METHOD AND APPARATUS FOR RECOVERING INDIUM FROM ETCHING WASTE SOLUTION CONTAINING INDIUM AND FERRIC CHLORIDE

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ABSTRACT

An object is to provide a method and an apparatus for recovering indium, the method and apparatus ensuring that it is unnecessary to recover indium in the form of indium hydroxide, indium can be recovered at a high concentration, indium can be recovered easily by a filter or the like without handling inferiors and also, the recovery rate of indium is greatly improved. The method includes adding a precipitation-inducing metal including a metal having higher ionization tendency than indium to an etching waste solution containing at least indium and ferric chloride, in which the concentration of ferric chloride is adjusted to 20% by weight or less to thereby precipitate indium contained in the etching waste solution on the surface of the precipitation-inducing metal, then, detaching the indium precipitated on the precipitation-inducing metal from the precipitation-inducing metal by a detaching means and separating the detached solid indium or indium alloy from the solution to recover the indium.
METHOD AND APPARATUS FOR RECOVERING INDIUM FROM ETCHING WASTE SOLUTION CONTAINING INDIUM AND FERRIC CHLORIDE

TECHNICAL FIELD

[0001] The present invention relates to a method and an apparatus for recovering indium from an etching waste solution containing indium and ferric chloride, and particularly, to a method and apparatus for recovering valuables, namely indium (In) in the form of an alloy, a metal simple substance or the like from an etching waste solution generated, for example, in the processes for manufacturing flat panel displays such as a liquid crystal display and plasma display.

BACKGROUND ART

[0002] Flat panel displays (FPD) such as liquid crystal displays and plasma displays are currently used for display and electronic devices such as displays for use in the display part of portable telephones. In a process for manufacturing such an FPD, it is necessary to note that waste solutions are produced and it is necessary to treat these waste solutions. This is the same to not only to liquid crystal manufacturing factories where such an FPD is treated but also to semiconductor manufacturing factories and plating factories. Then, there is an etching waste solution containing indium and ferric chloride as one of these waste solutions generated in the processes of manufacturing such an FPD.

[0003] Generally, industrial waste solutions sometimes contain various metals. In and the like are contained in waste solutions from liquid crystal manufacturing factories for manufacturing the FPD, copper (Cu), gallium (Ga) and the like are contained in waste solutions from semiconductor manufacturing factories, and nickel (Ni), Cu, zinc (Zn) and the like are contained in waste solutions from plating factories. An attempt is made to recover these metals as valuables. If these metals can be recovered in the form of metal or metal alloy, these metals may be, for example, reused.

[0004] As conventional technologies for treating waste solutions to recover heavy metals, the coagulation sedimentation treatment, coprecipitation treatment, or the like using chemicals is usually adopted. When the concentration of metals is lowered, these metals are removed by using an adsorbent. For example, as technologies utilizing the coagulation sedimentation treatment using chemicals, there is the invention described in the following Patent Document 1.

[0005] However, when the coagulation sedimentation treatment as mentioned above is applied to the etching waste solution containing indium and ferric chloride, indium can be recovered in the form of indium hydroxide. However, ferric chloride is also precipitated as a hydroxide, resulting in the problem that the amount of sludges of hydroxides generated is increased as a whole. Also, almost all sludges are put into iron-containing sludges, resulting in the problem that these metals are not recovered as valuables.

[0006] The present inventors and the like have researched prior art concerning a method of removing or recovering indium from an etching waste solution containing indium and ferric chloride, and as a result, have found that the patent application described in the following Patent Document 2 only exists. Specifically, the invention described in this Patent Document 2 relates to a method for removing or recovering indium, characterized in that iron and a nickel compound are added to an etching waste solution containing indium and ferric chloride as described in Claim 1 thereof.

