately this powder size range by reduction of a non-metallic feedstock it is preferred that a fraction of non-metallic powder is selected having a D10 particle diameter between 48 and 63 microns and a D90 particle diameter between 161 and 210 microns, for example D10 between 52 and 56 microns and D90 between 172 microns and 188 microns.

It may be desired to produce a metal powder for use in hot isostatic pressing (HIP). As stated above, an ideal powder for HIP processing may have a powder size range having D10 diameter of 45 microns and D90 diameter of 200 microns. In order to produce a metal powder with approximately this powder size range by reduction of a non-metallic feedstock it is preferred that a fraction of non-metallic powder is selected having a D10 particle diameter between 48 and 63 microns and a D90 particle diameter between 215 and 280 microns, for example D10 between 52 and 56 microns and D90 between 230 microns and 250 microns.

Feedstock particle size fractions can be made using any known method. A convenient method is sieving, but other methods of selecting specific particle size fractions, to an approximate accuracy, may be used.

For some applications, it may be preferable that the D90 diameter of the feedstock is no more than 200% greater than the D10 diameter of the feedstock, preferably no more than 150% greater than D10, or no more than 100% greater than D10. It may be beneficial if the feedstock has a narrow size distribution in which D90 is no more than 75% greater than D10 or no more than 50% greater than D10.

For some applications the D10 diameter of the feedstock is preferably between 10 microns and 80 microns. For some applications the D90 diameter of the feedstock is preferably between 80 microns and 300 microns. D90For some applications a metal powder having larger metal powder particles may be desired. Thus, one embodiment of a feedstock may have a population of particles in which D10 is 1 mm and D90 is 3 mm. Another embodiment of a feedstock may have a population of particles in which D10 is 1.5 mm and D90 is 2.5 mm. Another embodiment of a feedstock may have a population in which D10 is 250 microns and D90 is 400 microns. Another embodiment may have a population in which D10 is 0.5 mm and D90 is 0.75 mm.

Examples of minerals capable of yielding high value metals that may be found in naturally occurring sands and oxide ores include, rutile, ilmenite, anatase, and leucoxene (for titanium), scheelite (tungsten), cassiterite (tin), monazite (cerium, lanthanum, thorium), zircon (zirconium hafnium and silicon), cobaltite (cobalt), chromite (chromium), bertrandite and beryl (beryllium, aluminium, silicon), uranite and pitchblende (uranium), quartz (silicon), molybdenite (molybdenum and rhenium) and stibnite (antimony). One or more of these minerals may be suitable as a component of a feedstock for use in the present invention. This list of minerals is not exclusive. The invention may be used to reduce particles of material, for example sands or crushed ores, that contain one or more minerals not listed above.

The reduction time is advantageously as low as possible, to limit or prevent sintering of individual particles of the metal powder product. Advantageously, the reduction time may be

lower than 100 hours, preferably lower than 60 hours or lower than 50 hours. Particularly preferably the reduction time is lower than 40 hours.

The salt temperature is advantageously as low as possible, to limit or prevent sintering of individual particles of the metal product. Preferably, the molten salt temperature during reduction is maintained to be lower than 1100°C, for example lower than 1000°C, or lower than 950°C, or lower than 900°C.

Advantageously, the feedstock may be reduced with substantially no sintering between individual particles such that a metallic powder can be recovered having an average diameter that is lower than an average diameter of the particles making up the feedstock. The reason that the metallic particles are typically smaller than the feedstock particles is that the feedstock particles tend to have a ceramic structure that includes a non-metallic element such as oxygen or sulphur, whereas the reduced particles have a metallic structure from which much of this non-metallic element has been removed.

The reduced feedstock may form a friable mass of individual metallic particles. Advantageously, such a friable mass may be easily broken up to form a free-flowing metallic powder. Preferably, substantially every particle forming the metallic powder corresponds to a non-metallic particle from the feedstock.

The methods according to various embodiments of the invention described above may be particularly suitable for the production of metal powder by the reduction of a solid feedstock comprising particles of metal oxide or metal oxides. Pure metal powders may be formed by reducing pure metal oxides, and alloy powders and intermetallics may be formed by reducing feedstocks comprising particles of mixed metal oxides. The non-metallic powders used may be synthetically produced metal oxide powders. Preferably metal powders formed by processes embodying the invention have an oxygen content of lower than 5000 ppm, preferably lower than 4000 ppm, or lower than 3,500 ppm.

