



(11)

EP 4 317 537 A1

(12)

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

(43) Date of publication:

07.02.2024 Bulletin 2024/06

(51) International Patent Classification (IPC):

C25D 21/18 ^(2006.01) **C25D 21/06** ^(2006.01)
C25D 3/20 ^(2006.01)

(21) Application number: **21933323.4**

(52) Cooperative Patent Classification (CPC):

C25D 3/20; C25D 21/06; C25D 21/18

(22) Date of filing: **22.03.2021**

(86) International application number:

PCT/KR2021/003533

(87) International publication number:

WO 2022/203095 (29.09.2022 Gazette 2022/39)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

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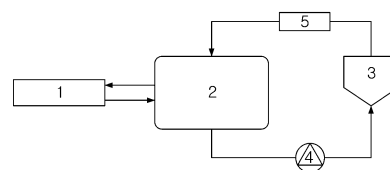
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(54) **METHOD FOR REMOVING FERRIC IONS FROM SULFATE-BASED IRON ELECTROPLATING SOLUTION**

(57) The present invention relates to a method for effectively removing ferric ions contained in an iron electroplating solution. The method for removing ferric ions contained in a sulfate-based iron electroplating solution comprises a step of regeneration for reduction of the ferric ions by circulating a ferric ion-containing sulfate-based iron electroplating solution in a solution bath containing ferrous metal charged therein, wherein the ferrous metal is charged in an amount that satisfies the following formula (1): $S \geq 0.01 I_{\text{conv}} / C_{\text{max}}$ (1). In formula (1), S indicates a total surface (m²) of ferrous metal, C_{max} indicates a maximum permissible ion concentration level (g/L) of the ferric ions in the solution, and I_{conv} indicates, as represented by the following formula (2), converted current (A) obtained by dividing the sum of current (I) applied to an electroplated cell during the plating time (t_p, sec) by the regeneration time (t_r, sec) for reduction of the ferric ions in an electrolyte.

$$I_{\text{conv}} = \frac{\int I dt_p}{\int dt_r}$$



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Description**Technical Field**

5 **[0001]** The present disclosure relates to a method for effectively removing ferric ions contained in an iron electroplating solution.

Background Art

10 **[0002]** Iron is a material made of steel sheets or steel materials and used as a general-purpose structural material, but since iron lacks corrosion resistance, appearance characteristics, and the like, compared to other metals, electroplating has been performed on a surface thereof for the purpose of utilizing magnetic characteristics or forming special-purpose alloys.

15 **[0003]** A conventional plating solution for iron electroplating on the surface of iron use ferrous ions to maintain high electroplating efficiency, but as ferrous ions are oxidized to ferric ions during a continuous electroplating process, there is a problem in that plating efficiency is rapidly reduced, and sludge is generated.

[0004] In order to solve this problem, conventionally, a method of reducing ferric ions to ferrous ions or periodically replacing the solution has been performed. However, in a large volume continuous electroplating process, it is difficult to periodically remove and replace the solution, and there is a problem of increasing manufacturing costs.

20 **[0005]** In addition, there is a method of reducing a production amount of ferric iron using a soluble anode. However, when electroplating is performed under a condition of a high current density exceeding 10 Ampere per Square Decimeter (ASD), oxidation of ferrous ions to ferric ions due to an increase in overvoltage cannot be fundamentally suppressed, and since dissolution efficiency of a soluble anode is higher than plating efficiency, a problem in which an iron ion concentration in the solution continuously increases, occurs. In addition, since the soluble anode is gradually dissolved and consumed as plating proceeds, a distance between electrodes and a surface state of the electrode changes, and accordingly, the soluble anode should be periodically replaced, so that it is very difficult to manage the soluble anode.

25 **[0006]** Meanwhile, in a sulfate-based iron electroplating solution to which an insoluble anode is applied, ferric ions are inevitably generated. Therefore, generally, a method of sludging ferric ions and filtering and removing the same from the plating solution, or reducing the ferric ions in the plating solution to ferrous ions by adding a reducing agent or through an electrolysis method, was used.

30 **[0007]** For example, Korean Patent Application No. 2011-0137463 discloses a method of reducing ferric ions to ferrous iron by containing ascorbic acid as a reducing agent in a sulfate-based iron electroplating solution. However, when ferric ions are reduced, ascorbic acid is oxidized to produce dehydroascorbic acid, which may cause a problem in that efficiency of iron electroplating may be significantly decreased, and dehydroascorbic acid may continuously accumulate.

35 **[0008]** As another example, Korean Patent Application No. 2015-0185858 and Japanese Patent Application Nos. 1994-181533 and 1988-259089, and the like disclose a method in which an anode and a cathode are installed in an electrolyte and a constant current is applied to reduce ferric ions to ferrous ions. However, when electricity is applied to an electrolyte containing both ferrous ions and ferric ions, a reaction in which ferrous iron is oxidized to ferric ions and a small amount of water decomposition reaction occur at an anode, while a reaction in which iron is mainly electroplated occurs and a reaction in which ferric ions is reduced to ferrous ions only partially occurs, at a cathode, resulting in a problem in which ferric ions are rather accumulated more occurs. That is, using this method, in an electrolyte solution, a reduction reaction rate of ferric ions may be increased at the cathode, using an additive suppressing iron electroplating, but in an iron electroplating solution requiring high plating efficiency, it is impossible to remove ferric ions in the solution using such an electrolysis method.

Summary of Invention**Technical Problem**

50 **[0009]** An aspect of the present disclosure is to provide a method of suppressing generation of sludge due to oxidation of iron ions by reducing ferric ions, generated during long-term continuous plating using an iron electroplating solution to ferrous ions and effectively removing the ferric ions, and maintaining plating efficiency to be constant, and effectively removing the ferric ions so that frequent solution replacement is not required.

Solution to Problem

55 **[0010]** According to an aspect of the present disclosure, provided is a method for removing ferric ions from a sulfate-based iron electroplating solution, the method including: a regeneration step of reducing ferric ions by circulating a

sulfate-based iron electroplating solution containing ferric ions in a solution bath containing metallic iron charged therein, wherein the metallic iron is charged in an amount satisfying the following formula (1):

$$S \geq 0.01 I_{\text{conv}} / C_{\text{max}} \dots (1)$$

[0011] In the formula (1), S indicates a total surface area (m²) of metallic iron, C_{max} indicates a maximum permissible ion concentration level (g/L) of the ferric ions in the solution, and I_{conv} indicates, as represented by the following formula (2), a converted current (A) obtained by dividing the sum of current (I) applied to an electroplated cell during a plating time (t_p, sec) by a regeneration time (t_r, sec) for reduction of the ferric ions in an electrolyte.

$$I_{\text{conv}} = \frac{\int I dt_p}{\int dt_r} \dots (2)$$

[0012] The regeneration step may be performed during a plating process.

[0013] The regeneration step may be performed during a plating process, and the regeneration step may be performed discontinuously two or more times.

[0014] The regeneration step may be initiated during a plating process, and may be terminated in a pause in the plating process, and the regeneration step may be performed continuously or discontinuously.

[0015] The regeneration step may be initiated in a pause in the plating process, and may be terminated in a pause during the plating process or after the plating process.

[0016] The regeneration step may be initiated during a pause in the plating process, and the regeneration step may be performed continuously or discontinuously.

[0017] The regeneration step may be performed discontinuously, including a pause in the plating process, and the regeneration step may be performed during two or more plating processes.

[0018] The metallic iron may be ferroalloy containing at least one alloying element selected from a group consisting of Mn, Al, Mg, Li, Na and K.

[0019] The ferroalloy may be ferroalloy containing an alloying element in an amount greater than 0% by weight and less than or equal to 3% by weight.

[0020] The metallic iron particles may be at least one of particles, a spiral chip, a plate shape, and a strip.