[0007] As for specific recovering means, there are the descriptions, in the paragraph [0022] of the specification of Patent Document 2, reading as follows “A nickel compound is added, then iron is added to the waste solution, and the mixture is stirred to precipitate nickel and also indium. From this fact, indium can be removed from the waste solution. In other words, indium can be recovered from the precipitate...”. There are also the descriptions in the paragraph [0023], reading as follows “The mixture consisting of indium and nickel precipitated by adding iron to the etching waste solution containing indium and ferric chloride is stuck to iron and can be therefore simply separated from the solution as a precipitate. Examples of a method of separating the precipitate includes the gravity type sedimentation, filtration and methods utilizing centrifugation such as a method using a cyclone.”.

[0008] Inferring from these descriptions, a nickel precipitation reaction is caused by the addition of nickel ions and this nickel precipitation reaction is accompanied by an indium precipitation reaction in the method of Patent Document 2. Therefore, the recovered indium alloy is much reduced in indium concentration and is recovered in the form of an alloy primarily containing nickel, and it is therefore difficult to utilize the recovered indium efficiently. In this point, Patent Document 2 does not refer to a method of recovering indium by increasing the concentration of indium in the alloy to a desired concentration or more. Therefore, though the method as described in Patent Document 2 may be used as technologies for removing indium from a waste solution, the method is unnecessarily regarded as technologies that can be effectively utilized as technologies for recovering only indium as a valuable. Also, indium is stuck to iron as a mixture with nickel and the like, and it is therefore necessary to separate indium as a precipitate by various separating methods and it is also very difficult to recover indium as a valuable by the usual separating method.


DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0011] The present invention has been made for solving such problems, and it is an object of the present invention to provide a method and an apparatus for recovering indium, in which the necessity to recover indium in the form of indium hydroxide can be omitted unlike the conventional methods, the concentration of indium in an alloy is not lowered so that indium can be recovered at a high concentration when recovering indium in the form of the alloy with other metals, therefore, indium can be recovered without handling sludges when in recovering unlike the case of indium hydroxide, so that it can be recovered easily by a filter or the like and also, the recovery rate of indium is greatly improved.

Means for Solving the Problems

[0012] To achieve the above object, the present invention has been made to provide a method and an apparatus for recovering indium from an etching waste solution containing indium and ferric chloride, with regard to the characteristics of a method for recovering indium, the present invention...
relates to a method for recovering indium from an etching waste solution containing indium and ferric chloride, wherein indium is recovered from an etching waste solution containing at least indium and ferric chloride, comprising adding a precipitation-inducing metal including a metal having higher ionization tendency than indium to an etching waste solution in which the concentration of ferric chloride in the waste solution is 20% by weight or less to precipitate indium contained in the etching waste solution on the surface of the precipitation-inducing metal, then, detaching the indium precipitated on the precipitation-inducing metal from the precipitation-inducing metal by a detaching means and separating the detached solid indium from the solution to recover it.

With regard to the characteristics of an apparatus for recovering indium, the present invention relates to an apparatus for recovering indium from an etching waste solution wherein indium is recovered from an etching waste solution containing at least indium and ferric chloride, comprising a recovering reactor 1 that introduces an etching waste solution adjusted such that the concentration of ferric chloride in the waste solution is 20% by weight or less thereinto or introduces an etching waste solution thereinto while adjusting the concentration of ferric chloride in the waste solution to 20% by weight or less, and adds a precipitation-inducing metal including a metal having higher ionization tendency than indium to cause a metal precipitation reaction to thereby precipitate indium contained in the etching waste solution on the surface of the precipitation-inducing metal, and a detachment means that detaches the indium precipitated on the precipitation-inducing metal from the precipitation inducing metal.

Indium to be recovered in the present invention may be recovered in the form of a metal simple substance and also in the form of an alloy or sometimes, in the form of a compound. Because indium contained in an etching waste solution is usually in the state of ions, compounds or the like, it is difficult to discriminate these materials from each other distinctly and clearly and also these materials are not necessarily discriminated from each other clearly. Therefore, the term “indium” in the present invention may include the case of an alloy or compound besides the case of meaning a metal simple substance.

The concentration of ferric chloride in the waste solution is preferably adjusted to 9% by weight or less, and more preferably adjusted to 6% by weight or less. Examples of the precipitation-inducing metal including a metal having higher ionization tendency than indium include zinc and aluminum.

