



(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
16.05.2018 Bulletin 2018/20

(51) Int Cl.:
B22F 9/26 (2006.01)

(21) Application number: **16821264.5**

(86) International application number:
PCT/JP2016/069030

(22) Date of filing: **27.06.2016**

(87) International publication number:
WO 2017/006795 (12.01.2017 Gazette 2017/02)

(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

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(30) Priority: **03.07.2015 JP 2015134743**

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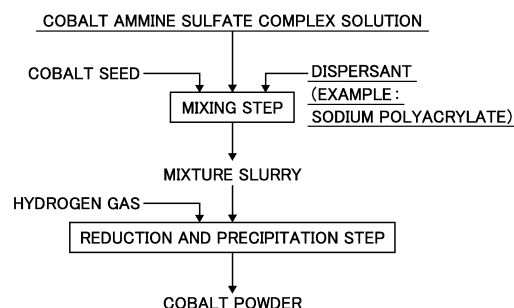
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(54) **METHOD FOR PRODUCING COBALT POWDER**

(57) Provided is a method for producing cobalt powder with high reaction efficiency by controlling the amount of added seed crystals when cobalt powder is produced from a solution containing a cobalt ammine sulfate complex. The method sequentially includes: a mixing step of adding, to the solution containing a cobalt ammine sulfate complex, cobalt powder as seed crystals in an amount of 1.5 times or more and 3.0 times or less the amount of cobalt contained in the solution and then adding a dispersant in an amount of 1.5% by weight to 3.0% by weight of the added seed crystals to form a mixture slurry; and a reduction and precipitation step of charging a reaction vessel with the mixture slurry and then blowing hydrogen gas into the mixture slurry to reduce cobalt complex ions contained in the mixture slurry to form cobalt precipitate on the surface of the seed crystals. (149 words)

Fig. 1



Description

Technical Field

[0001] The present invention relates to a method for producing cobalt powder having high reaction efficiency when cobalt powder is produced from a solution containing a cobalt ammine sulfate complex, and particularly, the present invention can be applied to the treatment of an in-process intermediate solution generated from a cobalt hydrometallurgical process.

Background Art

[0002] Examples of known methods for producing fine cobalt powder include dry methods such as an atomizing method of dispersing molten cobalt in a gas or in water to obtain fine powder and a CVD method of volatilizing cobalt and reducing it in a vapor phase to thereby obtain cobalt powder as disclosed in Patent Literature 1.

[0003] Further, examples of methods for producing cobalt powder by a wet process include a method of producing cobalt powder using a reducing agent as disclosed in Patent Literature 2 and a spray pyrolysis method in which cobalt powder is obtained by pyrolysis reaction by spraying a cobalt solution into a reducing atmosphere at high temperatures as disclosed in Patent Literature 3.

[0004] However, these methods are not economical because they require expensive reagents and a large amount of energy.

[0005] On the other hand, a method of obtaining cobalt powder by feeding hydrogen gas into a cobalt ammine sulfate complex solution to reduce cobalt ions in the complex solution as shown in Non Patent Literature 1 is industrially inexpensive and useful. However, there has been a problem that cobalt powder particles obtained by this method are easily coarsened.

[0006] Particularly, when particles are intended to be generated from an aqueous solution and grown, there is used a method of obtaining a powder having a predetermined particle size by allowing a small amount of fine crystals called seed crystals to coexist and feeding a reducing agent thereto to grow the seed crystals.

[0007] According to the above method, high reaction efficiency cannot be obtained, depending on the cobalt concentration in the aqueous solution to be used and the type of seed crystals, and the yield will decrease, which leads to an increase in cost.

[0008] Generally, in such a case, it is possible to improve reaction efficiency by reducing the particle size of seed crystals to increase the reaction field. However, time and effort are required in order to reduce the particle size of seed crystals. Further, in the case where seed crystals made of different types of metals are used, there arises a problem such that the purity of products decreases because the seed crystal component remains.

