

RECOVERY METHOD FOR HIGH PURITY PLATINUM

TECHNICAL FIELD

[0001]

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The present invention relates to a recovery method of high purity platinum for recovering high purity platinum, at a high yield, from a platinum alloy containing platinum and ruthenium as components, and in particular from scraps of a magnetic material target or the like.

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BACKGROUND ART

[0002]

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In recent years, pursuant to the considerable advancement of semiconductor integrated circuits, various thin films are being formed for circuit design and the formation of various electrical and electronic devices. Among the above, an alloy sputtering target containing platinum is also used for forming a specific thin film for use as a magnetic thin film for a recording medium or as a semiconductor material. This kind of platinum alloy target often also contains ruthenium as an alloy element.

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These thin films are formed by sputtering an alloy target containing platinum or the like in an inert atmosphere of argon gas or the like.

[0003]

During the stage that this kind of target is produced, a large amount of mill ends such as sawdust is generated. All of such mill ends become scraps. And the spent target also becomes a scrap.

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During the production process of the target, as a result of the plastic working such as forging/rolling or mechanical processing such as cutting of the ingot after the ingot is melted and cast, and due to the process of bonding the target to the backing plate, the portion that comes into contact with the target becomes contaminated. In particular, contamination is severe which is caused by heavy metals and the like from the material configuring the cutting tools used for the mechanical processing and peripheral processing tools is severe.

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Since platinum is an expensive material, it is necessary to recover and reuse the same, but there is a problem in that a material containing the foregoing contaminants cannot be used as is.

[0004] The foregoing impurities may cause the deterioration of performance of recording mediums, hard disks and semiconductor device elements, as well as cause the deterioration of performance of thin films as a result of generating splashes, abnormal discharges, particles and the like during the sputtering process.

5 Normally, platinum is recovered by dissolving platinum-containing scraps in acid such as aqua regia to eliminate residue, thereafter causing the acid with platinum dissolved therein and an ammonium chloride solution to react so as to precipitate/recover the product as ammonium hexachloroplatinate, and additionally roasting the ammonium hexachloroplatinate.

10 [0005] A magnetic thin film containing platinum as its main component of the constituent elements or as a part of the constituent elements often contains ruthenium also as a part of the constituent elements. Since ruthenium is a platinum group element, in addition to the properties being similar, there is also the problem of platinum and ruthenium being difficult to separate.

15 Excluding special cases where the inclusion of ruthenium in platinum will not cause any particular problem to the material properties, unless platinum and ruthenium are separated, ruthenium will become an impurity. Since platinum itself is an extremely expensive material, platinum must be recovered at a high yield.

20 Several techniques for recovering platinum have been proposed in patent documents, and these are introduced below. However, it cannot be said that these patent documents offer an efficient recovery method for separating ruthenium from platinum and recovering high purity platinum.

[0006] Patent Document 1 below discloses, upon precipitating platinum as an ammonium chloride salt and extracting platinum, technology of adjusting the pH of a chloride-containing aqueous solution which contains gold and platinum group metals and performing two-stage neutralization and filtering to separate tellurium.

25 Patent Document 2 below discloses technology of eliminating ruthenium as an impurity by heating ammonium hexachloroplatinate or platinum to a high temperature in an oxygen gas airflow.

30 [0007] Patent Document 3 below discloses, upon separating ruthenium from a solution containing a platinum group via oxidation/distillation, technology of adjusting the pH of the solution, and thereafter using sodium bromate to transform ruthenium into ruthenium tetroxide and performing oxidation/distillation thereto so as to

separate/recover ruthenium.

Patent Document 4 below discloses, upon forming ammonium hexachloroplatinate, a method of producing a platinum powder by using a dispersion stabilization agent in an ammonium chloride solution to obtain fine ammonium hexachloroplatinate, and burning the ammonium hexachloroplatinate at a low temperature.