As the means for detaching indium precipitated on the precipitation-inducing metal from the precipitation-inducing metal, for example, a means using ultrasonic wave to oscillate metal particles or a means using an electromagnet to stir metal particles to thereby collide these metal particles with each other may be adopted. The concentration of ferric chloride in the waste solution may be adjusted in an adjusting vessel 2 which may be installed at the stage preceding the recovering reactor 1 or in the recovering reactor 1.

**EFFECTS OF THE INVENTION**

According to the present invention, as mentioned above, a precipitation-inducing metal having higher ionization tendency than indium is added to an etching waste solution containing indium and ferric chloride such that the concentration of ferric chloride in the waste solution is 20% by weight or less, indium contained in the etching waste solution is precipitated on the surface of the precipitation-inducing metal, then, the indium precipitated on the precipitation-inducing metal is detached from the precipitation-inducing metal by a detaching means, and the detached solid indium is separated from the solution to be recovered. Therefore, the cementation reaction utilizing ionization tendency is combined with the detaching technologies for the recovery of indium from an etching waste solution and specifically, the use of the precipitation-inducing metal having higher ionization tendency than indium increases the total surface area of metal for a metal precipitation reaction and improves the precipitation reaction rate, and also, the precipitated metal grown to some extent is detached by the detaching means to always expose a new metal surface, thereby keeping the reaction rate. This produces such an effect that the indium recovery rate from a waste solution can be improved more outstandingly than any of the conventional methods.

In the case of an etching waste solution containing indium and ferric chloride which are the subjects of the present invention, the concentration of ferric chloride is usually as very high as 30% by weight or more. When intending to apply the cementation reaction utilizing the ionization tendency, the dissolution reaction of the precipitation-inducing metal is so strong that it is difficult to control the reduction precipitation reaction. Also, because the dissolution rate of the precipitation-inducing metal is higher than the precipitation rate of indium, zinc particles are all dissolved before iron and indium precipitate on the surface of zinc to terminate the dissolution reaction of zinc, with the result that the precipitated indium is dissolved again, making it impossible to recover the indium. In the present invention, on the contrary, the concentration of ferric chloride in the etching waste solution is adjusted to 20% by weight or less, preferably 9% by weight or less and more preferably 6% by weight or less as mentioned above, and therefore, the dissolution reaction of the precipitation-inducing metal is not so strong. Therefore, the control of the reduction precipitation reaction does not become difficult and also, the precipitation-inducing metal is not dissolved more than required.

Unlike the conventional methods, it is unnecessary to recover indium in the form of precipitates such as indium hydroxide, and also, even in the case where indium is recovered in the form of an alloy, the concentration of indium in the alloy is not reduced, so that indium is recovered at a high concentration. Therefore, such an effect is obtained that unlike the case of indium hydroxide, the precipitate obtained in this method is free from handling inferiors, enabling the precipitate to be recovered easily by a filter or the like.

As mentioned above, the present invention can provide a method for recovering indium at a high recovery rate and therefore, the present invention has the advantage that it can be applied as a method of recovering indium in the recycle process in the recycle factory of liquid crystal televisions even in the case where the recovery recycle of PDPs and the like is legally obligated, for example, by a household electric appliances-recycle law or a corresponding law.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic front view of an apparatus for recovering indium from an etching waste solution containing indium and ferric chloride in an embodiment.

FIG. 2 is a schematic front view of a recovering reactor in the apparatus for recovering indium.
FIG. 3 is a schematic front view of a recovering reactor of another embodiment.

DESCRIPTION OF REFERENCE NUMERALS

1 Recovering reactor
2 Adjusting vessel

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be explained in detail with reference to the drawings.

Embodiment 1

An apparatus for recovering indium (In) from an etching waste solution containing indium and ferric chloride is provided with a recovering reactor 1, an adjusting vessel 2 and a filter 3 as shown in FIG. 1.