In preferred embodiments the metal powder is a titanium powder or a titanium alloy powder. In these embodiments the feedstock consists of or comprises a titanium oxide, such as TiO2, or a titanium-bearing mineral such as rutile, synthetic rutile, or ilmenite.

Some reduction processes may only operate when the molten salt or electrolyte used in the process comprises a metallic species (a reactive metal) that forms a more stable oxide than the metallic oxide or compound being reduced. Such information is readily available in the form of thermodynamic data, specifically Gibbs free energy data, and may be conveniently determined from a standard Ellingham diagram or predominance diagram or Gibbs free energy diagram. Thermodynamic data on oxide stability and Ellingham diagrams are available to, and

understood by, electrochemists and extractive metallurgists (the skilled person in this case would be well aware of such data and information).

Thus, a preferred electrolyte for an electrolytic reduction process may comprise a calcium salt. Calcium forms a more stable oxide than most other metals and may therefore act to facilitate reduction of any metal oxide that is less stable than calcium oxide. In other cases, salts containing other reactive metals may be used. For example, a reduction process according to any aspect of the invention described herein may be performed using a salt comprising lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, barium, or yttrium. Chlorides or other salts may be used, including mixture of chlorides or other salts.

By selecting an appropriate electrolyte, almost any metal oxide particles may be capable of reduction using the methods and apparatuses described herein. Naturally occurring minerals containing one or more such oxides may also be reduced. In particular, oxides of beryllium, boron, magnesium, aluminium, silicon, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, germanium, yttrium, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, and the lanthanides including lanthanum, cerium, praseodymium, neodymium, samarium, may be reduced, preferably using a molten salt comprising calcium chloride.

The skilled person would be capable of selecting an appropriate electrolyte in which to reduce a particular metal oxide, and in the majority of cases an electrolyte comprising calcium chloride will be suitable.

Preferably, the reduction occurs by an electro-decomposition or electro-deoxidation process such as the FFC Cambridge process or the BHP Polar process and the process described in WO03/048399.

Specific embodiment of the invention

A specific embodiment of the invention will now be described with reference the accompanying drawings, in which;

Figure 1 is a schematic diagram illustrating an electrolysis apparatus arranged for performing a method according to an embodiment of the invention,

Figure 2A is a schematic cross-sectional view illustrating additional detail of the cathode structure of the electrolysis apparatus of figure 1,

Figure 2B is a plan view of the cathode illustrated in figure 2A, and

Figure 3 is a particle size distribution plot illustrating the particle size distributions of the feedstock and resulting metal powder from example 4.

Figure 1 illustrates an electrolysis apparatus 10 configured for use in performing a reduction on a feedstock comprising a plurality of non-metallic particles. The apparatus comprises a stainless steel cathode 20 and a carbon anode 30 situated within a housing 40 of an electrolysis cell. The anode 30 is disposed above, and spatially separated from, the cathode 20. The housing 40 contains 500 kg of a calcium chloride based molten salt electrolyte 50, the electrolyte comprising $CaCl_2$ and 0.4 wt % CaO (the electrolyte composition may be varied), and both the anode 30 and the cathode 20 are arranged in contact with the molten salt 50. Both the anode 30 and the cathode 40 are coupled to a power supply 60 so that a potential can be applied between the cathode and the anode.

The cathode 20 and the anode 30 are both substantially horizontally oriented, with an upper surface of the cathode 20 facing towards a lower surface of the anode 30.

The cathode 20 incorporates a rim 70 that extends upwards from a perimeter of the cathode and acts as a retaining barrier for a feedstock 90 supported on an upper surface of the cathode. The rim 70 is integral with, and formed from the same material as, the cathode. In other embodiments, the rim may be formed from a different material to the cathode, for example from an electrically insulating material.

The structure of the cathode may be seen in more detail in Figure 2A and Figure 2B. The rim 70 is in the form of a hoop having a diameter of 30 cm. A first supporting cross-member 75 extends across a diameter of the rim. The cathode also comprises a mesh-supporting member 71, which is in the form of a hoop having the same diameter as the rim 70. The mesh-supporting member has a second supporting cross-member 76 of the same dimensions as the supporting cross-member 75 on the rim 70. A mesh 80 is supported by being sandwiched between the rim 70 and the mesh-supporting member 71 (the mesh 80 is shown as the dotted line in Figure 2A). The mesh 80 comprises a stainless steel cloth of mesh-size 100 (the mesh size may be altered depending on the feedstock particle size; for example for smaller particles a smaller mesh size such as 635, which has 20 micron apertures, may be used) that is held in tension by the rim 70 and the mesh-supporting member. The cross-member 75 is disposed against a lower surface of the mesh 80 and acts to support the mesh. An upper surface of the mesh 80 acts as the upper surface of the cathode.