[0009] Therefore, there has been required a method

of having high reaction efficiency, without using different types of metals as seed crystals and not necessarily using seed crystals having a small particle size.

5 Citation List

Patent Literature

[0010]

10 Patent Literature 1:

Japanese Patent Laid-Open No. 2005-505695

15 Patent Literature 2:

Japanese Patent No. 5407495

Patent Literature 3:

20 Japanese Patent No. 4286220

Non Patent Literature

25 **[0011]**

Non Patent Literature 1:

"The Manufacture and properties of Metal powder produced by the gaseous reduction of aqueous solutions", Powder metallurgy, No. 1/2 (1958), pp 40-52.

Summary of Invention

35 Technical Problem

[0012] In such a situation, the present invention provides a method for producing cobalt powder by obtaining high reaction efficiency by controlling the amount of added seed crystals when cobalt powder is produced from a solution containing a cobalt ammine sulfate complex.

Solution to Problem

[0013] A first aspect of the present invention to solve such a problem is a method for producing cobalt powder, sequentially including: a mixing step of adding, to a solution containing a cobalt ammine sulfate complex, cobalt powder as seed crystals in an amount of 1.5 times or more and 3.0 times or less the amount of cobalt contained in the starting solution and then adding a dispersant in an amount of 1.5% by weight to 3.0% by weight of the added seed crystals to form a mixture slurry; and a reduction and precipitation step of charging a reaction vessel with the mixture slurry and then blowing hydrogen gas into the mixture slurry to reduce cobalt complex ions contained in the mixture slurry to form cobalt precipitate

on a surface of the seed crystals.

[0014] A second aspect of the present invention is a method for producing cobalt powder according to the first aspect of the invention, wherein the concentration of ammonium sulfate in the solution containing a cobalt ammine sulfate complex is in the range of 10 to 500 g/L.

[0015] A third aspect of the present invention is a method for producing cobalt powder according to the first and second aspects of the invention, wherein, in the reduction step, the temperature of the mixture slurry when hydrogen gas is blown is 150 to 200°C.

[0016] A fourth aspect of the present invention is a method for producing cobalt powder according to the first to third aspects of the invention, wherein, in the reduction step, the pressure of the gas phase part in the reaction vessel when hydrogen gas is blown is in the range of 1.0 to 4.0 MPa.

Advantageous Effect of Invention

[0017] According to the present invention, in the method of adding a dispersant to a cobalt ammine complex solution and subjecting the resulting mixture to hydrogen reduction under high temperatures and high pressures, cobalt powder can be produced at high reaction efficiency.

Brief Description of Drawings

[0018]

[Figure 1] Figure 1 is a production flow chart of the method for producing cobalt powder according to the present invention.

[Figure 2] Figure 2 is a SEM image showing the appearance of cobalt powder produced in Example 1.

Description of Embodiments

[0019] The method for producing high purity cobalt powder according to the present invention is a method for producing cobalt powder in which, when seed crystals are added to a cobalt ammine sulfate complex solution using a high-pressure vessel such as an autoclave and the resulting mixture is subjected to pressurized hydrogen reduction treatment including reduction treatment with hydrogen at high temperatures and high pressures, cobalt powder is produced by adding cobalt powder as seed crystals in an amount 1.5 times or more and 10.0 times or less the amount of cobalt in the starting solution, preferably 1.5 times or more and 3.0 times or less, and more preferably 2.0 times.

[0020] Hereinafter, the method for producing cobalt powder according to the present invention will be described with reference to the production flow chart shown in Figure 1.

