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(54) **METHOD FOR PRODUCING SEED CRYSTAL OF COBALT POWDER**

(57) Provided is a production method for obtaining cobalt powder efficiently by the way for increasing reduction reaction efficiency to produce the cobalt powder from a solution containing a cobalt ammine sulfate complex. The method for producing seed crystals of cobalt powder, sequentially including: a complexing step of adding ammonia, an ammonia compound solution, or both of ammonia and an ammonia compound solution to a cobalt sulfate solution to obtain a solution containing a cobalt ammine sulfate complex; a mixing step of adding a solid to the solution containing the cobalt ammine sulfate complex obtained in the complexing step to form a mixture

slurry; a reduction and precipitation step of charging a reaction vessel with the mixture slurry obtained in the mixing step, blowing hydrogen gas into the reaction vessel and reducing cobalt contained in the mixture slurry to obtain a cobalt powder slurry containing cobalt precipitate with a cobalt component precipitated on the surface of the solid as cobalt powder; and a solid-liquid separation step of performing solid-liquid separation on the cobalt powder slurry obtained in the reduction and precipitation step to obtain cobalt precipitate and a solution after reduction.

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## Description

### Technical Field

**[0001]** The present invention relates to a method for producing cobalt powder from a solution containing a cobalt ammine sulfate complex, and particularly relates to a method for obtaining seed crystals to use for crystal growth.

### Background Art

**[0002]** Various methods for obtaining cobalt, which is used as an electronic material or heat resistant alloys, have been known. In recent years, a demand for cobalt salts, which become raw materials such as battery materials, has been increased.

**[0003]** The cobalt salts are generally produced by dissolving a cobalt metal in an acid. However, sheet-shaped and massive forms such as conventionally common electrolytic cobalt are easily handled, but are extremely slowly dissolved in an acid. Meanwhile, the form of fine powder is easily dissolved in an acid, but has the handling disadvantage of being easily scattered and the like. Ones called briquets and obtained by consolidating or sintering grains or powder are preferred to make good use of the advantages of the both.

**[0004]** As a method for obtaining such a small size of cobalt grains or powder, an atomizing method for dispersing melted cobalt in gas or water to obtain fine powder and a dry method such as CVD for obtaining cobalt powder by volatilizing cobalt and reducing it in a gas phase as shown in Patent Literature 1 are known.

**[0005]** As a method for producing cobalt powder by a wet process, there are a method for generating it using a reducing agent as shown in Patent Literature 2 and a spray thermal decomposition method for obtaining cobalt powder by a thermal decomposition reaction by spraying a cobalt solution in a reduction atmosphere at a high temperature as shown in Patent Literature 3, and the like.

**[0006]** However, since these methods require expensive reagents and a large amount of energy, they are not economical as methods for industrially obtaining a large amount of material for the battery materials or the like.

**[0007]** There has remained a problem that in a method for growing using cobalt powder as seed crystals as shown in patent Literature 4, seed crystals and grown cobalt powder are remelted, resulting in a decrease in the recovery since the reaction is performed in an acidic solution having a pH of 4 or less.

**[0008]** Additionally, there has remained a problem that, in a method for adding a sodium hydroxide solution to a cobalt sulfate solution for a raw material and performing hydrogen reduction, the hydroxide of cobalt is generated and thereby allowing a reduction reaction not to proceed when the pH cannot be maintained at 4 and increases, and consequently the efficiency in the reduction reaction decreases.

**[0009]** Meanwhile, a method for feeding hydrogen gas to a cobalt ammine sulfate complex solution having cobalt in the form of an ammonia complex to reduce cobalt ions in the complex solution and obtain cobalt powder as shown in Non Patent Literature 1 is industrially low-priced and useful.

**[0010]** However, also in this method, there is a problem that many crystal nuclei are generated heterogeneously, resulting in the prevention of the growth in the same way as the above-mentioned prior arts since particles are intended to be generated from a solution and grow by a wet reaction. That is, it is essential to control the number of the derived nuclei of the crystal in a proper range, resulting in efficient growth.