The stainless steel cloth forming the mesh 80 is fabricated from 30 micrometre thick wires of 304 grade stainless steel that have been woven to form a cloth having square holes with a 150 micrometre opening. The mesh 80, cross-member 75 and rim 70 that form the cathode are all

electrically conductive. In other embodiments, the mesh may be the only electrically conductive component of the cathode.

Example 1

It was desired to form a titanium alloy powder optimised for use in hot isostatic pressing (HIP). A preferred powder for use in HIP is predominantly formed of discrete powder particles having a particle size between 45 microns and 200 microns.

A feedstock was prepared by sieving synthetic rutile particles and selecting the fraction falling between meshes of 150 microns and 250 microns. The median (D50) particle size of this synthetic rutile powder, as measured using a Malvern Mastersizer 2000MU, was 180 microns.

About 3 kg of the feedstock 90 was arranged on the upper surface of the cathode 20 and in contact with the molten salt 50 (which consisted of $CaCl_2$ and 0.4 wt % CaO). Thus, the feedstock 90 was supported by the mesh 80 of the cathode and retained at a depth of approximately 2 cm by the cathode-rim 70. The bed depth of the feedstock is approximately 100 times the average particle diameter of the synthetic rutile particles.

The molten salt was maintained at a temperature of about 950 °C and a potential was applied between the anode and the cathode. Thermal currents and gas lift effect generated by the buoyancy of the gases (which are predominantly CO and CO_2) generated at the anode cause the molten salt to circulate within the cell and generate flow through the bed of synthetic rutile supported on the cathode. The cell was operated in constant current mode, at a current of 400 A, for 52 hours. After this time, the cell was cooled and the cathode removed and washed to free salt from the reduced feedstock.

The reduced feedstock was removed from the cathode as a friable lump or cake of metallic powder particles that could be separated using light manual pressure. These metal powder particles were then dried and the average particle size was determined. The median (D50) particle size of the metallic powder, as measured using a Malvern Mastersizer 2000MU, was 160 microns. Thus, the median (D50) particle size of the reduced metallic powder is about 11 % smaller than that of the feedstock powder. In other words, the median (D50) particle size of the feedstock powder is about 12.5 % larger than that of the reduced metal powder.

Example 2

It was desired to form a titanium powder optimised for use in electron beam melting (EBM). A preferred powder for use in EBM is predominantly formed of discrete powder particles having a particle size between 50 microns (D10) and 100 microns (D90).

A feedstock was prepared by sieving pigment grade TiO_2 particles. The D10, D50, D90 particle size of this sieved pigment grade powder, as measured using a Malvern Mastersizer 2000MU, was 101 microns, 137 microns, and 188 microns respectively.

About 6.2 kg of the feedstock was arranged on the upper surface of the cathode and in contact with the molten salt (which consisted of $CaCl_2$ and 0.87 wt % CaO). Thus, the feedstock was supported by the mesh of the cathode. The bed depth of the feedstock was approximately 200 times the average particle diameter of the particles.

The molten salt was maintained at a temperature of about 950 °C and a potential was applied between the anode and the cathode. The cell was operated in constant current mode, at a current of 400 A, for 72 hours. After this time, the cell was cooled and the cathode removed and washed to free salt from the reduced feedstock.

The reduced feedstock was removed from the cathode as a friable lump or cake of metallic powder particles that could be separated using light manual pressure. These metallic powder particles were then dried and the particle characteristics of the metallic powder were determined. The D10, D50, D90 particle size of this metallic titanium powder, as measured using a Malvern Mastersizer 2000MU, was 71 microns, 111 microns, and 172 microns respectively. In other words, the median (D50) particle size of the feedstock powder is about 23 % larger than that of the reduced metal powder.

Example 3

It was desired to form a titanium alloy powder optimised for use in hot isostatic pressing (HIP) or cold isostatic pressing (CIP). A preferred powder for use in HIP or CIP is predominantly formed of discrete powder particles having a particle size between 45 microns and 200 microns.