[Cobalt Ammine Sulfate Complex Solution]

[0021] Examples of a suitable cobalt ammine sulfate complex solution used in the present invention include, but are not limited to, a cobalt ammine sulfate complex solution obtained by dissolving a cobalt-containing material such as an industrial intermediate including one or a mixture of two or more selected from cobalt and cobalt mixed sulfide, crude cobalt sulfate, cobalt oxide, cobalt hydroxide, cobalt carbonate, cobalt powder, and the like with sulfuric acid or ammonia to obtain a cobalt leaching solution (solution containing cobalt), subjecting the cobalt leaching solution to a purification step such as solvent extraction, ion exchange, and neutralization to obtain a solution from which impurity elements in the cobalt leaching solution have been removed, and adding ammonia to the resulting solution to form the cobalt ammine sulfate complex solution, in which cobalt is contained in the form of cobalt complex ions.

[Mixing Step]

[0022] In this step, a mixture slurry is produced by adding seed crystals to the cobalt ammine sulfate complex solution produced above and adding a dispersant thereto depending on the amount of the added seed crystals.

[0023] Cobalt powder is used as the seed crystals to be added here.

[0024] Although commercially available products may be used as the cobalt powder to be used as the seed crystals, it is more preferred to repeatedly use a part of products obtained by the production method of the present invention.

[0025] The particle size of the cobalt powder preferably has an average particle size of about 0.1 to 5 μm , and particularly preferably has a particle size of around 1 μm , where the particle size does not vary but is uniform.

[0026] If the particle size is too small, the cobalt powder obtained in the reaction will be too small, which has difficulty in handling and is not preferred. On the other hand, if the particle size is too large, the cobalt powder will easily settle during stirring, which poses a problem that uniform cobalt powder is not easily obtained.

[0027] The amount of cobalt powder to be added is 1.5 times or more and 3.0 times or less, preferably 2.0 times the amount of cobalt contained in the original solution, in order to maintain reaction efficiency.

[0028] If the amount of cobalt powder added is less than 1.5 times of the amount of cobalt contained in the original solution, high reaction efficiency cannot be obtained because the number of seed crystals is insufficient, reducing reaction fields. Further, even if the amount of cobalt powder added is more than 3.0 times, reaction efficiency will not be improved, and the efficiency will not be improved considering that too much time and effort and cost are required. The number of seed crystals will be rather too large, and the growth of the cobalt powder obtained will be insufficient, reducing the particle size.

Therefore, when the cobalt powder is used as products, a problem in use will easily occur, such as requiring time and effort in handling thereof. Further, a problem of properties, such as being easily dissolved or oxidized, will occur, which is not preferred.

[0029] Furthermore, when a dispersant is added so that it is contained at a concentration in the range of 1.5% by weight or more and 3.0% by weight or less relative to the amount of seed crystals added to the cobalt ammine sulfate complex solution, the added seed crystals are dispersed more uniformly, and desired nickel powder is thus more easily obtained, which is desirable.

[0030] Further, the concentration of ammonium sulfate in the solution is preferably in the range of 10 to 500 g/L.

[0031] If the concentration is 500 g/L or more, the solubility will be exceeded, and crystals will be precipitated. With respect to the lower limit, since ammonium sulfate is newly produced by reaction, it is difficult to achieve a concentration of less than 10 g/L.

[Reduction and Precipitation Step]

[0032] Next, a reaction vessel resistant to high pressure and high temperature is charged with the slurry formed by adding seed crystals in the previous step, and hydrogen gas is blown into the slurry stored in the reaction vessel to reduce cobalt complex ions in the slurry to precipitate cobalt on the seed crystals contained.

[0033] The temperature of the mixture slurry at this time, that is, reaction temperature, is preferably in the range of 150 to 200°C. If the reaction temperature is less than 150°C, reduction efficiency will be reduced, and even if it is 200°C or more, the reaction will not be affected, but the loss of thermal energy will increase. Therefore, these temperatures are not suitable.

[0034] Further, the pressure of the gas phase part in the reaction vessel (refers to a space in the reaction vessel remaining after the solution is stored in the reaction vessel) during the reaction is preferably maintained in the range of 1.0 to 4.0 MPa by controlling the feed rate of hydrogen gas. If the pressure is less than 1.0 MPa, reaction efficiency will be reduced, which is not preferred. Further, even if the pressure is higher than 4.0 MPa, the reaction efficiency will not be affected, but the loss of hydrogen gas will increase.