**[0011]** Then, as mentioned above, a method for feeding a reducing agent to a slurry in which a small amount of fine crystals called seed crystals coexist, and growing objects on the surfaces of the seed crystals to obtain powder having a predetermined particle size is commonly used.

**[0012]** The seed crystals added in the above are often used by conducting treatment such as grinding a portion of a product repeatedly. However, there has remained a problem that the processing also took time and effort and the yield decreased as the processing is repeated more times and therefore this lead to an increase in cost. There has also remained the problem of seed crystals having the optimal particle size and properties being capable of necessarily being obtained stably only by grinding simply, or the like.

**[0013]** That is, a method for stably obtaining seed crystals to use for crystal growth has been required.

### Citation List

#### Patent Literature

#### **[0014]**

Patent Literature 1: Japanese Patent Laid-Open No. 2005-505695

Patent Literature 2: Japanese Patent Laid-Open No. 2010-242143

Patent Literature 3: Japanese Patent No. 4286220

Patent Literature 4: Japanese Patent Laid-Open No. S57-54207

#### Non Patent literature

**[0015]** 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

## Technical Problem

**[0016]** In such a situation, the present invention provides a production method for obtaining cobalt powder efficiently by a way for increasing reduction reaction efficiency to produce the cobalt powder from a solution containing a cobalt ammine sulfate complex.

## Solution to Problem

**[0017]** A first aspect of the present invention to solve such a problem is a method for producing seed crystals of cobalt powder, sequentially including: a complexing step of adding ammonia, an ammonia compound solution, or both of ammonia and an ammonia compound solution to a cobalt sulfate solution to obtain a solution containing a cobalt ammine sulfate complex; a mixing step of adding a solid to the solution containing the cobalt ammine sulfate complex obtained in the complexing step to form a mixture slurry; a reduction and precipitation step of charging a reaction vessel with the mixture slurry obtained in the mixing step, and blowing hydrogen gas into the reaction vessel to reduce cobalt contained in the mixture slurry and obtain a cobalt powder slurry containing cobalt precipitate with a cobalt component precipitated on the surface of the solid as cobalt powder; and a solid-liquid separation step of subjecting the obtained cobalt powder slurry to solid-liquid separation treatment to obtain the cobalt precipitate and a solution after reduction.

**[0018]** A second aspect of the present invention is the method for producing seed crystals of cobalt powder, wherein the solid in the first aspect is a material insoluble or slightly soluble in the solution containing the cobalt ammine sulfate complex, and the solid has an average particle size of 0.1  $\mu\text{m}$  or more and 5  $\mu\text{m}$  or less.

**[0019]** A third aspect of the present invention is the method for producing seed crystals of cobalt powder, wherein the cobalt concentration in the solution containing the cobalt ammine sulfate complex in the first and second aspects is 75 g/L or less.

**[0020]** A fourth aspect of the present invention is the method for producing seed crystals of cobalt powder, wherein the solid in the first to third aspects is nickel powder.

**[0021]** A fifth aspect of the present invention is the method for producing seed crystals of cobalt powder, wherein the solid-liquid separation step in the first to fourth aspects has a solid-liquid separation treatment for separating the cobalt powder slurry into the cobalt precipitate and the solution after reduction, and a solid separation treatment for separating the obtained cobalt precipitate into the added solid and the cobalt powder that is precipitated on the surface of the solid, and thereby the solution after reduction, the solid and the cobalt powder are formed.

## Advantageous Effect of Invention

**[0022]** According to the present invention, seed crystals having a size suitable to be added to a cobalt ammine sulfate complex solution as seed crystals to form cobalt powder can be obtained efficiently when a cobalt ammine sulfate complex solution is reduced with hydrogen gas to produce cobalt powder.

## 10 Brief Description of Drawing

**[0023]** [Figure 1] Figure 1 is a production flow chart of the method for producing cobalt powder according to the present invention.

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## Description of Embodiment

**[0024]** The present invention is a method for efficiently producing seed crystals to be added when hydrogen gas is blown into a cobalt ammine sulfate complex solution to produce cobalt powder.