A feedstock was prepared by sieving natural rutile particles and selecting the fraction falling between meshes of 150microns and 212 microns. The D10, D50, D90 particle size of this pigment grade powder, as measured using a Malvern Mastersizer 2000MU, was 130 microns, 183 microns, and 258 microns respectively.

About 5 kg of the feedstock was arranged on the upper surface of the cathode and in contact with the molten salt (which consisted of $CaCl_2$ and 0.55 wt % CaO). Thus, the feedstock was supported by the mesh of the cathode. The bed depth of the feedstock was approximately 65 times the average particle diameter of the natural rutile particles.

The molten salt was maintained at a temperature of about 950 °C and a potential was applied between the anode and the cathode. The cell was operated in constant current mode, at a

current of 400 A, for 52 hours. After this time, the cell was cooled and the cathode removed and washed to free salt from the reduced feedstock.

The reduced feedstock was removed from the cathode as a friable lump or cake of metallic powder particles that could be separated using light manual pressure. These metallic powder particles were then dried and the particle characteristics of the metallic powder were determined. The D10, D50, D90 particle size of this metallic titanium alloy powder, as measured using a Malvern Mastersizer 2000MU, was 105 microns, 158 microns, and 238 microns respectively. Thus, the median (D50) particle size of the reduced metallic powder is about 14 % smaller than that of the feedstock powder. Alternatively, the median (D50) particle size of the feedstock powder can be said to be about 16 % larger than that of the reduced metal powder.

During trials, the powder was successfully used in a HIP process and a CIP process. Furthermore, a sample of the powder was also successfully used in an SLM process, although the laser power used was high and the deposition rate was low, to take account of the relatively large powder particle size.

Example 4

A feedstock was prepared by sieving pigment grade TiO_2 particles and selecting the fraction falling between meshes of 300 microns and 500 microns. The D10, D50, D90 particle size of this pigment grade powder, as measured using a Malvern Mastersizer 2000MU, was 291 microns, 406 microns, and 568 microns respectively.

About 7 kg of the feedstock was arranged on the upper surface of the cathode and in contact with the molten salt (which consisted of $CaCl_2$ and 0.55 wt % CaO). Thus, the feedstock was supported by the mesh of the cathode. The bed depth of the feedstock was approximately 200 times the average particle diameter of the particles.

The molten salt was maintained at a temperature of about 950 °C and a potential was applied between the anode and the cathode. The cell was operated in constant current mode, at a current of 400 A, for 92 hours. After this time, the cell was cooled and the cathode removed and washed to free salt from the reduced feedstock.

The reduced feedstock was removed from the cathode as a friable lump or cake of metallic powder particles, which were extracted and then dried. The particle characteristics of the metallic powder were then determined. The D10, D50, D90 particle size of this metallic titanium powder, as measured using a Malvern Mastersizer 2000MU, was 246 microns, 337 microns, and 462 microns respectively. Thus, the median (D50) particle size of the reduced metallic powder is about 17 % smaller than that of the feedstock powder. Alternatively, the median (D50)

particle size of the feedstock powder can be said to be about 20.5 % larger than that of the reduced metal powder.

Figure 3 illustrates the particle size distribution curves for both the feedstock (solid line) and resulting metal powder (dotted line) of this example.

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Claims

1. A method of producing a metal powder for a powder metallurgy process comprising the steps of,

identifying a first set of powder size characteristics defining a metal powder suitable for use in a powder metallurgy process,

obtaining a non-metallic powder comprising a plurality of non-metallic particles,

selecting a fraction of the non-metallic particles having a second set of powder size characteristics, and

reducing the selected fraction of non-metallic particles to a metal powder, the metal powder having powder size characteristics approximating the first set of powder size characteristics suitable for use in the powder metallurgy process.

2. A method of producing a metal powder according to claim 1 in which the powder size characteristics include one or more of the characteristics selected from the list consisting of average particle diameter, median (D50) particle diameter, D10 particle diameter, D90 particle diameter, particle diameter distribution, average particle volume, median particle volume, and particle volume distribution.

3. A method according to claim 1 or 2 in which the second set of powder size characteristics are between 7.5 percent and 40 percent larger in magnitude than the first set of powder size characteristics, when the first and second sets of powder characteristics are measured by the same measuring technique.

4. A method according to claim 3 in which the second set of powder size characteristics are between 10 percent and 30 percent larger in magnitude than the first set of powder size characteristics, for example between 15 percent and 25 percent larger in magnitude, preferably between 17 percent and 23 percent larger in magnitude.