[0021] The sulfate-based iron electroplating solution may further include a complexing agent.

[0022] The complexing agent is at least one amino acid selected from glycine, glutamic acid and glutamine, and at least one compound selected from a group consisting of formic acid, acetic acid, lactic acid, gluconic acid, oxalic acid, citric acid, nitrilotriacetic acid (NTA) and ethylenediamine-N, N, N', N'-tetraacetic acid (EDTA).

[0023] The sulfate-based iron electroplating solution has a temperature of 80 °C or lower and a pH of 1.0 to 4.0.

[0024] The method includes: an electroplated cell in which electroplating is performed by applying a current; a circulation bath for circulating the electroplated cell and an electroplating solution; a dissolution bath for circulating the circulation bath and the electroplating solution, containing the metallic iron charged therein, and dissolving the metallic iron to remove ferric ions from the electroplating solution, wherein the method may be performed by an iron-based electroplating apparatus having a pump for supplying the electroplating solution in the circulation bath to the dissolution bath and a filter for preventing the metallic iron in the dissolution bath from entering the circulation bath.

Advantageous Effects of Invention

[0025] As set forth above, according to an aspect of the present disclosure, by effectively removing ferric ions continuously accumulated during continuous electroplating, a decrease in electroplating efficiency may be prevented, and sludge due to the accumulation of ferric ions may be prevented.

[0026] In addition, since ferric ions are reduced to ferrous ions, and metallic iron is dissolved to supply ferrous ions, a concentration of the ferrous ions in an iron electroplating solution may be maintained to be constant.

[0027] Furthermore, since there is no need to periodically replace the solution for the solution management, an amount of wastewater in the solution may be reduced, so it is environmentally friendly, and the manufacturing cost may be greatly reduced.

Brief Description of Drawings

[0028]

FIG. 1 is a diagram schematically illustrating a temporal relationship between plating and regeneration of an electrolyte, and is a diagram schematically illustrating continuous regeneration of the electrolyte during a continuous plating process.

FIG. 2 is a diagram schematically illustrating a temporal relationship between plating and regeneration of an electrolyte, and a diagram schematically illustrating an example in which regeneration of the electrolyte is performed discontinuously during a continuous plating process.

FIG. 3 is a diagram schematically illustrating a temporal relationship between plating and regeneration of an electrolyte, and a diagram schematically illustrating an example in which regeneration of the electrolyte is initiated during a plating process, and a regeneration process of the electrolyte is terminated during a pause in the plating process.

FIG. 4 is a diagram schematically illustrating a temporal relationship between plating and regeneration of an electrolyte, and a diagram schematically illustrating an example in which regeneration of the electrolyte is initiated before a current is applied for plating, and regeneration of the electrolyte is terminated in a pause after the plating process is terminated.

FIG. 5 is a diagram schematically illustrating a temporal relationship between plating and regeneration of an electrolyte, and is a diagram schematically illustrating an example in which a regeneration process of the electrolyte is performed in a pause between plating processes.

FIG. 6 is a diagram schematically illustrating a temporal relationship between plating and regeneration of an electrolyte, and is a diagram schematically illustrating an example in which regeneration of the electrolyte is performed continuously in at least two plating processes and a pause between the plating processes.

FIG. 7 is a diagram schematically illustrating an apparatus according to the method of the present disclosure.

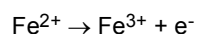
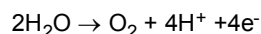
FIG. 8 is a photograph of an initial solution according to Example 1 and a solution after 1 hour, 2 hours and 3 hours after dissolving pure iron in the initial solution.

Best Mode for Invention

[0029] An aspect of the present disclosure is to provide a method of reducing a concentration of ferric ions accumulated in an electroplating solution, when iron electroplating is performed using a sulfate-based iron electroplating solution in an electroplating facility to which an insoluble anode is applied, and supplying ferrous ions consumed during plating.

[0030] When the concentration of ferric ions in the iron electroplating solution increases, the electroplating quality is deteriorated, so the present disclosure is intended to reduce the concentration of ferric iron in the iron electroplating solution by contacting ferric ions, generated during continuous plating operation in the electroplating facility using an insoluble anode, with metallic iron and reducing the same.

[0031] In performing iron electroplating in the electroplating facility to which an insoluble anode is applied, a sulfate-based electrolyte is usually used, and when electroplating is performed in the facility to which an insoluble anode is applied, the following reaction occurs at an anode.



[0032] That is, at the anode, a water decomposition reaction and a reaction in which ferrous ions are oxidized to ferric ions occur simultaneously. Since a potential at which an oxidation reaction of ferrous ions occurs is lower than a potential at which the water decomposition reaction occurs, when low-current operation is performed, a voltage is lowered and a rate at which the oxidation reaction of ferrous ions occurs is higher. In addition, when a complexing agent is used to prevent sludge, the oxidation reaction of ferrous ions is further accelerated because the ferric ions maintain a more stable state in an electrolyte.

[0033] Meanwhile, in performing iron electroplating in a sulfate-based electroplating solution, when a complexing agent is not used, high electroplating efficiency cannot be obtained, and when ferric ions are accumulated, they are easily sludged so that the solution becomes cloudy, which is difficult to be removed by a conventional filtration method.

[0034] However, when ferrous ions in the plating solution are oxidized to ferric ions, a concentration of ferrous ions participating in a plating reaction at a cathode decreases, and a current is consumed to reduce the ferrous ions to ferrous ions, so that the electroplating efficiency is greatly reduced. Therefore, in order to continuously perform iron electroplating, it is necessary to remove ferric ions in the solution.

[0035] The inventors of the present disclosure have attempted to provide a method for preventing a decrease in iron

electroplating efficiency by reducing ferric ions, generated during continuous plating in a sulfate-based iron electroplating solution again.

[0036] In particular, in the present disclosure, by suppressing generation of sludge in the solution by reducing and removing ferric ions, continuously accumulated in an iron electroplating facility to which an insoluble anode is applied, and supplying iron ions consumed during electroplating, a concentration of iron ions in the solution is maintained to be constant. Thereby, even when continuous plating is performed, the high electroplating efficiency may be maintained.

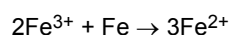
[0037] Furthermore, in the present disclosure, it is possible to maintain a pH of the electroplating solution to be constant, while reducing the concentration of ferric ions in the electroplating solution, and as a result, plating efficiency may be maintained to be constant, the iron electroplating solution may be easily managed, and may be used continuously for a long time.

[0038] Meanwhile, in order to prevent the accumulation of ferric ions in an electrolyte, when a reducing agent, other than metallic iron is introduced to reduce ferric ions to ferrous ions, components oxidized by the reducing agent are continuously increased and remain in the electrolyte, and in this case, components, unnecessary for electroplating, are accumulated, plating efficiency decreases and plating quality is affected.

[0039] In order to solve the above problems, the present inventors have devised a method of using metallic iron, which is a main component of an iron electroplating solution, as a reducing agent.

[0040] As a result of evaluating various types of reducing agents for the reduction of ferric ions in an iron electroplating solution, when metallic iron is used as a reducing agent, ferric ions may be effectively removed while maintaining solution homeostasis, and furthermore, iron ions consumed in an electroplating process are supplemented with ferrous ions eluted from metallic iron, so that a concentration of the iron ions in the electrolyte may be maintained to be constant so that an amount of the solution used may be drastically reduced.

[0041] When metallic iron and ferric ions are in contact with each other in a state in which no voltage is applied, a corrosion reaction in which the ferric ions are reduced to ferrous ions, and the metallic iron is oxidized and eluted as ferrous ions occurs. This reaction may be represented by the following equation.