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**[0025]** 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. In the present invention, cobalt powder is obtained by subjecting a cobalt sulfate solution serving as an original solution to a complexing step, a mixing step, a reduction and precipitation step and a solid-liquid separation step. The reduction rate mentioned in the present invention is defined as a rate obtained by dividing the weight (g) of the obtained cobalt powder by the cobalt amount (g/L) contained in the fed cobalt sulfate solution (L).

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## [Complexing Step]

**[0026]** A cobalt sulfate solution that can be used in the present invention is not particularly limited, but a cobalt leachate obtained by leaching/dissolving a cobalt-containing material such as an industrial intermediate comprising 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 can be used. Usually, various impurities are also industrially contained in the cobalt leachate. The leachate is generally used by removing impurity elements in the leachate by subjecting the leachate to a purification step such as solvent extraction, ion exchange, or neutralization.

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**[0027]** Next, aqueous ammonia and ammonium sulfate are added to the cobalt leachate to obtain a cobalt ammine sulfate complex solution.

**[0028]** The concentration of ammonium sulfate in the solution is preferably in the range of 10 to 500 g/L. If the concentration is 500 g/L or more, it is higher than the solubility, and crystals may be precipitated. This is not preferable since an operational trouble occurs. If the concentration is less than 10 g/L, since ammonium sulfate

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is newly produced by the reaction, it is industrially difficult to keep the concentration at a level of less than 10 g/L.

[0029] The cobalt concentration in the cobalt ammine sulfate complex solution is 75 g/L or less. It is because in the reaction of a solid after the addition in later steps, if the cobalt concentration in the cobalt ammine sulfate complex solution is too high, the reduction rate will be decreased due to the shortage of reaction sites.

#### [Mixing Step]

[0030] In this step, to the cobalt ammine sulfate complex solution prepared as described above is added a solid that is used as a matrix for precipitation.

[0031] The solid to be added is not particularly limited as long as it is insoluble or sparingly soluble with a low solubility in a cobalt ammine sulfate complex solution, an aqueous ammonium sulfate solution, or an alkali solution.

[0032] Specifically, it is preferable to use nickel powder.

[0033] When cobalt powder is used for a solid, it is the same as cobalt precipitate, and therefore these do not need to be separated. Cobalt powder is thus the most suitable to be used as seed crystals, but it is difficult to industrially obtain fine cobalt powder at a low price stably.

[0034] Although there is an advantage of iron powder being available at a low price easily, there is a disadvantage of iron powder being easily dissolved in an acidic solution and hardly serving as crystal nuclei. Because dissolved iron ions becomes a new cause of contamination, and the like, iron powder is not suitable.

[0035] In a method for using a slightly soluble or insoluble solid and precipitating cobalt thereon like the present invention, the influence of remelting is so avoidable as to be negligible and it is not necessary to repeat some of product, differently from a method for precipitating cobalt using seed crystals that is generally used conventionally and forming the cobalt including the seed crystals into a product. Therefore, there is a characteristic that cobalt complex ions contained in an ammine complex solution can be reduced nearly completely in a viewpoint of the balance between the amounts of materials in the process.

[0036] It is preferable that the solid have a smooth surface so that the precipitated cobalt powder can be separated effectively. As mentioned above, the amount of the solid added equivalent to the amount of cobalt existing in the solution or more is required. Specifically, when nickel powder is used for a solid, 75 g/L or more need to be added.

#### [Reduction and Precipitation Step]

[0037] Next, the reaction vessel of a pressure vessel is charged with the slurry formed by adding nickel powder in the mixing step, and cobalt complex ions in the slurry is reduced by blowing a reducing agent such as hydrogen gas into the reaction vessel to precipitate cobalt on the

surface of the solid.

[0038] Here, the temperature of the mixture slurry, namely, the reaction temperature, is preferably in the range of 150 to 200°C. If the reaction temperature is less than 150°C, reduction efficiency is decreased, and even if the reaction temperature is 200°C or more, the reaction is not affected, but the loss of thermal energy increases.