5. A method according to any preceding claim in which the metal powder formed by reduction of the selected fraction of non-metallic particles is suitable for use in a selected powder metallurgy process without any further size selection.

6. A method according to any preceding claim in which the plurality of non-metallic particles derive from a naturally occurring sand or ore.

7. A method according to any of claims 1 to 5 in which the plurality of non-metallic particles derive from a synthetically produced oxide.

8. A method according to any preceding claim in which the metal powder is titanium powder or a titanium alloy powder and the plurality of non-metallic particles comprise or consist of titanium oxide or titanium-bearing oxides.

9. A method according to any preceding claim in which reduction of the selected fraction of non-metallic particles is performed by an electrolytic reduction in a molten salt.

10. A method according to claim 9 in which the selected fraction of non-metallic particles are arranged in contact with a cathode in an electrolysis apparatus.

11. A method according to claim 10 in which the electrolysis apparatus is configured such that molten salt flows through a volume of the selected fraction of non-metallic particles during reduction.

12. A method according to any preceding claim comprising the steps of,

arranging a cathode and an anode in contact with a molten salt within an electrolysis cell,

arranging a feedstock consisting of a volume of the selected fraction of non-metallic particles within the electrolysis cell,

causing a molten salt to flow through the volume of feedstock, and

applying a potential between the cathode and the anode such that the feedstock is reduced to metal powder.

13. A method according to any preceding claim, in which the D90 particle size of the selected fraction of non-metallic particles is no more than 200% greater than the D10 particle size of the selected fraction of non-metallic particles.

14. A method according to any preceding claim in which the selected fraction of non-metallic particles comprises one or more naturally occurring minerals, for example in which the feedstock comprises one or more minerals selected from the list consisting of rutile, ilmenite, anatase, leucoxene, scheelite, cassiterite, monazite, lanthanum, zircon, cobaltite, chromite, bertrandite, beryl, uranite, pitchblende, quartz, molybdenite and stibnite.

15. A method according to any preceding claim in which the selected fraction of non-metallic particles are reduced in a molten salt and the temperature during reduction is maintained at less than 1100°C.

16. A method according to any preceding claim in which the reduction is an electrolytic reduction, for example in which the reduction occurs by an electro-decomposition according to the FFC Cambridge process or the BHP Polar process.

17. A method according to any preceding claim in which the step of selecting a fraction of non-metallic particles involved sieving.

18. A metal powder having predetermined powder size characteristics formed using a method according to any preceding claim.

19. A metal powder according to claim 18 comprising a plurality of discrete metallic particles, each of the metal particles formed by the direct reduction of a discrete non-metallic particle.