[0035] In this regard, when hydrogen gas is blown into the mixture slurry, the cobalt complex ions in the slurry can also be reduced either by directly blowing hydrogen gas into the liquid in the reaction vessel or by blowing hydrogen gas into the gas phase part in the reaction vessel.

[0036] A precipitate of cobalt is formed on the seed crystals by reduction and precipitation treatment of the present invention, and the cobalt contained in the solution can be recovered and repeatedly used as a precipitate of fine powdered cobalt.

[0037] As described above, by producing the seed crystals of cobalt powder in fine powder form which can

be used as seed crystals and repeating hydrogen reduction, particles in which cobalt precipitate is provided on the surface of the seed crystals are formed, and the particles can be grown up to produce high purity cobalt metal.

Examples

[0038] The present invention will be described below using Examples.

[Example 1]

[Mixing Step]

[0039] To a cobalt sulfate solution containing 75 g of cobalt, was added 465 g of ammonium sulfate, and there-to was added 191 ml of 25% aqueous ammonia to form an original solution. A mixture slurry containing a cobalt ammine sulfate complex containing seed crystals was prepared by adding, to the original solution, cobalt powder having an average particle size of about 0.1 to 5 μm , as seed crystals, in an amount of 150 g which is 2.0 times the amount of cobalt in the original solution, further adding 40 wt% polyacrylic acid, as a dispersant, in an amount 2.0% by weight relative to the amount of the seed crystals, and then adjusting the total volume of the solution to 1000 ml.

[Reduction and Precipitation Step]

[0040] Next, an inner cylinder of an autoclave was charged with the mixture slurry; the mixture slurry was heated to 185°C with stirring after the autoclave was sealed; hydrogen gas was blown into the mixture slurry while keeping the temperature; and hydrogen gas was fed from its cylinder so as to maintain the pressure in the inner cylinder of the autoclave at 3.5 MPa.

[0041] After a lapse of 60 minutes from the start of the feeding of hydrogen gas, the feeding of hydrogen gas was stopped, and the inner cylinder was cooled.

[0042] After cooling, when the mixture slurry in the inner cylinder was filtered and the recovered cobalt powder was observed with an electron microscope (SEM), it was verified that fine cobalt powder was produced as shown in Figure 2.

[0043] Further, the amount of precipitated cobalt obtained by deducting the amount of seed crystals from the amount of cobalt that was able to be recovered was divided by the amount of cobalt contained in the original solution to determine the yield of the cobalt powder produced by the reaction, that is, by reduction, which was found to be 72%.

(Comparative Example 1)

[0044] An original solution containing cobalt was prepared under the same conditions and in the same manner as in Example 1 above. A mixture slurry according to

Comparative Example 1 was prepared by adding, to the original solution, cobalt powder as seed crystals in an amount of 75 g which is 1.0 times the amount of cobalt in the original solution and adjusting the total volume of the solution to 1000 ml. Next, an inner cylinder of an autoclave was charged with the mixture slurry; the mixture slurry was then heated to 185°C with stirring; hydrogen gas was blown into the mixture slurry while keeping the temperature; and hydrogen gas was fed so as to maintain the pressure in the inner cylinder of the autoclave at 3.5 MPa.

[0045] After a lapse of 60 minutes from the start of the feeding of hydrogen gas, the feeding of hydrogen gas was stopped, and the inner cylinder was cooled.

[0046] After cooling, when the solution in the inner cylinder was filtered, fine cobalt powder was found to be produced.

[0047] However, the yield of the cobalt powder produced by the reaction was only 36%, and high efficiency as in Example 1 of the present invention was not obtained.