[0039] The pressure of the gas phase part, which is a space other than the solution in the reaction vessel, is preferably maintained in the range of 1.0 to 4.0 MPa by feeding hydrogen gas. If the pressure is less than 1.0 MPa, reaction efficiency is reduced since the amount of gas migrating from the gas phase part into the solution is little. Meanwhile, even if the pressure is higher than 4.0 MPa, there is no influence such as the reaction being enhanced, but the loss of hydrogen gas just increases, resulting in no advantage.

[0040] Hydrogen gas may be blown into the gas phase part in the reaction vessel or blown directly into the slurry.

#### [Solid-Liquid Separation Step]

[0041] The solid having cobalt precipitate on the surface obtained in the reduction and precipitation step is taken out of the pressure vessel with the solution after reduction in the pressure vessel and subjected to solid-liquid separation from the solution after reduction.

[0042] This solid-liquid separation may be any of, for example, a method using a nutsche and a vacuum flask, a method using a centrifuge, a method using a filter press.

[0043] Then, when a substance other than cobalt is used for the solid, operation of separating the cobalt precipitate on the surface from the solid may be performed.

[0044] Specific separation method can be properly performed by applying a shock to the solid and the cobalt precipitate, or the like.

[0045] When the size of the cobalt precipitate still including the solid or the cobalt precipitate after separation from the solid is still smaller than that used for seed crystals, the size of the cobalt precipitate can be increased by repeating the mixing step again.

[0046] The solid collected here can be reused for the mixing step repeatedly.

[0047] The solution after reduction can be used repeatedly as a complexing agent in the complexing step without any treatment or by the recycling thereof into ammonia by treatment such as heating and distillation.

#### Examples

[0048] Examples for generating seed crystals for obtaining cobalt powder of the present invention will be described below.

[0049] The average particle size was measured using a commercial laser particle size analyzer (Microtrac).

## Example 1

[0050] A solution containing a cobalt ammine sulfate complex was prepared by adding 191 ml of 25% aqueous ammonia to cobalt sulfate equivalent to 75 g of cobalt and 330 g of ammonium sulfate, dissolving them and adjusting the total volume of the solution to 1000 ml.

[0051] To this solution was added 75 g of nickel powder having an average particle size of 1  $\mu\text{m}$  and used as a matrix for precipitation to obtain a mixture slurry.

[0052] Next, an inner cylinder of an autoclave having a volume of 3 L 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 further fed so as to maintain the pressure in the inner cylinder of the autoclave at 3.5 MPa. 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.

[0053] After cooling to room temperature, the mixture slurry in the inner cylinder was filtered, and the insoluble solid having cobalt precipitate formed on the surface was removed. Then, solid-liquid separation was conducted by suction filtration using a vacuum flask and a nutsche.

[0054] The reduction reaction rate of cobalt at this time was 99%.

## (Comparative Example 1)

[0055] A solution containing a cobalt ammine sulfate complex was prepared by obtaining a solution containing 75 g of cobalt, 330 g of ammonium sulfate and 191 ml of 25% aqueous ammonia, adding 3.73 g of polyacrylic acid having a concentration of 40 wt% as a dispersant instead of a solid of seed crystals of the present invention thereto, and adjusting the total volume of the solution to 1000 ml.

[0056] To this solution was added 75 g of cobalt powder used as a matrix for precipitation to prepare a mixture slurry.

[0057] The same inner cylinder of the autoclave as Example 1 was charged with the prepared mixture slurry, which was then heated to 185°C with stirring, hydrogen gas was blown into the mixture slurry while keeping the temperature, and hydrogen gas was further fed so as to maintain the pressure in the inner cylinder of the autoclave at 3.5 MPa.

[0058] After a lapse of 60 minutes from the start of the feeding of hydrogen gas, feeding hydrogen gas was stopped, and the inner cylinder was cooled.

[0059] After cooling to room temperature, the mixture slurry in the inner cylinder was filtered, and the insoluble solid having cobalt precipitate formed on the surface was removed. Then, solid-liquid separation was conducted by suction filtration using the vacuum flask and the nutsche. The cobalt reduction reaction rate at this time was 72%, and as high efficiency as that of Example of the present invention was not obtained.

