(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 530 385 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
28.08.2019 Bulletin 2019/35

(51) Int Cl.:
B22F 9/08 *(2006.01)* ***B33Y 70/00*** *(2015.01)*
B22F 3/105 *(2006.01)*

(21) Application number: **18020079.2**

(22) Date of filing: **26.02.2018**

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

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(54) **METHOD FOR THE PRODUCTION OF METALLIC POWDERS**

(57) The invention relates to a method for the manufacturing of a metal powder wherein a liquid metal is atomized with a gas or a liquid and wherein the liquid metal is exposed to a controlled gas atmosphere. The controlled atmosphere comprises at least 95% by volume of an inert gas as well as carbon monoxide (CO) and carbon dioxide (CO_2).

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Description

[0001] The invention pertains to a method for producing metal powders according to claim 1.

[0002] Additive manufacturing is a rapidly growing market for metallic powders. It essentially consists of the distribution of a thin layer of a metal powder from a reservoir followed by fusion/sintering of the powder using an energy source (e. g. laser or electron beam). This is repeated building up the final product layer by layer. Powder size and morphology are critical characteristics that significantly impact the product quality. Generally speaking fine powders with a uniform particle size are preferred as this enables greater consistency as individual layers are deposited. Smaller particle sizes allow for thinner layers which determine the resolution of the component detail. From W. J. Sames, F. A. List, S. Pannala, R. R. Dehoff and S. S. Babu (2016: The metallurgy and processing science and metal additive manufacturing, International Material Reviews) an overview over different methods of additive manufacturing can be derived.

[0003] Powder raw materials for these additive manufacturing processes are produced using a variety of atomisation processes. A description of the main methods is available from J. Davis, R. Bowerman and R. Trepleton (2015, 59 (3): Introduction to the additive manufacturing powder metallurgy supply chain; Johnson Matthey Technology Review, 243-256) common routes of powder production are known.

[0004] These routes include water atomisation, gas atomisation, plasma atomisation the hydride-dehydride process and the TiRO™ process.

[0005] As it is mentioned in the article, all atomisation processes begin with melting the feedstock alloy. The melting process has a number of variations but generally, when atomizing using water, the feedstock is first melted in a furnace before being transferred to a tundish (a crucible that regulates the flow rate of the melt into the atomizer). The liquid alloy enters the atomisation chamber from above, in which it is free to fall through the chamber. Water jets are symmetrically positioned around the stream of liquid metal, atomizing and solidifying the particles. The final powder exits at the bottom of the chamber, where it is collected. Additional processing steps are then required to dry the powder. Metal powder produced in this way is typically highly irregular in morphology, which reduces both packing properties and flow properties. Water atomisation is the main method for producing iron and steel powders and typically feeds into the press-and-sintered industries rather than the additive manufacturing industry.

[0006] Gas atomisation processes mimic water atomisation, with the differentiator being the use of gas instead of water during the processing. Air can be used as the atomizing medium, but it's more preferred that an inert gas (nitrogen or argon) will be used to reduce the risk of oxidation and contamination of the metal. The process of melting the metal ingots can be the same as described for water atomisation, however for powders produced for high end applications such as aerospace, the need to control interstitial elements has led to increased use of vacuum induction melting furnaces. In this case the molten stream of liquid enters the atomisation chamber directly from the furnace rather than through a tundish. The stream of liquid metal is atomized by high pressure jets of gas. Due to the lower heat capacity of the gas in comparison with water the metal droplets have an increased solidification time which results in comparatively more spherical powder particles. Whilst it is not possible to have complete control over the particle size of atomized powder, the distribution can be influenced by varying the ratio of the gas to melt flow rate.

[0007] In plasma atomisation it is possible to produce highly spherical particles. The feedstock used in the process can either be in wire form such as the method by AP & C Advanced Powders and Coatings Inc, Canada, or in powder form such as the method used by Tekna Plasma Systems Inc, Canada. The spool of wire or powder feedstock is fed into the atomisation chamber where it is simultaneously melted and atomized by coaxial plasma torches and gas jets. Plasma rotating electrode process is a variation of plasma atomisation whereby a bar of rotating feedstock is used instead of a wire feed. As the rotating bar enters the atomisation chamber plasma torches melt the end of the bar, ejecting material from its surface. The metal solidifies before hitting the walls of the chamber.

[0008] Oxygen content of the powders is a key quality parameter. Surface oxidation can adversely impact the shape and size distribution of powders produced during atomisation and residual oxygen content can lead to embrittlement of welds during the laser processing of powders. This can result in the final product failing to meet mechanical specifications and consequently there is significant pressure to reduce the oxygen content of the precursor powders. As a result there is an interest in using controlled atmospheres to prevent or dramatically reduce the extent of oxidation that occurs during atomisation. Such atmospheres can be used to avoid oxidation during melting, or to prevent oxidation after liquid metal has been transferred to a tundish or indeed there is potential to use such atmospheres to avoid oxidation during atomizing of a liquid metal stream by gas jets.