Claims

1. A method of producing cobalt powder, sequentially comprising:

a mixing step of adding, to a solution containing a cobalt ammine sulfate complex, cobalt powder as seed crystals in an amount of 1.5 times or more and 3.0 times or less an amount of cobalt contained in the solution and then adding a dispersant in an amount of 1.5% by weight to 3.0% by weight of the seed crystals added to form a mixture slurry; and

a reduction and precipitation step of charging a reaction vessel with the mixture slurry and then blowing hydrogen gas into the mixture slurry to reduce cobalt complex ions contained in the mixture slurry to form cobalt precipitate on a surface of the seed crystals.

2. The method of producing cobalt powder according to claim 1, wherein a concentration of ammonium sulfate in the solution containing a cobalt ammine sulfate complex is in a range of 10 to 500 g/L.

3. The method of producing cobalt powder according to claim 1 or 2, wherein, in the reduction step, a temperature of the mixture slurry when hydrogen gas is blown is 150 to 200°C.

4. The method of producing cobalt powder according to any one of claims 1 to 3, wherein, in the reduction step, a pressure of a gas phase part in the reaction vessel when hydrogen gas is blown is in a range of 1.0 to 4.0 MPa.

Fig.1

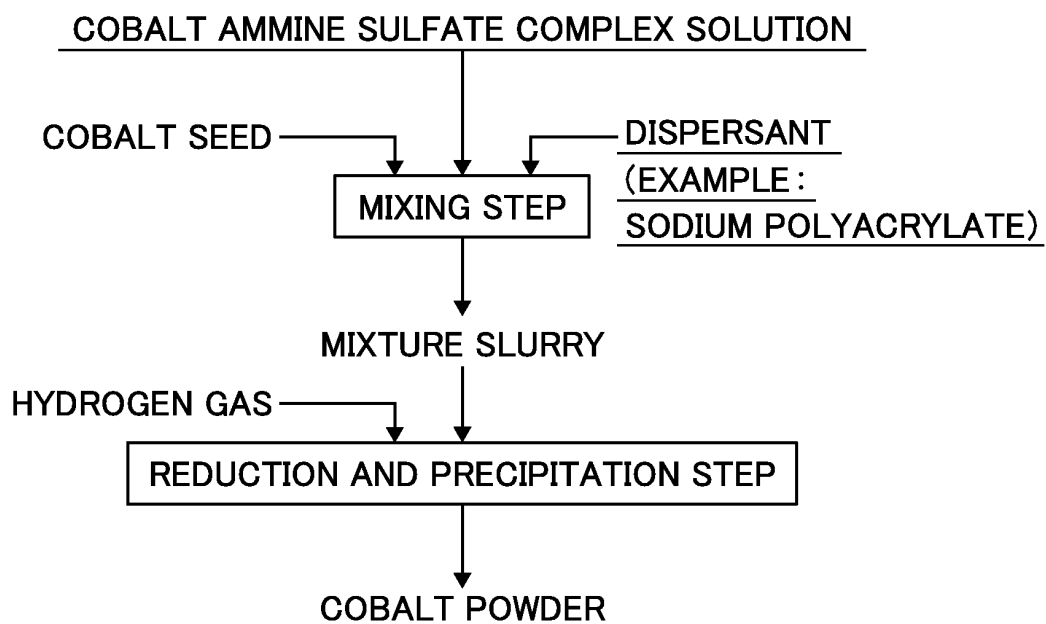
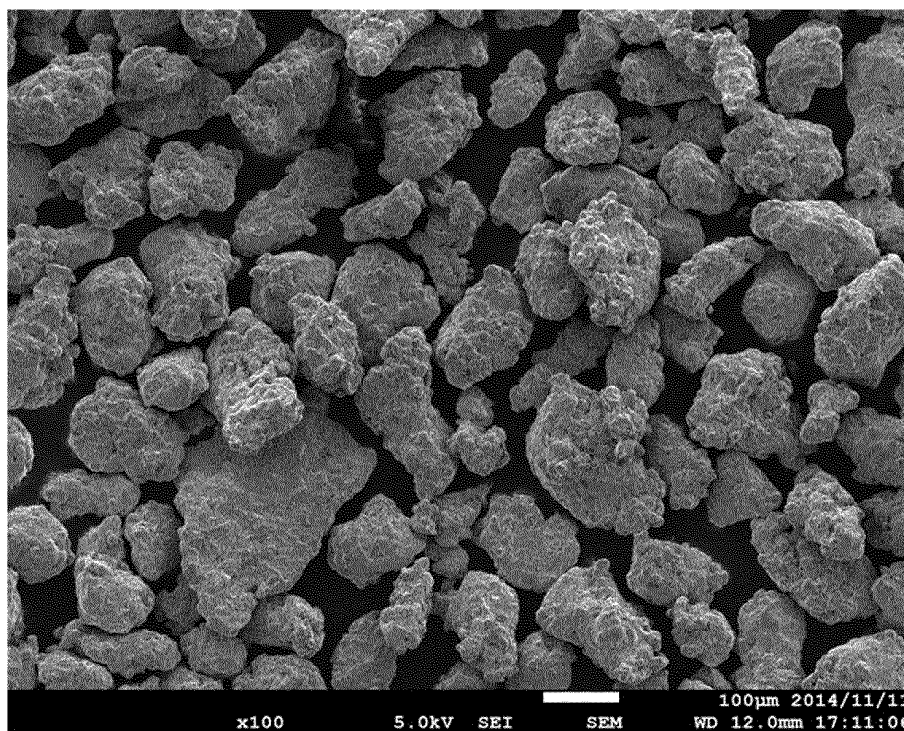