[0042] As a reducing agent for removing ferric ions in the iron electroplating solution, in the present disclosure, metallic iron is preferably used. When iron is used as a reducing agent, iron is eluted by reacting with hydrogen ions or ferric ions in the solution, thereby reducing the ferric ions in the solution to ferrous ions, and further supplying ferrous ions.

[0043] Metallic iron used as the reducing agent may be pure iron or ferroalloy. An alloying element of the ferroalloy may be an element, which is more oxidizable than iron and is not easily precipitated in electroplating, and for example, at least one selected from a group consisting of Mn, Al, Mg, Li, Na, and K. When such ferroalloy is used, it reacts with hydrogen ions or ferric ions in the solution to further increase an elution rate. More preferably, the alloying element may be at least one selected from a group consisting of Mn and Al.

[0044] In the present disclosure, the metallic iron used as the reducing agent preferably has an alloying element content of 3% by weight or less. When ferroalloy in which the content of the alloying element exceeds 3% by weight is used, even if there is almost no ferric ions in the solution, an alloying element with strong oxidizing characteristics may be continuously eluted by reacting with oxygen introduced from the air and hydrogen ions in the solution, and in this case, a pH of a plating solution is excessively increased. Furthermore, when such ferroalloy is used as a reducing agent for a long time, a concentration of ions of alloying elements in the solution increases, and is incorporated into an iron electroplating layer during an electroplating process, an electroplating layer of pure iron to be obtained may not be obtained.

[0045] In the present disclosure, metallic iron used as a reducing agent is pure iron or ferroalloy, and a shape thereof is not limited, and may be in a form of particles such as spheres, spiral chips, plates, or strips. When the shape of the metallic iron is a form of plates or strips, when put into a dissolution bath, it can be put into a dissolution bath at an appropriate size by cutting, or the like, and as a result, it is possible to prevent a problem in which metallic iron is stacked with each other to reduce a flow of the solution or to reduce an actual contact area with the solution, and furthermore, by-products generated in the manufacturing process such as a steel sheet, or the like, may be used as a reducing agent, thereby reducing manufacturing costs, so which is more preferable. In addition, when metallic irons in a form of particles are used as the reducing agent, a filling rate is high, and a contact area with the solution can be increased, and thus, a volume of the dissolution bath can be prevented from being excessively increased, which is preferable.

[0046] A size of the metallic iron used as the reducing agent is not particularly limited as it can be appropriately selected in consideration of plating facility, reduction efficiency, or the like. For example, plate-shaped or strip-shaped metallic iron having a thickness of 0.1 to 5 mm may be used, the metallic iron is cut into appropriate size, or if they are arranged so as not to hinder the flow of the solution, such as stacking and arranging the plate-shapes or strips at equal intervals, a reduction effect of ferric iron may be equally obtained, and an area of the plate-shape or strip is not particularly limited.

[0047] When used in a form of particles, particles having an average diameter of 0.1 mm to 10 mm, for example 0.5

mm, 0.7 mm, 1 mm or more and 5 mm, 7 mm or 10 mm or less may be used.

[0048] As the size of the metallic iron used is smaller, a contact area between the metallic iron and the solution may be maximized, which is effective for the reduction of ferric ions, but when metallic iron having an excessively small size rather hinder a flow of the solution, and when an excessive amount thereof is added, a pH may be excessively increased by reacting with hydrogen ions in the solution even when there are no ferric ions, and iron particles may flow into an electroplated cell and damage a plating surface. On the other hand, when the size of the metallic iron is too large, a reaction area may be reduced so that ferric ions may not be effectively removed, and addition of a large amount of metallic iron is required. Therefore, it is preferable to select metallic iron having an appropriate size within the above range according to a capacity of the iron electroplating facility and a plating speed.

[0049] Ferrous ions in the electroplating solution are reduced to metallic iron at -0.44V or lower compared to a standard hydrogen electrode, and oxidized to ferric ions at 0.77V or higher. Meanwhile, water is electrolyzed at 1.23V or higher and oxygen gas is generated. Therefore, when iron electroplating is performed in an electroplating facility having an insoluble anode, an oxidation reaction of ferrous ions in which ferrous ions are oxidized to ferric ions and a water decomposition reaction in which water is decomposed occur at the anode, and at the cathode, ferrous ions are reduced to metallic iron and plated, and ferric ions are partially reduced to ferrous ions.

[0050] In the electrode reaction as described above, a rate of occurrence of each of the reactions may be slightly different depending on the current density, electrode and solution characteristics, but when iron electroplating is performed in an electroplating facility having an insoluble anode, a rate of the amount of iron electroplating at a cathode is greater than an amount of reduction reaction of ferric iron, and an oxidation reaction of ferrous iron and water decomposition reaction occur at an anode. Therefore, when electroplating is performed by applying an electric current, the concentration of ferric ions in the solution inevitably increases continuously.

[0051] A rate at which ferric ions are generated in the iron electroplating solution increases in proportion to an amount of current applied for iron electroplating or a plating speed. Therefore, it is preferable to control the rate at which ferric iron is generated by electroplating so as not to exceed a rate at which ferric iron is removed by metallic iron so that ferric ions do not continuously increase.

[0052] The present inventors have confirmed that ferric ions can be prevented from continuously being accumulated and increased, when metallic iron is used as a reducing agent in an appropriate amount according to the electroplating speed, through numerous experiments. That is, when a contact area between metallic iron and the solution is sufficiently great, an amount of reaction in which ferric ions are reduced to ferrous iron increases, and thus an increase in ferric ions can be suppressed.

[0053] When a current is applied for iron plating, ferric ions are generated in proportion to the current. In this case, as represented by the following formula, a production rate of the ferric ions may be represented as $a \cdot I_{conv}$, where a is a constant of the production rate of ferric ions, I_{conv} is a converted current per unit time, and the converted current I_{conv} is a value obtained by dividing the sum of the current (I) applied during a plating time (t_p , sec) by regeneration of an electrolyte, that is, a regeneration time (t_r , sec) for reduction of the ferric ions, where, and a unit thereof is A.

$$I_{conv} = \frac{\int I dt_p}{\int dt_r}$$

[0054] In this case, a time when the current (I) is applied (a current application time, that is, a plating time (t_p) and a regeneration time (t_r)) may be the same or different. That is, the plating process and the regeneration process can be performed in various forms. For example, the plating process and the regeneration process may have a form such as continuous plating and continuous regeneration, continuous plating and discontinuous regeneration, discontinuous plating and continuous regeneration, discontinuous plating and discontinuous regeneration, and the like. The plating process and the regeneration process may be performed in various forms, and some examples thereof will be more exemplarily described with reference to FIGS. 1 to 6.

[0055] FIG. 1 illustrates a case in which regeneration for reduction of ferric ions is performed continuously while a plating process is performed by applying a current (I), as an embodiment of continuous plating and continuous regeneration, and the regeneration process may be performed during the plating process. In this case, the current application time t_p and the regeneration time t_r are the same, and in this case, the converted current I_{conv} is equal to an average current applied to a plating cell per unit time.

[0056] FIG. 2 illustrates a case in which a regeneration process intermittently performed when a concentration of ferrous iron ions in an electrolyte solution exceeds an allowable value while a plating process is continuously performed by applying a current (I), as an embodiment of continuous plating and discontinuous regeneration. In this case, the

current application time t_p and the regeneration time ($t_r = t_{r1} + t_{r2}$) are different. FIG. 2 illustrates an example in which regeneration is performed twice, but may be performed three or more time if necessary.

[0057] FIG. 3 illustrates a case in which a regeneration process is initiated when a concentration of ferrous ions in an electrolyte solution exceeds an allowable value during a plating process by applying a current (I), and a regeneration process is continued for a certain period of time and then the regeneration process is terminated in a pause in the regeneration process, as an embodiment of discontinuous plating and continuous regeneration. In this case, the current application time t_p and the regeneration time (t_r) may be the same or different. FIG. 3 illustrates a case in which a regeneration process is performed continuously, but it can be easily understood by those skilled in the art that the regeneration process may be performed intermittently by combining the embodiment of FIG. 2.