[0008] Patent Document 5 below discloses a high purity platinum recovery method including the steps of dissolving platinum-containing scraps in acid, thereafter causing the product to react with an ammonium chloride solution, precipitating/recovering the product as ammonium hexachloroplatinate, and roasting the ammonium hexachloroplatinate to obtain a platinum sponge.

Patent Document 6 below describes technology of dissolving platinum-containing scraps in acid, thereafter causing the product to react with an ammonium chloride solution, precipitating/recovering the product as ammonium hexachloroplatinate, and thereafter recovering the platinum remaining in the liquid by using ion-exchange resin and activated carbon.

[0009] [Patent Document 1] Japanese Unexamined Patent Application Publication No. H10-102156

[Patent Document 2] Japanese Unexamined Patent Application Publication No. 2006-183099

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 2006-161096

[Patent Document 4] Japanese Unexamined Patent Application Publication No. 2008-106349

[Patent Document 5] Japanese Unexamined Patent Application Publication No. 2003-27154

[Patent Document 6] Japanese Unexamined Patent Application Publication No. 2003-129145

SUMMARY OF THE INVENTION

[Problems to be Solved by the Invention]

[0010] Based on the above, the present invention provides a method of enabling recovery of high purity platinum as a result of efficiently eliminating cobalt, chromium, copper, iron, nickel, silicon and the like which become included in a platinum alloy used for sputtering particularly in a target scrap (spent target) containing platinum used for forming a magnetic thin film or in scraps such as mill ends, sawdust, and surface grinding scraps generated in the production process of such a target. Especially, since it is possible to separate ruthenium contained in the platinum alloy scraps used for sputtering, recovery of high purity platinum which can be reused in platinum and a platinum-containing target can be achieved at a high yield and at a low cost.

[Means for Solving the Problems]

[0011] The present invention provides:

1) A high purity platinum recovery method including the steps of dissolving a platinum alloy containing ruthenium in aqua regia and eliminating residue, thereafter causing acid with platinum dissolved therein and an ammonium chloride solution to react so as to deposit chloroplatinic ammonium salt, and reducing the chloroplatinic ammonium salt to obtain a platinum sponge, wherein the acid with platinum dissolved therein and the ammonium chloride solution are caused to react at a temperature of 40°C or higher;

2) The high purity platinum recovery method according to 1) above, wherein a platinum concentration of a liquid resulting from dissolving the platinum alloy containing ruthenium in the aqua regia is 15 g/L or more; and

3) The high purity platinum recovery method according to 1) or 2) above, wherein a ruthenium concentration of a liquid resulting from dissolving the platinum alloy containing ruthenium in the aqua regia is 6 g/L or less.

[0012] The present invention additionally provides:

4) The high purity platinum recovery method according to any one of 1) to 3) above, wherein a ruthenium content as an impurity in the platinum sponge obtained by roasting the chloroplatinic ammonium salt is 2% or less;

5) The high purity platinum recovery method according to 4) above, wherein the ruthenium content is 1% or less; and

6) The high purity platinum recovery method according to any one of 1) to 5) above, wherein the platinum alloy containing ruthenium is a scrap of a magnetic

material target, and a platinum recovery rate from the scrap is 99% or higher.

[Effect of the Invention]

[0013] The present invention yields a superior effect of being able to eliminate, with a relatively simple process, cobalt, chromium, copper, iron, nickel, silicon and the like which become included in a platinum-containing target scrap (spent target) for use in sputtering or in scraps such as mill ends, sawdust, and surface grinding scraps generated during the production process of such a target, and efficiently separate, from platinum, ruthenium as a platinum group element contained in the magnetic material target.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present invention foremost dissolves, in acid, scraps containing platinum and ruthenium and additionally containing cobalt, chromium, copper, iron, nickel, silicon and the like as impurity elements. Aqua regia is used as the acid for dissolving the scraps. While other acids can also be used for dissolving the scraps, for instance, if hydrochloric acid is used for dissolving the scraps, the dissolution will be incomplete. In addition, hydrogen will be generated; which is a possibility of hydrogen explosion.