## (Comparative Example 2)

[0060] A solution containing a cobalt ammine sulfate complex was prepared by adding a solution containing 330 g of ammonium sulfate to a cobalt sulfate solution containing 75 g of cobalt, adding 191 ml of 25% aqueous ammonia to the resulting solution, and adjusting the total volume of the solution to 1000 ml.

[0061] To this solution was added 75 g of commercial iron powder having an average particle size of 1  $\mu\text{m}$  as a solid soluble in the solution to prepare a mixture slurry.

[0062] The inner cylinder of the autoclave used in Example 1 was charged with the prepared 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 further fed so as to maintain the pressure in the inner cylinder of the autoclave at 3.5 MPa. 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.

[0063] After cooling to room temperature, the mixture slurry in the inner cylinder was filtered, and the iron powder having cobalt precipitate formed on the surface was removed. Then, solid-liquid separation was conducted by suction filtration using the vacuum flask and the nutsche.

[0064] It was found that the cobalt reduction reaction rate as to this Comparative Example 2 was 76%, which was higher than that in the case where a conventional dispersant was used, but as high effect as that of Example of the present invention was not obtained even if easily soluble solid was added.

## Claims

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

a complexing step of adding ammonia, an ammonia compound solution, or both of ammonia and an ammonia compound solution to a cobalt sulfate solution to obtain a solution containing a cobalt ammine sulfate complex;  
a mixing step of adding a solid to the solution containing the cobalt ammine sulfate complex obtained in the complexing step to form a mixture slurry;  
a reduction and precipitation step of charging a reaction vessel with the mixture slurry obtained in the mixing step, and blowing hydrogen gas into the reaction vessel to reduce cobalt contained in the mixture slurry and obtain a cobalt powder slurry containing cobalt precipitate with a cobalt component precipitated on a surface of the solid as cobalt powder; and  
a solid-liquid separation step of subjecting the

cobalt powder slurry obtained to solid-liquid separation treatment to obtain the cobalt precipitate and a solution after reduction.