[0058] FIG. 4 illustrates a case in which a regeneration process is initiated before a plating process is performed, that is, in a pause in which a current (I) is not applied, in the plating process by applying a current (I), and the regeneration process is maintained during the plating process, and the regeneration process is continued for a certain period of time until the pause after the plating process is terminated, and then terminated, as another embodiment of discontinuous plating and continuous regeneration. This embodiment may be suitably performed in the case of using the electrolyte solution used in the previous plating process. In this case, the current application time t_p and the regeneration time t_r may be different. FIG. 4 illustrates that one regeneration process is continuously performed, but it can be easily understood by those skilled in the art that the regeneration process may be performed intermittently by combining the embodiment of FIG. 2. In this case, the current application time t_p and the regeneration time t_r may be the same.

[0059] FIG. 5 illustrates a case in which a regeneration process is performed in a pause in a plating process in which a current (I) is not applied. In this case, a current application time t_p and a regeneration time t_r may be the same or different, as another embodiment of discontinuous plating and continuous regeneration. FIG. 5 illustrates that one regeneration process is performed continuously, it can also be performed intermittently by combining the embodiment of FIG. 2. In this case, the current application time t_p and the regeneration time t_r may be the same or different.

[0060] FIG. 6 illustrates a case in which a plating process is performed discontinuously from plating process-pause-plating process, and a regeneration process is continuously performed during the plating process and pause. In this case, the current application time t_p and the regeneration time t_r may be different, as another embodiment of discontinuous plating and continuous regeneration. FIG. 6 illustrates that one regeneration process is performed continuously, but the regeneration process may be performed intermittently by combining the embodiment of FIG. 2, and the regeneration process may be initiated or terminated during the plating process. In this case, the current application time t_p and the regeneration time t_r may be the same.

[0061] Meanwhile, when a concentration of ferric ions in the iron electroplating solution is C (g/L) and a total surface area of metallic iron added as a reducing agent is S(m²), ferric ions are reduced by the reducing agent, so that the concentration of the ferric ions decreases, and in this case, a rate of a decrease in ferric ions may be expressed as bCS (b= a reaction rate constant between ferric ions and metallic iron).

[0062] In the case of a state in which the concentration of ferric ions is maintained to be constant during continuous plating, it has the following relationship.

$$a \cdot I_{\text{conv}} = b \cdot C \cdot S$$

$$S = (a/b) \cdot I_{\text{avg}}/C$$

[0063] When having such a relationship, the C represents an equilibrium concentration.

[0064] Meanwhile, a / b is a value that can be obtained experimentally. As a result of measurements thereof by the present inventors, even when if a solution is changed, a has an almost constant value regardless of the solution and the electrode, and b tends to increase as a content of alloying elements such as Mn and Al in metallic iron added as a reducing agent increases, and in the case of pure iron, it was confirmed that a/b was 0.01.

[0065] When ferric ions are generated by an electrode reaction, a is almost constant because the ferrous ions in the solution are directly oxidized and other additive components do not participate in the reaction, while when ferric ions and metallic iron react with each other and are reduced, a reaction rate is changed greatly depending on a composition of metallic iron, so it was determined that b increases significantly.

[0066] From the above relationship, when the current I_{conv} per unit time is applied to an electroplated cell and a maximum permissible concentration level of ferric ions in the solution is C_{max} , it is preferable that metallic iron is contained so that a total surface area S of the metallic iron satisfies the following relational expression.

$$S \geq 0.01 \times I_{\text{conv}}/C_{\text{max}}$$

[0067] When metallic iron containing an alloying element is used as a reducing agent, even if the surface area of metallic iron as a reducing agent is smaller compared to the case where pure iron is used as a reducing agent under the same conditions, the ferroalloy has a faster reaction rate for reducing ferric ions into ferrous ions, the reaction rate constant b becomes high, so a/b becomes low. Therefore, when the surface area S of the reducing agent satisfies the condition for the surface area of metallic iron, an effect of reducing ferric ions in the iron electroplating solution into ferrous ions and removing the same may be provided, and thus, it is possible to achieve a predetermined purpose of managing a permissible concentration of ferric ions below a critical value.

[0068] For example, when it is intended to maintain the concentration of ferric ions to be 3g/L or less in an operation pattern in which electroplating is performed by applying a current of 9000 A for 20 minutes, and then paused without applying a current for 40 minutes, which are repeatedly performed, and when metallic iron is added so that the converted current is 3000A and the total surface area is 10m² or more, the average concentration of ferric ions in the solution may be maintained to be 3 g/L or less.

[0069] Meanwhile, when a large amount of ferric ions are contained in the sulfate-based iron electroplating solution, ferric ions form hydroxide and sludge is generated, and the sludge of ferric ions does not cause a reduction reaction by metallic iron even when the sludge is in contact with metallic iron, so reducing force of metallic iron is not generated in a normal plating solution. Therefore, in order for ferric ions to be reduced by a corrosive reaction with metallic iron, it is preferable to use a complexing agent to prevent the ferric ions from precipitating in a form of sludge.

[0070] As the complexing agent that can be used in the present disclosure, as long as it is commonly used in electroplating, it can be suitably used in the present invention, and is not particularly limited, but, for example, a compound having a carboxyl group may be used, and specifically, amino acids such as glycine, glutamic acid, and glutamine; acids containing one carboxyl group, such as formic acid, acetic acid, lactic acid, and gluconic acid; and acids having two or more carboxyl groups, such as oxalic acid, citric acid, nitrilotriacetic acid (NTA), and ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA), and the like.

[0071] A method of effectively removing ferric ions in an iron sulfate-based electroplating solution using metallic iron according to the method of the present disclosure will be described in detail.

[0072] As illustrated in FIG. 7, the method of the present disclosure includes an electroplated cell 1 in which iron electroplating is performed by applying a current, and a circulation bath 2 supplying an electroplating solution to the electroplated cell 1, and receiving an electroplating solution from the electroplated cell 1. That is, the electroplating solution circulates between the electroplated cell 1 and the circulation bath 2.

[0073] More specifically, ferrous ions are supplied to the circulation bath 2, and an electroplating solution containing the ferrous ions is supplied to the electroplated cell 1, so that a concentration of ferrous ions contained in the electroplating solution in the electroplated cell 1 may be maintained to be constant. Furthermore, an electroplating solution in which a concentration of ferric ions is increased by electroplating in the electroplated cell 1 is transferred to the circulation bath 2.

[0074] Meanwhile, an electroplating solution containing ferric ions supplied from the electroplated cell 1 to the circulation bath 2 is circulated to a dissolution bath 3. The dissolution bath 3 contains metallic iron charged therein. The electroplating solution supplied to the dissolution bath 3 dissolves metallic iron in the dissolution bath 3, and in this process, ferric ions in the electroplating solution are reduced to ferrous ions by metallic iron, so that a content of ferric ions in the electroplating solution is reduced.

[0075] In circulating the electroplating solution from the circulation bath 2 to the dissolution bath 3, which may be performed by driving a pump 4 as illustrated in FIG. 1.

[0076] The electroplating solution in the dissolution bath 3 in which the content of ferric ions is reduced is supplied to the circulation bath 2, and then supplied to the electroplated cell 1.

[0077] In supplying the electroplating solution in the dissolution bath to the circulation bath 2, it is preferable to pass through a filtration means 5. The filtering means 5 is to prevent metallic iron particles or impurity particles, charged into the dissolution bath 3 from flowing into the circulation bath 2 together with the electroplating solution. In particular, in a continuous electroplating process in which a strip passes between rolls, when metallic iron particles are present in the electroplating solution, the metallic iron particles intervene between the rolls and the strip to stamp the strip, causing dent defects.