The recovering reactor 1 serves to precipitate In from the waste solution by the cementation reaction (metal precipitation reaction) as explained later. The adjusting vessel 2 serves to adjust the concentration of ferric chloride in the waste solution ahead of the reaction. The filter 3 serves to separate and recover the In precipitated in the recovering reactor 1. Such a structure may be adopted in which the separated process solution is returned to the adjusting vessel 2. In the case of adopting the structure in which the separated process solution is returned to the adjusting vessel 2, a pump or the like that circulates a solution to be processed is required.

A reactor body 5 of the recovering reactor 1 is an oval type as shown in FIG. 2 and is constituted of a reactor upper part 6, a reactor middle part 7 and a reactor lower part 8, which are each connected via connecting parts 9 and 10. Although the reactor upper part 6, reactor middle part 7 and reactor lower part 8 are respectively formed in the same width, they are formed such that the sectional area of the reactor upper part 6 is larger than the sectional area of the reactor middle part 7 and the sectional area of the reactor lower part 8. As a result, the reactor 1 has a structure in which the sectional area of the reactor body 5 is discontinuously increased towards the upper side as a whole. In this case, the connecting parts 9 and 10 are formed in a taper form spread upward.

An intake chamber 11 having a substantially cone shape for introducing the etching waste solution containing In and ferric chloride to be treated is disposed on the lower side of the reactor lower part 8 and a intake tube 12 is disposed at the lower part of the intake chamber 11. The intake tube 12 is provided with a stop valve though not shown. Also, an upper chamber 13 is installed on the upper side of the upper part 6 and a discharge pipe 14 that discharges the recovered flake or microparticle In which is a recovery subject metal is installed on the side of the upper chamber 13.

The upper chamber 13 is a part that discharges the metal (In) recovered through the discharge tube 14 and also a part that introduces metal particles of a precipitation-inducing metal having a higher ionization tendency than In in order to cause the so-called cementation reaction (metal precipitation reaction) based on a difference in ionization tendency between the precipitation-inducing metal and In. In actual, the cementation reaction between the introduced metal and the recovered metal (In) is caused in the whole part of the reactor body 5. Then, the reactor has a structure in which a fluidized bed is formed by metal particles while the etching waste solution introduced from the intake tube 12 is made to flow up in a vertical direction until the etching waste solution reaches the discharge tube 14. Moreover, ultrasonic oscillators 15a, 15b and 15c as the detaching means that detaches the recovery subject metals which are the metals contained in the etching waste solution and precipitated on the introduced metal particles by the cementation reaction are disposed on the reactor upper part 6, reactor middle part 7 and reactor lower part 8, respectively.

In this embodiment, particles of zinc (Zn) or aluminum (Al) are used as the metal particles to be introduced. As for the average particle diameter of the metal particles to be introduced, metal particles having an average particle diameter of 2 mm are used in this embodiment though it is preferable to use metal particles having an average particle diameter of 0.1 to 8 mm. In this case, the average particle diameter is measured by, for example, the image analysis method or JIS Z 8801 Sieve Analysis Test.

Explained is a method of recovering In by the In-recovering apparatus having such a structure, first, a waste solution to be treated is supplied to the adjusting vessel 2 and the concentration of ferric chloride in the waste solution is adjusted in this adjusting vessel 2. Specifically, the etching waste solution is diluted by adding water in the adjusting vessel 2 such that the concentration of ferric chloride is 0% by weight or less.

Next, the etching waste solution in which the concentration of ferric chloride has been thus adjusted is flown into the reactor body 5 from the intake tube 12 through the intake chamber 11. On the other hand, metal particles (Zn or Al particles) producing the cementation reaction are introduced from the upper chamber 13. In the reactor body 5, the introduced etching waste solution is made to flow upward in a vertical direction, whereas the metal particles introduced from the upper chamber 13 are put into a fluidized state so as to form a fluidized bed.