2. The method of producing seed crystals of cobalt powder according to claim 1, wherein the solid is a material insoluble or slightly soluble in the solution containing the cobalt ammine sulfate complex, and the solid has an average particle size of 0.1 to 5  $\mu\text{m}$ .
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3. The method of producing seed crystals of cobalt powder according to claim 1 or 2, wherein a cobalt concentration in the solution containing the cobalt ammine sulfate complex is 75 g/L or less.
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4. The method of producing seed crystals of cobalt powder according to any one of claims 1 to 3, wherein the solid is nickel powder.
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5. The method of producing seed crystals of cobalt powder according to any one of claims 1 to 4, wherein the solid-liquid separation step has:
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  - a solid-liquid separation treatment for separating the cobalt powder slurry into the cobalt precipitate and the solution after reduction; and
  - a solid separation treatment for separating the cobalt precipitate obtained into the solid added and the cobalt powder that is precipitated on the surface of the solid, to form the solution after reduction, the solid and the cobalt powder.
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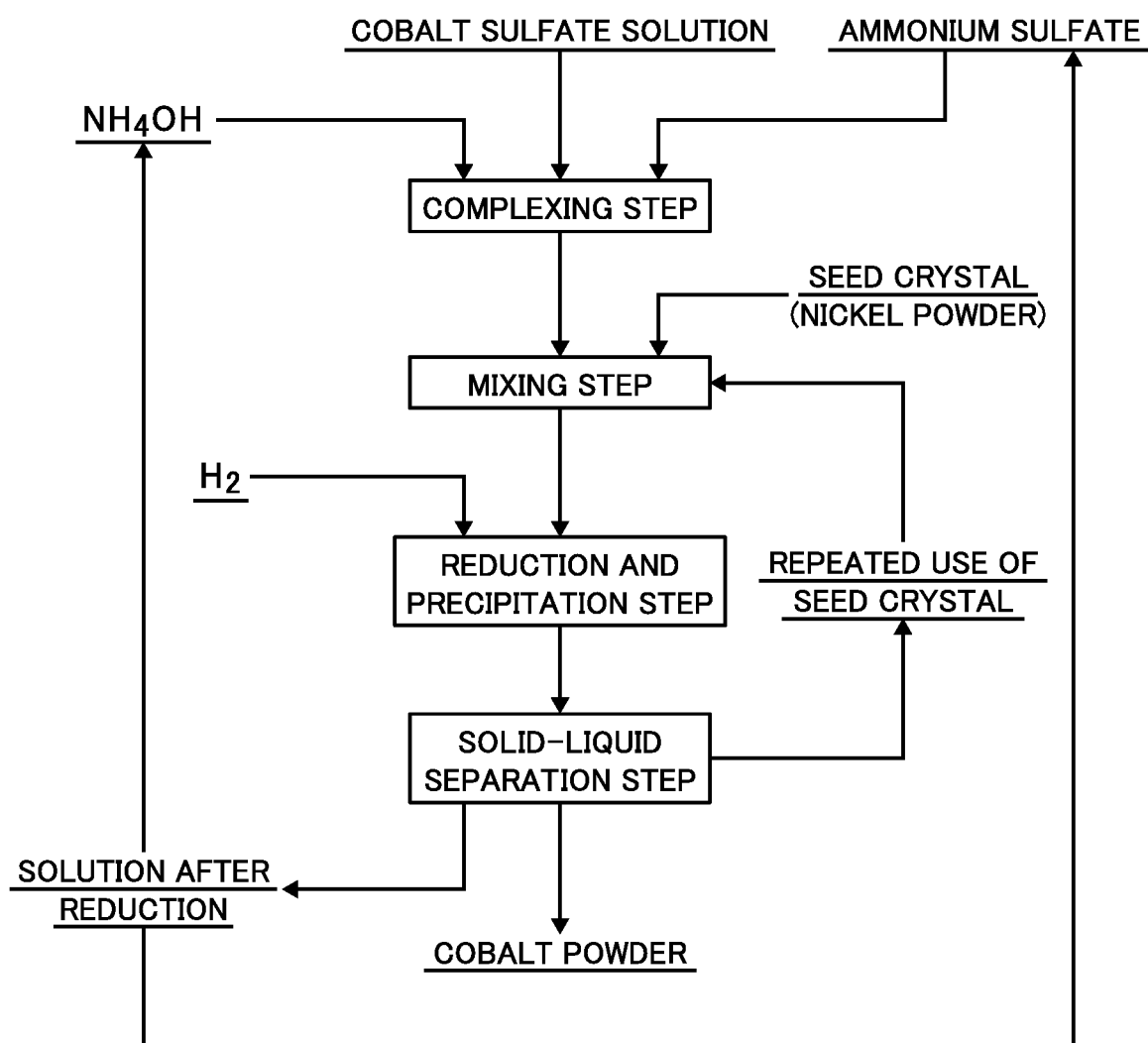
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Fig.1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/080690

## 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

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)

JSTPlus/JMEDPlus/JST7580 (JDreamIII)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 32-9051 B2 (Chemical Construction Corp.), 24 October 1957 (24.10.1957), example 3 (Family: none)	1-3 4-5
X A	W.KUNDA et al., THE REDUCTION OF COBALT FROM ITS AQUEOUS AMMINE AMMONIUM SULPHATE SYSTEM USING HYDROGEN UNDER PRESSURE, Hydrometallurgy, 1979, Vol.4 No.4, Page.347-375	1-3 4-5
A	JP 8-503999 A (Sherritt Inc.), 30 April 1996 (30.04.1996), claim 1 & US 5246481 A claim 1 & WO 1994/10350 A1	1-5

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

## \* Special categories of cited documents:

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Date of the actual completion of the international search  
21 December 2016 (21.12.16)Date of mailing of the international search report  
10 January 2017 (10.01.17)Name and mailing address of the ISA/  
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/080690

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4761177 A (CHOU, Eddie C), 02 August 1988 (02.08.1988), examples (Family: none)	1-5
A	US 3775098 A (KUNDA, Wasył), 27 November 1973 (27.11.1973), examples (Family: none)	1-5

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

## REFERENCES CITED IN THE DESCRIPTION

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- JP 2010242143 A [0014]
- JP 4286220 B [0014]
- JP S5754207 B [0014]

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