Sufficient dissolution can be achieved by using aqua regia, and there is an advantage in that there is no danger of the hydrogen becoming diluted and exploding since nitrogen oxide and hydrogen are simultaneously generated during the dissolution. When aqua regia is used, while platinum will not dissolve easily at first, platinum will gradually dissolve more easily.

[0015] After dissolving the platinum-containing scraps in acid, impurities such as tantalum oxide (Ta_2O_5) and boron oxide (B_2O_3), as residue, are eliminated.

After eliminating the residue, caustic alkali such as sodium hydroxide (NaOH) is added to the solution containing platinum, the pH is adjusted to be 3 to 6 to achieve neutralization, cobalt, copper and the like are precipitated as hydroxide, and these are filtered and eliminated.

When the solution contains palladium, hydroxides of cobalt, copper and the like are precipitated and eliminated, and palladium is extracted via solvent

extraction. After palladium is extracted, the extracted palladium is subject to back extraction with ammonia, and the palladium-containing fluid is reduced with a reducing agent such as hydrazine so as to recover a high purity palladium sponge.

[0016] Subsequently, the acid with platinum dissolved therein and an ammonium chloride solution are caused to react so as to precipitate ammonium hexachloroplatinate $((\text{NH}_4)_2\text{PtCl}_6)$ crystals. In the foregoing case, desirably, aqua regia that dissolved the platinum is added to the ammonium chloride solution.

Normally, common knowledge is to add an ammonium chloride solution to the aqua regia with platinum dissolved therein, but when this technique is adopted, ammonium hexachloroplatinate becomes re-dissolved and cannot be deposited easily; thus phenomena are observed in that platinum remains in the solution and the yield of platinum deteriorates.

[0017] Accordingly, in order to increase the yield of platinum, it is important to add the aqua regia that dissolved the platinum to the ammonium chloride solution.

Subsequently, the ammonium hexachloroplatinate $((\text{NH}_4)_2\text{PtCl}_6)$ crystals obtained as described above are roasted at 600 to 1000°C to obtain a high purity platinum sponge. Consequently, the yield of platinum reaches 97%, and high purity platinum can be recovered at a high yield with a relatively simple method. The foregoing process is a method that is disclosed in Patent Document 6 developed by Nikko Materials, which is the name of the predecessor of the Applicant before the name change, and is an efficient recovery method for high purity platinum.

[0018] The problem is that the separation of ruthenium is not considered in the foregoing scraps. This is because the separation of ruthenium was not considered a major problem since the addition of ruthenium for forming a magnetic film or as a constituent element of the target was not being conducted generally. Nevertheless, the separation of ruthenium is an urgent necessity under the current circumstances.

Meanwhile, since ruthenium is a platinum group element as described above, it cannot be separated from platinum easily. The present invention provides technology for easily and efficiently separating ruthenium from platinum.

[0019] The high purity platinum recovery method of the present invention includes the steps of dissolving a platinum alloy containing ruthenium in aqua regia and eliminating residue, thereafter causing acid with platinum dissolved therein and an ammonium chloride solution to react so as to deposit chloroplatinic ammonium

salt, and reducing the chloroplatinic ammonium salt to obtain a platinum sponge, wherein the acid with platinum dissolved therein and the ammonium chloride solution are caused to react at a temperature of 40°C or higher.

While there is no particular limit in the upper limit of the temperature, it could be said that the temperature is preferably 100°C or less where the solution does not evaporate.

[0020] It could be said that, up to the process of obtaining the sponge, conventional technology may be used. Nevertheless, it is difficult to separate ruthenium, and the intended separation could not be realized. Nevertheless, by raising the temperature by merely 10 to 20°C or so higher than ordinary temperature, the platinum recovery rate improved, and it became possible to reduce the content rate of ruthenium in the platinum salt. This was an extremely unexpected result.

[0021] In other words, the technique of reducing the foregoing chloroplatinic ammonium salt and obtaining a platinum sponge is a relatively simple and efficient production process, and the separation of ruthenium became possible as an extension of the foregoing technology.