Then, a so-called cementation reaction based on a difference in ionization tendency between In contained in the waste solution and the introduced metal particles, that is, Zn or Al particles, is caused. To explain this in more detail, the reduction reaction of each metal ion is as shown in the following equations (1) to (3), showing the standard electrode potential (E°) of each metal ion. Since ferric chloride is contained in the waste solution and Fe also participates in the cementation reaction, the reduction reaction of Fe ions is shown in the following equation (4) and its standard electrode potential (E°) is also shown.

\[ \text{In}^{3+} + 3e^- \rightarrow \text{In} \quad -0.34 \text{V} \]  \hspace{1cm} (1)

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad -0.76 \text{V} \]  \hspace{1cm} (2)

\[ \text{Al}^{3+} + 3e^- \rightarrow \text{Al} \quad -1.66 \text{V} \]  \hspace{1cm} (3)

\[ \text{Fe}^{2+} + 2e^- \rightarrow \text{Fe} \quad -0.44 \text{V} \]  \hspace{1cm} (4)

As is clear from the above (1) to (4), the standard reduction potentials of \( \text{Zn}^{2+} \) and \( \text{Al}^{3+} \) are smaller than the standard reduction potentials of \( \text{In}^{3+} \) and \( \text{Fe}^{2+} \). In other words, the ionization tendencies of Zn and Al are larger than those of In and Fe. Therefore, in the above fluidized state, Zn and Al each having a larger ionization tendency are ionized into \( \text{Zn}^{2+} \) and \( \text{Al}^{3+} \) and eluted in the waste solution. At the same time, \( \text{In}^{3+} \) and \( \text{Fe}^{2+} \) contained in the waste solution are deionized.
into In and Fe, respectively, and then, In and Fe are precipitated on the surface of Zn and Al.

In this case, ferric chloride is contained in the etching waste solution. Therefore, if the concentration of ferric chloride is high, the dissolution reaction of Zn particles or Al particles is strong when the cementation reaction is run and there is a fear that it is difficult to control the reduction precipitation reaction. Also, Zn particles and Al particles are dissolved more than required, bringing about an economical loss.

However, in this embodiment, the dissolution reaction of Zn particles or Al particles is not so strong because the concentration of ferric chloride in the etching waste solution is adjusted to 6% by weight or less as mentioned above, and therefore, it is not difficult to control the reduction precipitation reaction and Zn particles and Al particles are not dissolved more than required. Moreover, the precipitate is obtained in the state of an alloy of In and Fe in the above cementation reaction. However, the etching waste solution introduced into the reactor body 5 is diluted in advance such that the concentration of ferric chloride is 6% by weight or less and therefore, the obtained alloy of In and Fe contains In in an amount as very high as 90% by weight or more, making it possible to obtain an alloy having highly concentrated In.

After In is precipitated on the surface of Zn or Al particles by the cementation reaction, the ultrasonic oscillators 15a, 15b and 15c are allowed to operate. When allowing these ultrasonic oscillators 15a, 15b and 15c to operate, ultrasonic wave produced by the oscillation of the ultrasonic oscillators 15a, 15b and 15c give oscillation force and agitation force to the Zn particles or Al particles precipitating the In to thereby forcibly detach the precipitated In from these Zn particles or Al particles.

In the case of utilizing an ultrasonic oscillation for detaching the precipitated In in this manner, the existence of the ultrasonic oscillator can be visually confirmed on the reactor part from the outward appearance of the treating apparatus. Even in the case where the existence of the ultrasonic oscillator cannot be visually confirmed, it can be easily confirmed that treatment utilizing ultrasonic wave is performed because high noises at about over ten kHz are generated when Zn or Al metal particles are made to be in contact with each other and oscillated by the ultrasonic wave oscillator during treatment.

The process solution containing the In detached in this manner is discharged out of the reactor body 5 from the upper chamber 13 through the discharge tube 14 and separated by the filter 3, and the separated In is recovered resultantly. In this embodiment, a granular metal is used as the precipitation-inducing metal introduced to precipitate In which is a recovery subject metal in this case, and therefore, the surface area of the metals (Zn and Al) causing the cementation reaction is more increased than in the case of introducing, for example, scraps of Zn and Al, resulting in an improvement in the rate of In precipitation reaction. Then, after the precipitation of metals grown to some extent is recognized, a new metal surface (surface of Zn particles) is always exposed by the detachment forced by the oscillation of ultrasonic wave as mentioned above, making it possible to maintain reaction rate. The recovered metal contains very smaller amount of impurities other than In as compared with the case of the conventional method.