Fig.2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/069030

A. CLASSIFICATION OF SUBJECT MATTER

B22F9/26(2006.01) i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B22F9/26, C22B23/00

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016

Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 32-9051 B1 (Chamical Construction Corp.), 24 October 1957 (24.10.1957), page 1, left column, lines 1 to 4; page 1, right column, lines 15 to 19; page 3, left column, lines 17 to 25; page 3, left column, lines 36 to 41 (Family: none)	1-4

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search
05 August 2016 (05.08.16)Date of mailing of the international search report
16 August 2016 (16.08.16)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/069030

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 8-503999 A (Sherritt Inc.), 30 April 1996 (30.04.1996), claim 1 & US 5246481 A claim 1 & WO 1994/010350 A1 & EP 665900 A1 & FI 951955 A & KR 10-0220627 B & KR 10-0229917 B & AU 676862 B & NZ 257319 A & AU 5367494 A & BR 9307308 A & ZA 9307947 A & AT 138110 T & CA 2147760 A & RU 95112580 A	1-4
A	JP 3-51764 B2 (Inco Ltd.), 07 August 1991 (07.08.1991), & EP 47076 A1 & DE 3170282 D & CA 1151881 A & NO 812809 A & PH 18541 A & FI 812559 A & ZA 8105530 A & ZW 19981 A & AU 542235 B	1
A	JP 43-022395 B1 (Sumitomo Metal Mining Co., Ltd.), 26 September 1968 (26.09.1968), (Family: none)	1
A	JP 30-8915 B1 (Chamical Construction Corp.), 07 December 1955 (07.12.1955), (Family: none)	1
A	JP 50-26750 A (Sherritt Gordon Mines Ltd.), 19 March 1975 (19.03.1975), & US 3994716 A & US 3975217 A & GB 1436595 A & DE 2415442 A & FR 2223119 A & PH 10513 A & PH 11716 A & AU 6713974 A & FI 66435 B & CA 1013595 A & ZA 7401828 A & AU 475404 B	1

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2005505695 A [0010]
- JP 5407495 B [0010]
- JP 4286220 B [0010]

Non-patent literature cited in the description

- The Manufacture and properties of Metal powder produced by the gaseous reduction of aqueous solutions. *Powder metallurgy*, 1958, 40-52 [0011]