[0078] The filtering means 5 is generally applicable to the present disclosure as long as it is a means for separating solids in the solution, and is not particularly limited, and examples thereof include a filter, a filter net, or the like.

[0079] As described above, in the present disclosure, by circulating a sulfate-based iron electroplating solution containing ferric ions into a solution bath containing metallic iron charged therein, ferric ions present in the iron electroplating solution react with metallic iron to reduce the ferric ions to ferrous ions and the metallic iron is eluted as ferrous ions, thereby removing ferric ions in the solution.

[0080] In this case, the sulfate-based iron electroplating solution to which the present disclosure is applied is not particularly limited as long as it does not cause freezing of the plating solution, a change in viscosity, or the like, at a temperature of 80 ° C or lower, more preferably, it may be performed at 0 ° C or higher, and at 80 ° C or lower.

[0081] Meanwhile, a pH of the electroplating solution does not have a significant effect on the reduction of ferric iron,

and is not particularly limited, but the pH of the electroplating solution is preferably from 1.0 to 4.0, and more preferably from 2.0 to 3.0, in terms of electroplating efficiency.

Mode for Invention

[0082] Hereinafter, it will be described in more detail through examples of the present disclosure.

Reference Examples 1 and 2

[0083] Ferrous sulfate was used as a raw material for ferrous iron, and ferric sulfate was used as a raw material for ferric iron, a sulfate-based iron electroplating solution was prepared in which a concentration of ferrous ions, a concentration of ferric ions, and the sum (T-Fe) of the concentration of ferrous ions and the concentration of ferric ions are illustrated in Table 1 below.

[0084] A pH of the iron electroplating solution was adjusted as illustrated in Table 1 using sulfuric acid and sodium hydroxide, and glutamine was added as a complexing agent to be 0.5 times a molar concentration of iron ions so that ferric ions would not precipitate as sludge.

[0085] In the solution described above, 10 sheets of metallic iron plates formed of pure iron having an area of 1dm² and a thickness of 0.7 mm were immersed in the solution at regular intervals so as not to overlap each other, maintained for 3 hours, and then a total iron concentration (total Fe, T-Fe), obtained by summing a concentration of ferric ions in the iron electroplating solution and a concentration of ferrous ions and a concentration of ferric ions, was measured respectively.

[0086] In addition, plating efficiency was measured by performing electroplating at a current density of 40ASD immediately after preparing a solution and in a solution in which ferric iron was removed using a metallic iron plate as a reducing agent.

[0087] Each measurement result was illustrated in Table 1.

[Table 1]

Division	Initial solution				
	T-Fe(g/L)	Ferric ions(g/L)	Complexing agent	pH	Plating efficiency(%)
Reference Example 1	50.1	9.3	Glutamine	2.3	54
Reference Example 2	49.8	9.9		2.9	63

[0088] As can be seen from Table 1, an iron electroplating solution prepared to contain a large amount of ferric ions in Reference Examples 1 and 2 had plating efficiency of 54% and 63%, respectively, and the lower the pH, the lower the plating efficiency.

Examples 1 to 2

[0089] A metallic iron plate formed of pure iron having an area of 1dm² and a thickness of 0.7 mm was contained as a reducing agent to initial solutions of Reference Examples 1 and 2 in which a large amount of ferric ions illustrated in Table 1 are contained, and the ferric ions were reduced and removed for 3 hours, and then a reduced iron electroplating solution was obtained. An example using the initial solution of Reference Example 1 was Example 1, and an example using the initial solution of Reference Example 2 was Example 2.

[0090] A concentration of ferric ions and a T-Fe concentration, obtained by summing a concentration of ferrous ions and a concentration of ferric ions for the obtained iron electroplating solution, were measured, respectively, and the results thereof were illustrated in Table 2.

[0091] Furthermore, a pH of the iron electroplating solution was adjusted as illustrated in Table 2 using sulfuric acid and sodium hydroxide, and amino acids or citric acid were added to a molar concentration of iron ions 0.5 times so that ferric ions would not precipitate as sludge.

[0092] In addition, plating efficiency was measured by performing electroplating at a current density of 40ASD immediately after preparing a solution and in a solution in which ferric iron was removed using a reducing agent.

[0093] Each measurement result thereof was illustrated in Table 2.

[Table 2]

Division	Reducing agent	Reduced solution				
		T-Fe (g/L)	Ferric ions (g/L)	pH	Sludge	Plating efficiency (%)
Example 1	Metallic iron	55.8	0.4	3.1	Not generated	82
Example 2	Metallic iron	54.2	1.0	3.7	Not generated	85

[0094] As can be seen from Table 2, when metallic iron was used as a reducing agent as in Examples 1 and 2, a concentration of ferric iron decreased, a pH increased, and plating efficiency was 82% and 85%, respectively, which were significantly increased. Meanwhile, a state of the solution after maintaining the solution prepared in Example 1 for 1 hour, 2 hours, and 3 hours, respectively, was illustrated in FIG. 8. As can be seen from FIG. 8, it was confirmed that a color gradually changed from reddish brown due to ferric iron to light green due to ferrous iron over time.

Comparative Examples 1 to 2

[0095] Comparative Examples 1 to 2, a reduced iron electroplating solution, subjected to reduction treatment in the same manner as in Example 1, except that 16 g/L of ascorbic acid was added to initial solutions of Reference Examples 1 and 2 as a reducing agent to reduce ferric ions to ferrous ions, was obtained. An example using the initial solution of Reference Example 1 was Comparative Example 1, and an example using the initial solution of Reference Example 2 was Comparative Example 2.

[0096] A concentration of ferric ions and a T-Fe obtained by summing a concentration of ferrous ions and a concentration of ferric ions for the prepared iron electroplating solution were measured, respectively, and the results thereof were illustrated in Table 3.

[Table 3]

Division	Treatment method	Reduced solution				
	Reducing agent	T-Fe (g/L)	Ferric ions (g/L)	pH	Sludge	Plating efficiency (%)
Comparative Example 1	Ascorbic acid 16g/L	50.0	2.2	2.0	Not generated	46
Comparative Example 2	Ascorbic acid 16g/L	50.2	2.1	2.6	Not generated	49

[0097] Immediately after adding ascorbic acid, and the plating solution changed a color from reddish brown to light green, and the concentration of ferric ions significantly decreased. However, after maintaining the same for 3 hours, it reacted with oxygen in the air and slowly showed a red color. Meanwhile, as can be seen from Table 3, as a result of performing iron electroplating with a solution maintained for 3 hours after adding ascorbic acid, although the ferric ion concentration was greatly reduced, the plating efficiency rather decreased.

Comparative Examples 3 to 4

[0098] In Comparative Examples 3 and 4, a reduced iron electroplating solution, obtained by subjecting to reduction treatment in the same manner as in Example 1, except that 12 g/L of ascorbic acid was contained to initial solutions of Reference Examples 3 and 4 as a reducing agent, and then maintained for 3 hours at 50°C was obtained. An example using the initial solution of Reference Example 1 is Comparative Example 3, and an example using the initial solution of Reference Example 2 is Comparative Example 4.

[0099] A concentration of ferric ions and a T-Fe concentration, obtained by summing a concentration of ferrous ions and a concentration of ferric ions for the prepared iron electroplating solution, were measured, respectively, and the results thereof were illustrated in Table 4.

[Table 4]

Division	Treatment method	Reduced solution				
	Reducing agent	T-Fe (g/L)	Ferric ions (g/L)	pH	Sludge	Plating efficiency (%)
Comparative Example 3	Sodium sulfite 12g/L	50.1	10.2	2.2	Not generated	49
Comparative Example 4	Sodium sulfite 12g/L	50.1	10.9	2.8	Not generated	57

[0100] Even when sodium sulfite was added, a color of the solution did not change. In addition, as can be seen from Table 4, there was no significant change in the concentration of ferric ions compared to Reference Examples 1 and 2, and the plating efficiency was rather decreased.