Since the metal particles consisting of Zn or Al are fluidized in the reactor body 5 and Zn^{2+} and Al^{3+} are eluted by the cementation reaction, the particle diameter of the metal particles introduced into the upper chamber 13 at the initial stage after the metal particles are introduced is inevitably decreased with time. As a result, because, originally, the waste solution flows upward at almost the same flow rate in the reactor body 5, there is a fear that the metal particles whose particle diameter is decreased as the waste solution comes close to the top overflows unexpectedly from the reactor body 5.

However, since the reactor body 5 is formed such that its sectional area is discontinuously increased with decrease in distance from the top of the reactor body 5 in this embodiment, the upward flow rate of the waste solution in the reactor body 5 is gradually decreased and therefore, the metal particles reduced in particle diameter by the cementation reaction or the like as mentioned above do not unexpectedly overflow over the upper part of the reactor body 5 whose sectional area increases but are kept within the reactor body 5 highly possibly.

When the etching waste solution is introduced from the lower side of the reactor body 5 and passes through the reactor body 5 in which is a recovery subject metal is precipitated on the metal particles constituted of Zn or Al by the cementation reaction, and therefore, the concentration of the recovery subject metal is reduced as the waste solution is nearer to the top of the reactor body 5.

In this embodiment, however, finer Zn or Al particles exist as the position is nearer to the top of the reactor body 5, and also, the rate of the upward flow of the etching waste solution is gradually decreased, so that it is recognized that the number of Zn or Al particles is increased. Therefore, the total surface area of Zn or Al particles is larger with decrease in distance from the top of the reactor body 5. As a result, because the reaction rate (efficiency of precipitation of In) of the cementation reaction is improved, In which is the recovery subject metal can be recovered efficiently also at the upper part of the reactor body 5 where the concentration of In is lower.

**Embodiment 2**

This embodiment is different from the embodiment 1 in the structure of the reactor body 5. Specifically, in this embodiment, a reactor body 5, as shown in FIG. 3, has a structure in which the entire peripheral surface forms a taper spread upward, so that the sectional area of the reactor body 5 is increased continuously with decrease in distance from the top of the reactor body 5. This embodiment 2 is different in this point from the embodiment 1 in which the sectional area of the reactor body 5 is discontinuously increased with decrease in distance from the top of the reactor body 5. Since the reactor body 5 of this embodiment is structured such that it is not discontinuously but continuously increased in its sectional area, the reactor body 5 of this embodiment is not divided into the reactor upper part 6, the reactor middle part 7 and the reactor lower part 8 in its structure unlike the embodiment 1.

However, this embodiment is in common with the embodiment 1 in the point that the ultrasonic oscillators 15a, 15b and 15c are installed at three points extending from the upper part to lower part of the reactor body 5. Accordingly, also in this embodiment, such an effect is obtained that In precipitated as the recovery subject metal on the metal particles (Zn, Al and the like) of the precipitation-inducing metal
can be forcibly detached by the ultrasonic wave oscillated from the ultrasonic oscillators 15a, 15b and 15c in the same manner as the embodiment 1.

[0048] Also, though there is a difference in whether the increase in sectional area is continuous or discontinuous, this embodiment is in common with the embodiment 1 in the point that the sectional area is increased towards the upper part of the reactor body 5. Therefore, also in this embodiment, fine metal particles decreased in particle diameter are kept at the upper part of the reactor body 5, producing such an effect that the phenomenon that the metal particles unexpectedly overflow over the reactor body 5 can be prevented and such an effect that the recovery subject metal can be efficiently recovered at the upper part of the reactor body 5 where the concentration of the recovery subject metal is low.