While this may appear to be simple, as described above, it is difficult to anticipate this result, and a dramatic effect was obtained.

[0022] Moreover, with the high purity platinum recovery method of the present invention, preferably, the platinum concentration of the liquid resulting from dissolving the platinum alloy containing ruthenium in the aqua regia is 15 g/L or more. This is because the solubility of the platinum salt will increase and the platinum recovery rate from scraps will deteriorate (to less than 99%), if the platinum concentration is reduced to less than 15 g/L.

25 The platinum content rate in the scraps is usually 30 wt% or higher, and, when the scraps are dissolved in aqua regia under normal conditions, the platinum concentration in the solution becomes a concentration that becomes considerably greater than 15 g/L; the concentration will not fall below 15 g/L unless the product is diluted in a large volume of water. However, in cases where the ruthenium content rate is high and the platinum content rate is relatively low, and the concentration will fall below 15 g/L as is, it will suffice to mix the scraps with scraps having a high platinum content rate and dissolve the scraps in aqua regia.

[0023] With the high purity platinum recovery method of the present invention,

preferably, the ruthenium concentration of the liquid resulting from dissolving the platinum alloy containing ruthenium in the aqua regia is 6 g/L or less.

In addition to the foregoing reaction temperature being affected, this is because ruthenium tends to easily enter into the deposit when the ruthenium concentration exceeds 6 g/L. In order to lower the ruthenium concentration, dilution with water will suffice. Nevertheless, mutual adjustment is required since dilution will contrarily lower the platinum concentration of the liquid.

[0024] Based on the above, the high purity platinum recovery method of the present invention can cause the ruthenium content as an impurity in the platinum sponge, which is obtained by roasting the chloroplatinic ammonium salt, to be 2% or less, and even 1% or less. In addition, the present invention can achieve a platinum recovery rate of 99% or higher from scraps of a magnetic material target containing a platinum alloy containing ruthenium. The present invention provides this kind of high purity platinum recovery method.

[0025] [Examples]

The present invention is now explained based on the following Examples. Note that these Examples are described for facilitating the understanding of the present invention, and the present invention is not limited by the Examples. In other words, the present invention is only limited by the ensuing patent claims and the technical concept described in this specification.

[0026]
(Example 1)

In Example 1, scraps of a magnetic material target containing platinum, cobalt, chromium, and ruthenium were dissolved in aqua regia and residue was eliminated, and the resulting product was diluted in water to obtain an aqua regia solution having a platinum concentration of 30 g/L and a ruthenium concentration of 5 g/L.

The aqua regia solution and ammonium chloride were caused to react at 45°C to obtain chloroplatinic ammonium salt $((\text{NH}_4)_2\text{PtCl}_6)$ crystals. Subsequently, the crystals were roasted at 800°C to obtain a platinum sponge, and the platinum recovery rate from the aqua regia solution and the ruthenium content rate as an impurity were measured. The results are shown in Table 1.

[0027]

[Table 1]

	platinum recovery rate (%)	ruthenium content rate in the platinum salt (wt%)
Example 1	99.5	0.5
Example 2	99.3	0.3
Example 3	99.2	1.7
Comparative Example 1	96.0	0.6
Comparative Example 2	99.5	2.3
Comparative Example 3	99.2	3.5

[0028] As shown in Table 1, the platinum recovery rate reached 99.5%, and the
5 ruthenium content rate in the platinum salt decreased to 0.5 wt%. This ruthenium
content was sufficiently decreased to use the recycled platinum as a target.
Moreover, similar platinum purity and ruthenium reduction could be achieved as long
as the reaction temperature of the aqua regia solution and ammonium chloride was
40°C or higher. Note that there is no particular limitation to the roast temperature
10 and may be adjusted as needed, and the temperature capable of normally obtaining
a platinum sponge may be arbitrarily selected; hereinafter the same.