Examples 3 to 5 and Comparative Examples 5 to 12

[0101] In the iron electroplating solution, ferrous sulfate was dissolved so that the iron ion (T-Fe) concentration was about 50 g/L, and glutamine, a kind of amino acid, was added as a complexing agent to be 0.5 times a molar concentration of iron ions. Sulfuric acid was added to adjust a pH to 2 to 3 to prepare initial solutions as illustrated in Table 5 below.

[0102] As a reducing agent, as illustrated in Table 5 below, pure iron having a thickness of 0.5 mm or metallic steel plates of ferroalloy having different contents of Mn were cut into a size of 1dm², and charged into a dissolution bath at regular intervals so as not to overlap each other. A surface area of metallic iron in contact with the solution was adjusted by varying the number of metallic iron plates charged into the dissolution bath, and an input area (dm²) of the reducing agent accordingly was illustrated in Table 5.

[0103] As a base metal for plating, a copper plate having a plating area of 1dm² was degreased in advance, and continuously plated for 2 minutes at a current of 40 A at regular time intervals, and plated a total of 5 times per hour so that an average current was 6.7 A.

[0104] After plating at regular time intervals for 3 hours by the above method, iron ion concentration in the solution (T-Fe and ferric ion, unit: g / L), manganese ion concentration (mg / L), pH and plating efficiency (%) was measured, and whether or not sludge was generated in the plating solution (O: sludge generated, X: sludge not generated) was observed, and the results thereof are illustrated in Table 5.

[0105] Furthermore, the results according to the above formula (1) for an area (S, unit: m²) of metallic iron used as a reducing agent, a converted current (I_{conv}), and a maximum allowable ion concentration (C_{max}) of ferric ions in the solution (unit: m²·g/L·A) was calculated, and the results thereof were illustrated together in Table 5.

[Table 5]

Division	Initial solution				Reducing agent		Solution after 3 hours plating						SC/I
	T-Fe	Ferric ions	pH	Plating efficiency	Type	Char- ging area	T-Fe	Ferric ions	Mn	pH	Plating efficiency	Generation of sludge	
Comparative Example 5	49.2	1.44	2.7	75	-		44.7	9.69	-	2.1	37	X	0
Comparative Example 6					Fe	2	46.5	3.14	-	2.4	54	X	0.004
Comparative Example 7					Fe	4	46.7	1.64	-	2.6	68	X	0.009
Example 3					Fe	8	46.9	0.91	-	2.8	79	X	0.017
Example 4					Fe	16	47.5	0.41	-	2.9	82	X	0.035
Comparative Example 8	50.1	1.68	2.8	78	Fe-3%Mn	2	46.9	2.07	32.3	2.5	58	X	0.005
Example 5					Fe-3%Mn	4	47.1	1.05	40	2.8	74	X	0.010
Example 6					Fe-3%Mn	8	47.3	0.52	42.5	2.9	81	X	0.020
Example 7					Fe-3%Mn	16	47.9	0.15	40.8	3.0	85	X	0.040
Comparative Example 9	49.8	1.61	2.7	76	Fe-5%Mn	2	51.3	0.57	173.6	3.4	83	O	0.005
Comparative Example 10					Fe-5%Mn	4	51.6	0.39	174.6	3.5	82	O	0.010
Comparative Example 11					Fe-5%Mn	8	52.3	0.03	178.9	3.8	85	O	0.019
Comparative Example 12					Fe-5%Mn	16	52.4	0.06	181.1	4.1	82	O	0.039

[0106] Examples 3 to 4 and Comparative Examples 6 and 7 are examples in which an iron plate, obtained by cutting pure iron into a size of 1dm² as a reducing agent is charged at regular intervals by varying the added number thereof, and an effect of inhibiting production of ferric ions according to a surface area of metallic iron may be confirmed.

[0107] Specifically, Comparative Examples 6 to 7 illustrate a case in which metallic iron was charged so that a surface area of the metal iron plate was 2dm² and 4dm², and unlike Comparative Example 5 in which metallic iron was not charged, a concentration of ferric ions did not increase significantly, and plating efficiency did not significantly decrease, but the concentration of ferric ions tended to increase slowly compared to that of the initial solution.

[0108] On the other hand, in the case of Examples 3 and 4 in which metallic iron was charged so that a surface area of the iron plate was 8 and 16dm², the concentration of ferric ions in the electroplating solution gradually decreased compared to that of the initial solution as the plating proceeded, and the plating efficiency also slightly increased. Furthermore, no sludge was generated in the solution during electroplating.

[0109] Examples 5 to 7 and Comparative Example 8 are examples in which a metallic iron plate, obtained by cutting an alloy iron plate containing about 3% Mn into a size of 1dm² as a reducing agent and charged at regular intervals by varying the added number thereof, and it can be confirmed that an effect of inhibiting production of ferric ions according to a surface area of Mn ferroalloy.

[0110] As in Examples 5 to 7, the concentration of ferric ions decreased compared to that of the initial solution even though only an Mn-containing alloy iron plate having a surface area of 4dm² or more is charged. However, in Comparative Example 8 in which metallic iron was charged so that an area of the alloy iron plate was 2dm², the pH decreased and the concentration of ferric ions gradually increased as the plating progressed.

[0111] In Comparative Examples 9 to 12 were examples in which an iron alloy sheet containing about 5% by weight of Mn as a reducing agent was used, and it can be confirmed that an effect of suppressing production of ferric ions according to a content of Mn. As such, when the iron alloy sheet containing a large amount of Mn was used, even when a small amount of ferroalloy Mn was used, the concentration of ferric ions was greatly reduced, and the plating efficiency was also maintained to be constant. However, the content of Mn in a solution increased, the pH rapidly increased, and fine sludge was generated in the electroplating solution during plating.

[0112] From the above results, when a dissolution bath containing pure iron charged therein or ferroalloy containing 3% or less of Mn is installed in an iron electroplating apparatus and circulated, it is possible to prevent the accumulation of ferric ions in an iron electroplating solution, suppress a decrease in a pH, and supply iron ions exhausted by electroplating, so that plating efficiency may be maintained to be constant, when iron electroplating is continuously performed using an insoluble anode, and homeostasis of the iron electroplating solution may be maintained.

[0113] While example embodiments have been shown and described above, it will be apparent to those skilled in the art that modifications and variations could be made without departing from the scope of the present disclosure as defined by the appended claims.