[0009] EP 2 050 528 B1 describes the use of gaseous boranes or silanes as dopants in Ar or N2 as a method to avoid such oxidation. These are pyrophoric gases that demand specialist handling and infrastructure and hence their application as described in EP 2 050 528 B1 is not practically viable due to the necessary investment and precautionary measures that would be required in a foundry environment. Furthermore, boranes are highly toxic at concentrations much lower than those proposed for the application described in EP 2 050 528 B1.

[0010] CN1174108 discloses an atomisation process for producing a metal powder. In order to reduce oxidation of the powder it is suggested to use a reducing atomisation atmosphere by adding one or more of hydrogen, carbon

monoxide, methane, ethane, propane and the like to the atmosphere. The reducing atmosphere will react with the oxygen present in the atomisation atmosphere, thereby reducing oxidation of the powder.

[0011] However, the addition of substances like CO to the atomisation atmosphere creates a safety issue and leakage of atomizing gas to the environment could easily result in maximum permitted concentrations being exceeded in the working environment.

[0012] Another concern is related to the phenomenon of carbon dusting'. Carbon dusting is a catastrophic form of corrosion associated with carburization of metals and alloys exposed to carbonaceous atmospheres at carbon activities > 1. Dusting has potential to rapidly destroy metallic components of the atomizing system. The carbon activity of a CO:CO2 mixture is related to the thermodynamics of the reaction

$$2CO = CO2 + C \qquad [1]$$

$$\text{Carbon activity} = a_c = \frac{pCO^2}{(PCO_2)\ x\ K}$$

[0013] Where K is the temperature dependent equilibrium constant for reaction 1.

[0014] Kinetics of dusting reactions increase in the presence of hydrogen (Thermodynamics, mechanisms and kinetics of metal dusting, H.J. Grabke, Materials and Corrosion, Vol 49, 303-308, 1998) which means the risk is enhanced for gas mixtures containing hydrocarbons as suggested by CN1174108.

[0015] It is an object of the invention to provide a method for manufacturing a metal powder by atomisation which avoids or at least reduces the abovementioned problems.

[0016] This is achieved by a method for the manufacturing of metal powders according to claim 1.

[0017] According to the invention a metal powder is manufactured by atomisation of a liquid metal with a gas or a liquid. The liquid metal is exposed to a controlled gas atmosphere which comprises at a mixture of inert gas (at least 50% by volume) as well as carbon monoxide (CO) and carbon dioxide (CO2).

[0018] The invention relates to a safe method for minimizing or avoiding oxidation during liquid metal atomisation. Pyrophoric gases such as silane or borane can be avoided. The explosion hazards associated with silanes and boranes can be completely avoided. Relative to the suggestions of EP 2 050 528 B1 the application of the invention will be considerably safer, less expensive and more effective. Silane of borane utilization will result in contamination of the metal powders with SiO2, B2O3 or BN dependent upon the choice of inert gas. Further, the infrastructure associated with the atomizing process would be essentially unchanged. There would be no requirement to modify electrical equipment to be spark free or explosion proof as there would if pyrophoric gases were employed.

[0019] In practice commercially pure inert gas, e. g. inert gas of 99.999% purity, often has a high enough (ppm level) oxygen content to dramatically lower surface tension of liquid metals and to lead to surface oxidation. Adding CO can avoid these undesirable consequences.

[0020] It has further been found that under the conditions employed during atomisation CO additions to the gas can result in carbon activities in the gas mixture that exceed one risking destructive metal carburization. Thus, the invention suggests to add CO and CO2 to the inert gas in ratios that avoid the corrosion issue by reducing carbon potential of the gas to levels below 1.

[0021] In addition, the inventive addition of CO and CO2 is safer than just adding only CO. The concentration of CO required to avoid oxidation can be reduced because adding CO and CO2 to the inert gas allows the oxygen potential to be tailored to avoid oxidation of the metal alloy system being processed.

[0022] A gas mixture of CO and CO2 defines a specific oxygen potential at a given temperature. The relevant reaction is

$$2CO + O2 = 2CO2$$

for which the equilibrium constant is (PCO2)2/(PCO)2 x (PO2). Hence for a given temperature there is a unique PO2 that is given by the CO:CO2 ratio and the Gibbs Energy change for that reaction at the specified temperature.

[0023] So basically a mixture of CO and CO2 provides an oxygen potential anywhere between that associated with CO at one end of the spectrum and that associated with CO2 at the other. The addition of an appropriate mixture of CO and CO2 to an inert gas can therefore be used to reduce its oxygen potential to levels below those required to oxidize metallic species of the metal or alloys to be atomized whilst simultaneously controlling the carbon potential of the gas to avoid potentially catastrophic metal dusting of atomizing equipment If one wants to replicate the conditions associated with an inert gas doped with CO only, the inert gas could be doped with a CO:CO2 mix of a sufficiently high ratio.

[0024] Considering the residual oxygen contained in the inert gas the ratio of CO:CO2 could for example be between

2:1 and 50:1 in order to achieve the same practical impact as doping with CO alone, but avoiding the above-mentioned safety issues related to CO.

[0025] In an embodiment of the invention the controlled atmosphere contains an inert gas, CO, CO2 and SO2. Such an atmosphere would allow to control both oxygen and sulphur partial pressures which can be used to moderate liquid metal surface tension.