[0029] (Example 2)

In Example 2, scraps of a magnetic material target containing platinum,
15 cobalt, chromium, and ruthenium were dissolved in aqua regia and residue was
eliminated, and the resulting product was diluted in water to obtain an aqua regia
solution having a platinum concentration of 18 g/L and a ruthenium concentration of 3 g/L.

The aqua regia solution and ammonium chloride were caused to react at
90°C to deposit chloroplatinic ammonium salt, and the deposited chloroplatinic
20 ammonium salt was roasted at 800°C to obtain a platinum sponge, and the platinum
recovery rate from the aqua regia solution and the ruthenium content rate as an
impurity were measured. The results are shown in Table 1.

[0030] As shown in Table 1, the platinum recovery rate reached 99.3 %, and the
ruthenium content rate in the platinum salt decreased to 0.3 wt%. This ruthenium
25 content was sufficiently decreased to use the recycled platinum as a target.
Moreover, similar platinum purity and ruthenium reduction could be achieved so as
long as the reaction temperature of the aqua regia solution and ammonium chloride

was 40°C or higher.

[0031]

(Example 3)

In Example 3, scraps of a magnetic material target containing platinum, cobalt, chromium, and ruthenium were dissolved in aqua regia and residue was eliminated, and the resulting product was diluted in water to obtain an aqua regia solution having a platinum concentration of 16 g/L and a ruthenium concentration of 5 g/L.

The aqua regia solution and ammonium chloride were caused to react at 50°C to deposit chloroplatinic ammonium salt, and the deposited chloroplatinic ammonium salt was roasted at 800°C to obtain a platinum sponge, and the platinum recovery rate from the aqua regia solution and the ruthenium content rate as an impurity were measured. The results are shown in Table 1.

[0032]

As shown in Table 1, the platinum recovery rate reached 99.2 %, and the ruthenium content rate in the platinum salt decreased to 1.7 wt%. This ruthenium content was sufficiently decreased to use the recycled platinum as a target. Moreover, similar platinum purity and ruthenium reduction could be achieved so as long as the reaction temperature of the aqua regia solution and ammonium chloride was 40°C or higher.

20 [0033]

(Comparative Example 1)

Scraps of a magnetic material target containing platinum, cobalt, chromium, and ruthenium were dissolved in aqua regia and residue was eliminated, and the resulting product was diluted in water to obtain an aqua regia solution having a platinum concentration of 12 g/L and a ruthenium concentration of 2 g/L. In the foregoing case, the platinum concentration was low and lower than the 15 g/L of the present invention.

The aqua regia solution and ammonium chloride were caused to react at 70°C to deposit chloroplatinic ammonium salt, and the deposited chloroplatinic ammonium salt was roasted at 800°C to obtain a platinum sponge, and the platinum recovery rate from the aqua regia solution and the ruthenium content rate as an impurity were measured.

[0034]

The results are shown in Table 1. As shown in Table 1, the ruthenium

content rate in the platinum salt decreased to 0.6 wt% and the ruthenium content satisfied the conditions of the object of the present invention, but the platinum recovery rate deteriorated to 96.0%. It was confirmed that a low platinum concentration is unfavorable since it deteriorates the platinum recovery rate.

5 [0035]

(Comparative Example 2)

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Scraps of a magnetic material target containing platinum, cobalt, chromium, and ruthenium were dissolved in aqua regia and residue was eliminated, and the resulting product was diluted in water to obtain an aqua regia solution having a platinum concentration of 48 g/L and a ruthenium concentration of 8 g/L. In the foregoing case, the ruthenium concentration exceeded 6 g/L, which is the upper limit of the present invention.

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The aqua regia solution and ammonium chloride were caused to react at 70°C to deposit chloroplatinic ammonium salt, and the deposited chloroplatinic ammonium salt was roasted at 800°C to obtain a platinum sponge, and the platinum recovery rate from the aqua regia solution and the ruthenium content rate as an impurity were measured.