20. A metallic article formed from a metal powder according to claim 18 or 19.

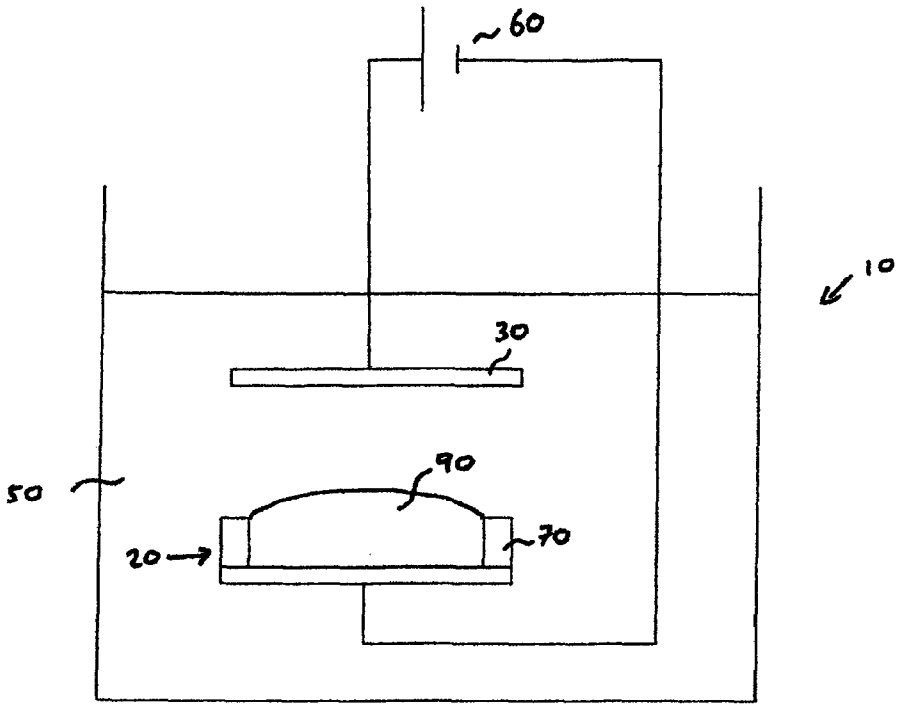


FIGURE 1

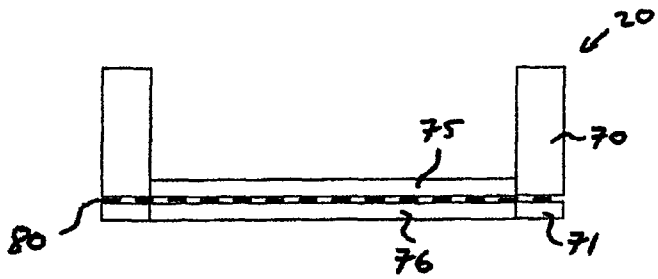


FIGURE 2A

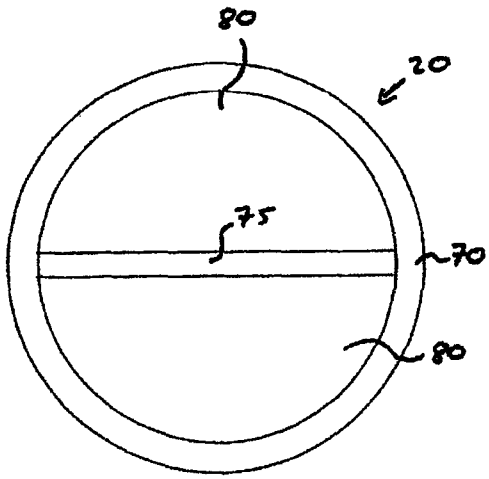


FIGURE 2B

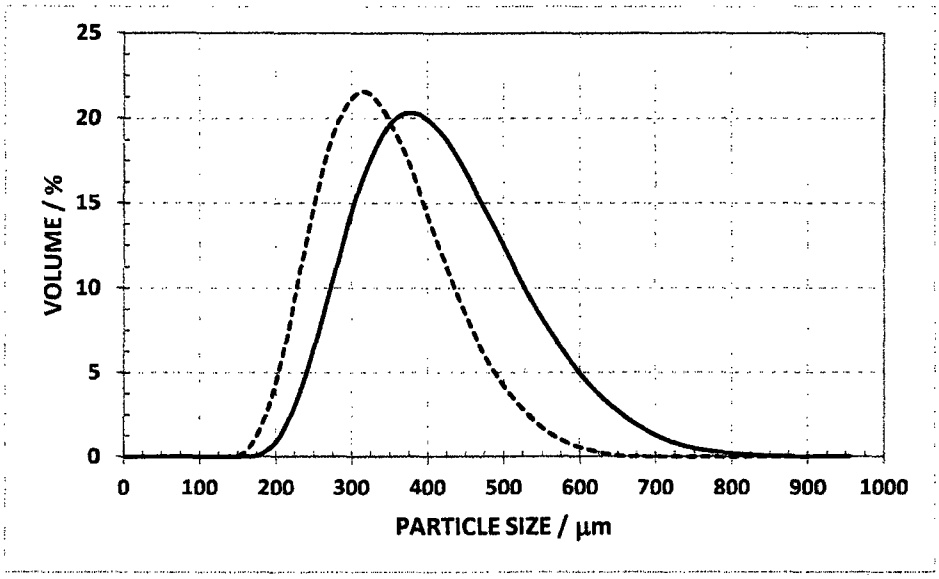

25
20
15
10
5
0
VOLUME / %
0
100
200
300
400
500
600
700
800
900
1000
PARTICLE SIZE / µm

FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/000463

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F9/20 C25C3/26 C25C3/28
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F C25C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X Y	WO 2010/036131 A1 (TITANOX DEV LTD [NZ]; LIANG JING [NZ]) 1 April 2010 (2010-04-01) page 1 page 8, lines 3-10 -----	1-8, 17-20 9-16
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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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	Date of mailing of the international search report
24 January 2014	31/01/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Forestier, Gilles

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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

Information on patent family members

International application No
PCT/GB2013/000463

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