Other Embodiments

[0049] Since, in the above embodiments, the concentration of ferric chloride in the etching waste solution is designed to be 6% by weight or less, the desired effect that the recovery rate of In is improved is obtained. However, the concentration of ferric chloride in the etching waste solution is not limited to that of the embodiments. It is only necessary that the concentration of the ferric chloride be 20% by weight or less. In the case where the concentration of ferric chloride in the etching waste solution is designed to be 6% by weight or less, the ratio of In to Fe to be recovered can be made to be about 9:1. When the concentration of ferric chloride is about 10 to 20% by weight, on the contrary, the ratio of In to Fe is about 1:1. Also in this case, the object of the present invention, that is, the object of recovering In or an alloy of In and Fe as valuable can be attained.

[0050] Also, the above embodiments were described by taking, for example, the case in which the adjusting vessel 2 is installed on the upstream side of the recovering reactor 1 and the concentration of ferric chloride in the waste solution is adjusted in this adjusting vessel 2. The present invention is not limited thereto, and the concentration of ferric chloride in the waste solution may be adjusted by, for example, adding a diluent directly in the recovering reactor 1.

[0051] The explanations in above embodiment are furnished as to the case where Zn or Al particles are added to recover In. However, the metal particles to be added in the recovering reactor are not limited to Zn or Al particles used in above embodiments and it is only necessary to use a metal having a higher ionization tendency than In.

[0052] In this embodiment, the particle diameter of the metal particles is designed to be about 2 mm. However, the particle diameter of the metal particles is not limited thereto and is preferably 0.1 to 8 mm. This reason is as follows. Specifically, when the particle diameter is less than 0.1 mm, the cementation reaction is unnecessarily properly run and there is also a fear that the precipitation-inducing metal detached from the metal particles cannot be recovered with ease. Particularly, when the concentration of ferric chloride is high, there is a fear that the cementation reaction is not properly run. When the particle diameter exceeds 8 mm, the number of metal particles which can be retained in the reactor body 5 is reduced, with the result that the total surface area of the metal particles is reduced, and there are fears as to a reduction in the efficiency of the precipitation reaction and as to precipitation of metals other than valuable metals, which are the recovery subject, in the form of metal particles.

[0053] The average particle diameter of the metal particles is measured by, for example, the image analysis method or JIS Z 8801 Sieve Analysis Test. For the measurement of the average particle diameter by the image analysis method, for example, MILLITRACK JPA manufactured by Nikkiso Co., Ltd. is used. When the average particle diameter is designed to be in the range of 1 to 2 mm as one example, it is only necessary to use metal particles having a screening size under a nominal dimension of 2000 µm and over a nominal dimension of 1000 µm.

[0054] In the embodiments 1 and 2, the reactor body 5 is formed such that its sectional area is increased with decrease in distance from the top of the reactor body 5 and therefore, the desirable effect is obtained. However, it is not essential in the present invention to form the reactor body 5 having such a structure.

[0055] Also, the means for detaching the recovery subject metal from the metal particles is not limited to the means using the ultrasonic wave in the embodiments 1 and 2 and to the means using an electromagnetic of the embodiment 3, but may be other means. Although metal particles are utilized as the precipitation-inducing metal in above embodiments, the precipitation-inducing metal is not limited thereto and, for example, metal wires, materials obtained by processing metal wires into a mesh structure or plate metals may be used.

EXAMPLES

[0056] The correlation between the concentration of ferric chloride in the etching waste solution as a process solution and the concentration of In in the precipitated metal was examined. Specifically, as shown in Table 1, solutions obtained by diluting the etching waste solution (concentration of ferric chloride: about 36% by weight) being a raw solution, two times, four times, six times and ten times by utilizing water were prepared and these solutions different in concentration were examined by using an apparatus such as those used in above embodiments. The test results are shown in Table 1.

<table>
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<tr>
<th>Magnification of dilution</th>
<th>Concentration of In in the precipitate (% by weight)</th>
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<tbody>
<tr>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
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<tr>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

[0057] As being clear from Table 1, the concentration of In in the precipitate was about 50% by weight in the solutions diluted two times (concentration of ferric chloride: about 18% by weight) and four times (concentration of ferric chloride: about 9% by weight), and the concentration of In in the precipitate was about 90% by weight in the solutions diluted six times (concentration of ferric chloride: about 6% by weight) and ten times (concentration of ferric chloride: about 3.6% by weight). It was found from this result that the concentration of In was increased, that is, the recovery rate of In is increased, with decrease in the concentration of ferric chloride in the solution.