DESCRIPTION OF REFERENCE NUMERALS

[0114]

- 1: ELECTROPLATED CELL
- 2: CIRCULATION BATH
- 3: DISSOLUTION BATH
- 4: PUMP
- 5: FILTERING MEANS

Claims

1. As a method for removing ferric ions from a sulfate-based iron electroplating solution, the method comprising:

a regeneration step of reducing ferric ions by circulating a sulfate-based iron electroplating solution containing ferric ions in a solution bath containing metallic iron charged therein, wherein the metallic iron is charged in an amount satisfying the following formula (1):

$$S \geq 0.01 \cdot I_{\text{conv}} / C_{\text{max}} \quad \dots (1),$$

where S indicates a total surface (m²) of metallic iron, C_{max} indicates a maximum permissible ion concentration level (g/L) of the ferric ions in the solution, and I_{avg} indicates, as represented by the following formula (2),

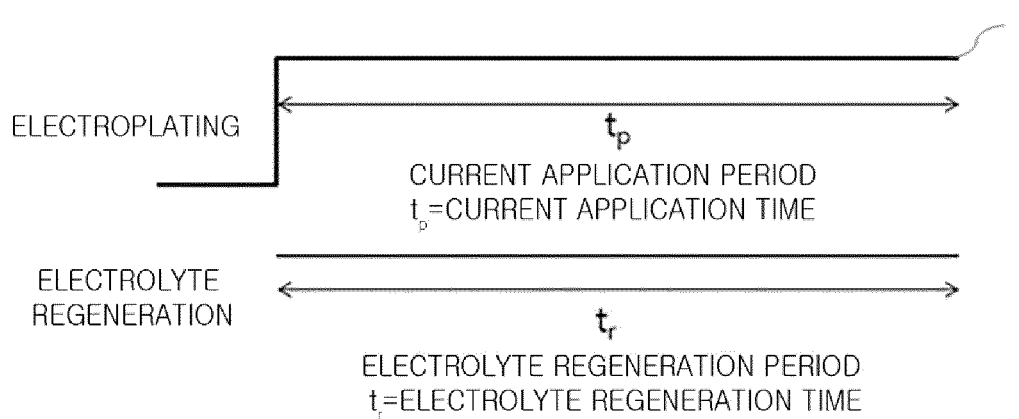
converted current (A) obtained by dividing the sum of current (I) applied to an electroplated cell during a plating time (t_p , sec) by a regeneration time (t_r , sec) for reduction of the ferric ions in an electrolyte

$$I_{conv} = \frac{\int I dt_p}{\int dt_r} \dots (2)$$

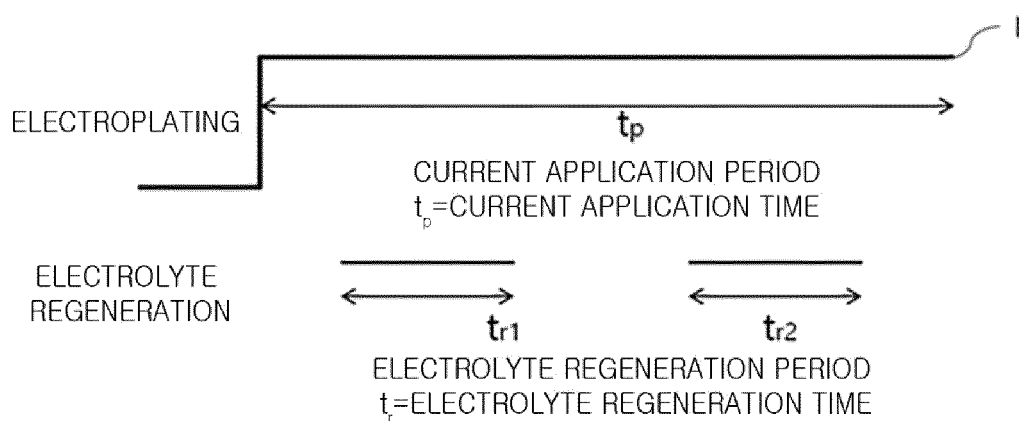
2. The method of claim 1, wherein the regeneration step is performed during a plating process.
3. The method of claim 1, wherein a regeneration step is performed during a plating process, and the regeneration step is performed discontinuously two or more times.
4. The method of claim 1, wherein a regeneration step is initiated during a plating process, the regeneration step is terminated in a pause in the plating process, and the regeneration step is performed continuously or discontinuously.
5. The method of claim 1, wherein a regeneration step is initiated in a pause in the plating process, and the regeneration step is terminated in a pause during or after the plating process.
6. The method of claim 1, wherein a regeneration step is performed during a pause in the plating process, and the regeneration step is performed continuously or discontinuously.
7. The method of claim 1, wherein a plating process is performed discontinuously, including a pause, and a regeneration step is performed during two or more plating processes.
8. The method of claim 1, wherein the metallic iron is ferroalloy containing at least one alloying element selected from a group consisting of Mn, Al, Mg, Li, Na and K.
9. The method of claim 8, wherein the ferroalloy is ferroalloy containing an alloying element in an amount greater than 0% by weight and less than or equal to 3% by weight.
10. The method of claim 1, wherein the metallic iron particles are at least one of particles, spiral chips, plates, and strips.
11. The method of claim 1, wherein the sulfate-based iron electroplating solution further comprises a complexing agent.
12. The method of claim 11, wherein the complexing agent is at least one amino acid selected from glycine, glutamic acid and glutamine, and at least one compound selected from a group consisting of formic acid, acetic acid, lactic acid, gluconic acid, and oxalic acid, citric acid, nitrilotriacetic acid (NTA), ethylenediamine-N, N, N', N'-tetraacetic acid (EDTA).
13. The method of claim 1, wherein the sulfate-based iron electroplating solution has a temperature of 80 °C or lower and a pH of 1.0 to 4.0.
14. In any one of claims 1 to 13, wherein the method comprises

an electroplated cell in which electroplating is performed by applying a current;
 a circulation bath for circulating the electroplated cell and an electroplating solution;
 a dissolution bath for circulating the circulation bath and the electroplating solution containing the metallic iron charged therein, and dissolving metallic iron to remove ferric ions from the electroplating solution,
 wherein the method is performed by an iron-based electroplating apparatus having a pump for supplying the electroplating solution in the circulation bath to the dissolution bath and a filter for preventing metallic iron in the dissolution bath from entering the circulation bath.

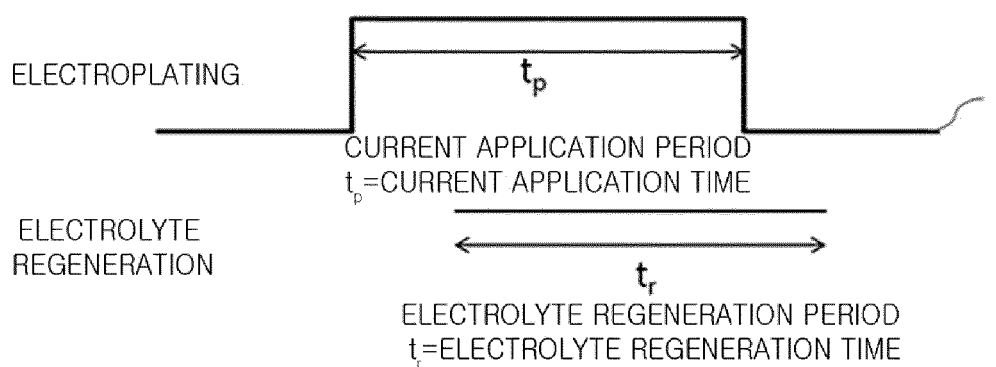
[FIG. 1]



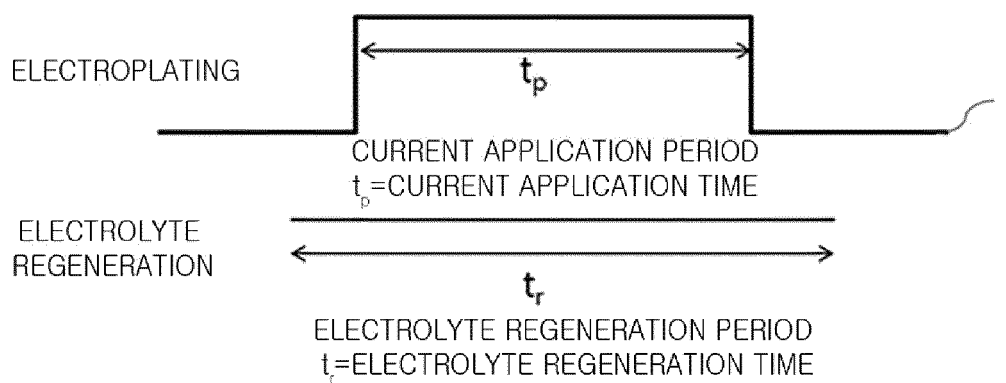
[FIG. 2]