[0026] In another embodiment, the liquid metal contained in the crucible/tundish or furnace is exposed to a controlled atmosphere containing the inert gas, CO and CO2. Additional tensioactive species or microalloying elements which lower the surface tension could be added to the liquid metal in concentrations which are capable of reducing surface tension but having no or negligible impact on other physical or chemical properties of the metal.

[0027] Atomisation of a liquid metal results in a huge increase in the surface to volume ratio of the metal being processed. This requires that energy be provided to generate the increased surface energy of the product phase. If the surface tension of the liquid is reduced by equilibration with a gas atmosphere capable of introducing tensioactive species and/or adding microalloying elements to the liquid metal it is possible to lower the average particle size generated for given atomisation conditions. Alternatively it is possible to retain a desired mean particle size but to do so by means of lower momentum or lower pressure gas (or water) jets.

[0028] According to a preferred embodiment of the invention argon is used as inert gas.

[0029] The inert gas has a purity of at least 95% by volume, preferably at least 99% by volume or at least 99.5% by volume.

[0030] According to another embodiment the liquid metal is exposed to the controlled gas atmosphere during the atomisation step.

[0031] According to another embodiment the inventive method comprises a step of melting a metal to get the liquid metal. In this case it is preferred to expose the liquid metal to the controlled gas atmosphere during said melting step.

[0032] According to another embodiment the controlled atmosphere consists of Ar, CO and CO2.

Examples:

[0033] It is well known that sulphur and oxygen are highly surface active in iron and consequently ferrous alloys are subject to dramatic reductions of surface tension at very low concentrations of these species even at the ppm level. One way of introducing the levels of oxygen or sulphur required to bring this about without influencing the physical properties of the final product would be to equilibrate the melt in the crucible or tundish or in the melting furnace with, for example, a CO:CO2:SO2 mixture ahead of atomisation. The oxygen and sulphur potentials of such mixtures are very low.

[0034] In addition, it is possible to micro-alloy the respective metal with microalloying elements which have been mentioned above or with group V and Vi elements which are known to be surface active in liquid metal solutions. The alloying can take place according to the manufacturing route of the metal. This can be a metallurgical ladle or in the crucible or tundish before casting the metal into the atomisation chamber.

Claims

1. Method for the manufacturing of a metal powder wherein a liquid metal is atomized with a gas or a liquid, wherein the liquid metal is exposed to a controlled gas atmosphere, **characterized in that** the controlled atmosphere comprises at least 50% by volume an inert gas as well as carbon monoxide (CO) and carbon dioxide (CO2).

2. Method according to claim 1, **characterized in that** the controlled atmosphere comprises at least 80% by volume, at least 90% by volume or at least 95% by volume of an inert gas.

3. Method according to any of the preceding claims, **characterized in that** the inert gas is argon (Ar).

4. Method according to any of the preceding claims, **characterized in that** the liquid metal is exposed to the controlled gas atmosphere during the atomisation step.

5. Method according to any of the preceding claims, further comprising a step of melting a metal to get the liquid metal and wherein the liquid metal is exposed to the controlled gas atmosphere during said melting step.

6. Method according to any of the preceding claims, **characterized in that** the controlled atmosphere comprises more than 99% by volume argon (Ar).

7. Method according to any of the preceding claims, **characterized in that** the controlled atmosphere comprises SO2.

8. Method according to any of the preceding claims, **characterized in that** the controlled atmosphere consists of Ar, CO and CO2.

9. Method according to any of the preceding claims, **characterized in that** the volume ratio of CO to CO2 is between 2:1 and 50:1.

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EUROPEAN SEARCH REPORT

Application Number
EP 18 02 0079

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	CA 852 097 A (REYNOLDS METALS CO) 22 September 1970 (1970-09-22)	1-5	INV. B22F9/08
A	* page 2, lines 1-8 * * page 4, lines 13-15 * * page 5, lines 7-16, 23-27 *	6-9	B33Y70/00 ADD. B22F3/105
X	CN 104 308 170 B (UNIV LIAONING TECHNICAL) 11 January 2017 (2017-01-11)	1,3-6,8	
A	* page 5, paragraph [0023] *	2,7,9	

TECHNICAL FIELDS SEARCHED (IPC)
B22F B33Y

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	13 September 2018	Helgadóttir, Inga

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 18 02 0079

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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13-09-2018

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA 852097 A	22-09-1970	NONE	
CN 104308170 B	11-01-2017	NONE	

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

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- CN 1174108 **[0010] [0014]**

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- **W. J. SAMES ; F. A. LIST ; S. PANNALA ; R. R. DEHOFF ; S. S. BABU.** The metallurgy and processing science and metal additive manufacturing. *International Material Reviews,* 2016 **[0002]**
- **J. DAVIS ; R. BOWERMAN ; R. TREPLETON.** Introduction to the additive manufacturing powder metallurgy supply chain. *Johnson Matthey Technology Review,* 2015, vol. 59 (3), 243-256 **[0003]**
- **H.J. GRABKE.** *Materials and Corrosion,* 1998, vol. 49, 303-308 **[0014]**