[0058] Metals other than In in the precipitate are almost Fe. Accordingly, when the concentration of In is about 50% by weight, the rough composition of the precipitate is In: Fe=1:1,
and when the concentration of In is about 90% by weight, the rough composition of the precipitate is In: Fe=9:1.

1. A method for recovering indium from an etching waste solution containing at least indium and ferric chloride, comprising adding a precipitation-inducing metal including a metal having higher ionization tendency than indium to an etching waste solution with the concentration of ferric chloride of the etching waste solution adjusted to 20% by weight or less in the waste solution to thereby precipitate indium contained in the etching waste solution on the surface of the precipitation-inducing metal, then, detaching the indium precipitated on the precipitation-inducing metal from the precipitation-inducing metal by a detaching means and separating the detached solid indium from the solution to recover the indium.

2. The method for recovering indium according to claim 1, wherein the concentration of ferric chloride in the waste solution is adjusted to 9% by weight or less.

3. The method for recovering indium according to claim 1, wherein the concentration of ferric chloride in the waste solution is adjusted to 6% by weight or less.

4. The method for recovering indium according to claim 1, wherein the precipitation-inducing metal is added to the etching waste solution after the concentration of ferric chloride in the waste solution is adjusted.

5. The method for recovering indium according to claim 1, wherein the precipitation-inducing metal including a metal having higher ionization tendency than indium is any one of zinc and aluminum.

6. The method for recovering indium according to claim 1, wherein the means that detaches indium from the precipitation-inducing metal is a means that oscillates the metal particles by ultrasonic wave.

7. The method for recovering indium from an etching waste solution containing indium and ferric chloride according to claim 1, wherein the precipitation-inducing metal is metal particles having a particle diameter of 0.1 to 8 mm.

8. An apparatus for recovering indium from an etching waste solution containing at least indium and ferric chloride, comprising a recovering reactor (1) that introduces an etching waste solution with the concentration of ferric chloride of the etching waste solution adjusted to 20% by weight or less in the waste solution thereinto and adds a precipitation-inducing metal including a metal having higher ionization tendency than indium to cause a metal precipitation reaction to thereby precipitate indium contained in the etching waste solution on the surface of the precipitation-inducing metal, and a detachment means that detaches the indium precipitated on the precipitation-inducing metal from the precipitation inducing metal.

9. The apparatus for recovering indium according to claim 8, further comprising an adjusting vessel (2) disposed on the upstream side of the recovering reactor (1) to adjust the concentration of ferric chloride in the waste solution.

10. An apparatus for recovering indium from an etching waste solution containing at least indium and ferric chloride, comprising a recovering reactor (1) that introduces an etching waste solution thereinto, adjusts the concentration of ferric chloride in the waste solution to 20% by weight or less and adds a precipitation-inducing metal including a metal having higher ionization tendency than indium to cause a metal precipitation reaction to thereby precipitate indium contained in the etching waste solution on the surface of the precipitation-inducing metal, and a detachment means that detaches the indium precipitated on the precipitation-inducing metal from the precipitation inducing metal.

11. The apparatus for recovering indium according to claim 8, wherein the precipitation-inducing metal including a metal having higher ionization tendency than indium is any one of zinc and aluminum.

12. The apparatus for recovering indium according to claim 8, wherein the means that detaches indium from the precipitation-inducing metal is a means that oscillates the metal particles by ultrasonic wave.

13. The apparatus for recovering indium according to claim 10, wherein the precipitation-inducing metal including a metal having higher ionization tendency than indium is any one of zinc and aluminum.

14. The apparatus for recovering indium according to claim 10, wherein the means that detaches indium from the precipitation-inducing metal is a means that oscillates the metal particles by ultrasonic wave.

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