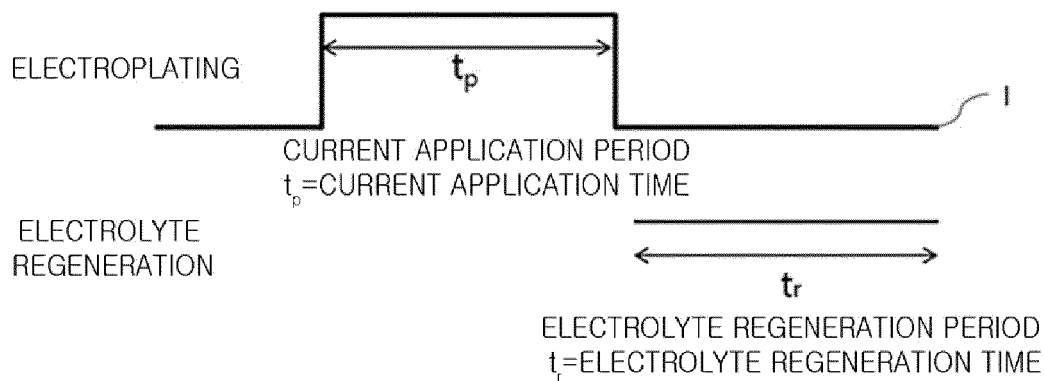
[FIG. 3]



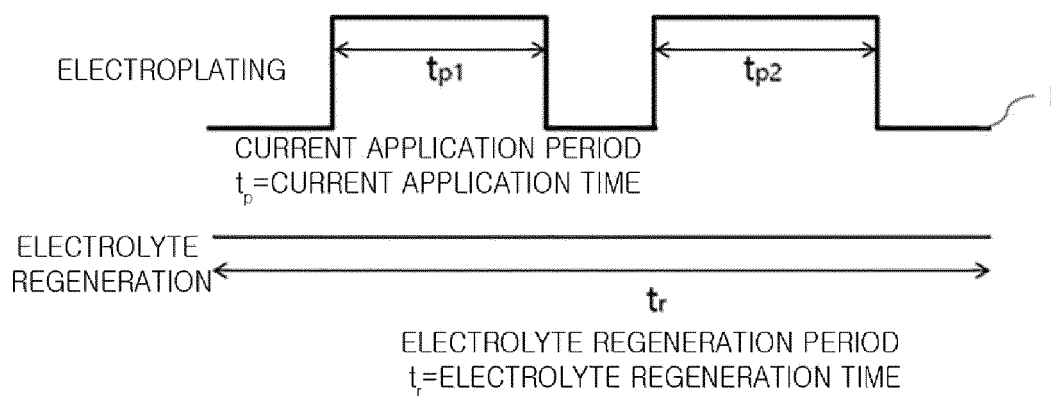
[FIG. 4]



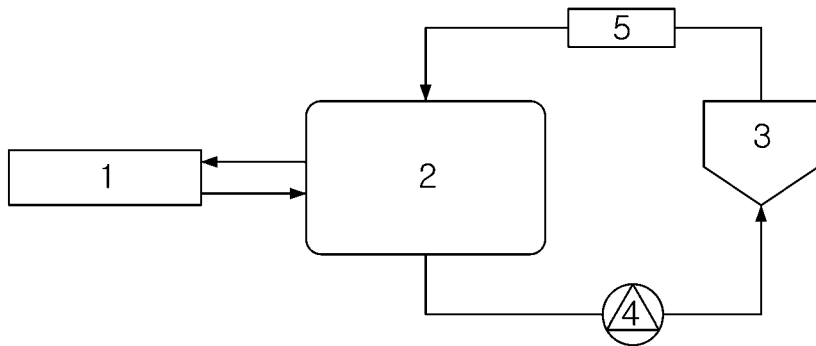
[FIG. 5]



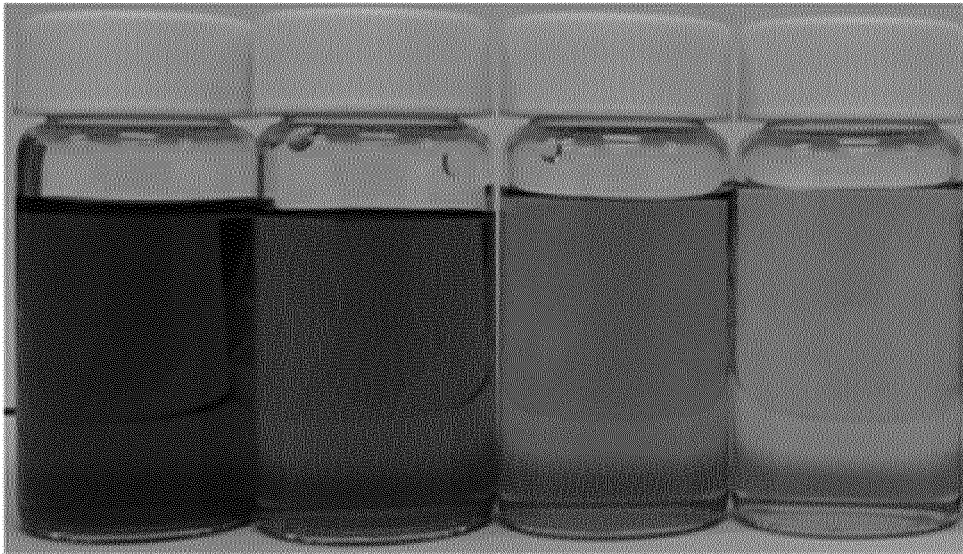
[FIG. 6]



[FIG. 7]



[FIG. 8]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2021/003533

A. CLASSIFICATION OF SUBJECT MATTER

C25D 21/18(2006.01)i; C25D 21/06(2006.01)i; C25D 3/20(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)

C25D 21/18(2006.01); C02F 1/461(2006.01); C25B 1/00(2006.01); C25D 21/14(2006.01); C25D 3/00(2006.01);
C25D 3/20(2006.01)

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

Korean utility models and applications for utility models: IPC as above

Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 환원(reduction), 제2철(ferric iron), 제1철(ferrous iron), 전기 도금(electroplating),
황산(sulfuric acid)**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 06-306697 A (KAWASAKI STEEL CORP.) 01 November 1994 (1994-11-01) See paragraphs [0016]-[0019] and claim 1.	1-14
A	JP 10-102300 A (NIPPON PARKERIZING CO., LTD. et al.) 21 April 1998 (1998-04-21) See paragraph [0013] and claims 1-2.	1-14
A	JP 09-165698 A (TOYOTA MOTOR CORP.) 24 June 1997 (1997-06-24) See claims 1-3.	1-14
A	CN 210163184 U (SHANDONG SHENLONG WATER CO., LTD.) 20 March 2020 (2020-03-20) See claim 1.	1-14
A	KR 10-0138617 B1 (POHANG IRON & STEEL CO., LTD.) 15 July 1998 (1998-07-15) See paragraph [0031] and claim 1.	1-14

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

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"D" document cited by the applicant in the international application	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"E" earlier application or patent but published on or after the international filing date	"&" document member of the same patent family
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 26 November 2021	Date of mailing of the international search report 29 November 2021
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208 Facsimile No. +82-42-481-8578	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2021/003533

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 06-306697 A	01 November 1994	JP 3234671 B2	04 December 2001
JP 10-102300 A	21 April 1998	None	
JP 09-165698 A	24 June 1997	None	
CN 210163184 U	20 March 2020	None	
KR 10-0138617 B1	15 July 1998	KR 10-1996-0023232 A	18 July 1996

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REFERENCES CITED IN THE DESCRIPTION

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- KR 20150185858 [0008]
- JP 6181533 A [0008]
- JP 63259089 A [0008]