[0036]

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The results are shown in Table 1. As shown in Table 1, while the platinum recovery rate was high at 99.5%, the ruthenium content rate in the platinum salt increased to 2.3 wt%. It was confirmed that a high ruthenium concentration in the aqua regia solution is unfavorable.

[0037]

(Comparative Example 3)

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Scraps of a magnetic material target containing platinum, cobalt, chromium, and ruthenium were dissolved in aqua regia and residue was eliminated, and the resulting product was diluted in water to obtain an aqua regia solution having a platinum concentration of 30 g/L and a ruthenium concentration of 5 g/L. The aqua regia solution and ammonium chloride were caused to react at 30°C to deposit chloroplatinic ammonium salt, and the deposited chloroplatinic ammonium salt was roasted at 800°C to obtain a platinum sponge, and the platinum recovery rate from the aqua regia solution and the ruthenium content rate as an impurity were measured. In the foregoing case, the temperature for causing the aqua regia solution and ammonium chloride to react did not satisfy 40°C or higher, which is a condition of the

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present invention.

[0038] The results are shown in Table 1. As shown in Table 1, while the platinum recovery rate was high at 99.2%, the ruthenium content rate in the platinum salt increased to 3.5 wt%. It was confirmed that a low temperature for causing the aqua regia solution and ammonium chloride to react is unfavorable since it increases the ruthenium content.

[0039] Accordingly, in addition to platinum, cobalt, chromium, and ruthenium as the magnetic materials as scraps, it was possible to eliminate most of the numerous other impurities such as copper, iron, nickel, silicon and the like that result from the mill ends, sawdust, and surface grinding scraps arising during the production process of a target containing platinum, and the platinum yield of obtaining high purity platinum reached 99%.

Moreover, it was also possible to yield an effect of being able to reduce ruthenium, which is difficult to separate from platinum.

15 In the foregoing description, while scraps of a magnetic material target containing platinum, cobalt, chromium, and ruthenium were used for explaining the present invention, the present invention can be similarly applied to scraps containing other impurities.

[Industrial Applicability]

20 [0040] The present invention yields a superior effect of being able to eliminate, with a relatively simple process, cobalt, chromium, copper, iron, nickel, silicon and the like which become included in scraps such as mill ends, sawdust, and surface grinding scraps generated during the production process of a platinum and platinum-containing target for use in sputtering, and recover, at a high yield, high purity platinum that can be reused as platinum or as a target containing platinum. Moreover, since the present invention also yields an effect of being able to reduce ruthenium, which is said to be difficult to separate from platinum, using a relatively simple method, the present invention can provide a method that is useful for recovering high purity platinum at a low cost and at a high yield.

CLAIMS

1. A high purity platinum recovery method including the steps of dissolving a platinum alloy containing ruthenium in aqua regia and eliminating residue, thereafter causing acid with platinum dissolved therein and an ammonium chloride solution to react so as to deposit chloroplatinic ammonium salt, and reducing the chloroplatinic ammonium salt to obtain a platinum sponge, wherein the acid with platinum dissolved therein and the ammonium chloride solution are caused to react at a temperature of 40°C or higher.

2. The high purity platinum recovery method according to claim 1, wherein a platinum concentration of a liquid resulting from dissolving the platinum alloy containing ruthenium in the aqua regia is 15 g/L or more.

3. The high purity platinum recovery method according to claim 1 or claim 2, wherein a ruthenium concentration of a liquid resulting from dissolving the platinum alloy containing ruthenium in the aqua regia is 6 g/L or less.

4. The high purity platinum recovery method according to any one of claims 1 to 3, wherein a ruthenium content as an impurity in the platinum sponge obtained by roasting the chloroplatinic ammonium salt is 2% or less.

5. The high purity platinum recovery method according to claim 4, wherein the ruthenium content is 1% or less.

6. The high purity platinum recovery method according to any one of claims 1 to 5, wherein the platinum alloy containing ruthenium is a scrap of a magnetic material target, and a platinum recovery rate from the scrap is 99% or higher.