



(11)

EP 3 633 074 A1

(12)

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

(43) Date of publication:

08.04.2020 Bulletin 2020/15

(51) Int Cl.:

C25C 7/02 (2006.01)

C23F 1/02 (2006.01)

C25C 1/08 (2006.01)

C25D 17/12 (2006.01)

(21) Application number: 18809926.1

(86) International application number:

PCT/JP2018/013187

(22) Date of filing: 29.03.2018

(87) International publication number:

WO 2018/220979 (06.12.2018 Gazette 2018/49)

(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

(30) Priority: 29.05.2017 JP 2017105796

(71) Applicant: **Sumitomo Metal Mining Co., Ltd.**
Tokyo 105-8716 (JP)

(72) Inventors:

- **WATANABE Hiroto**
Niihama-shi
Ehime 792-0002 (JP)

- **MATSUOKA Itsu**
Niihama-shi
Ehime 792-0002 (JP)

- **SENBA Yusuke**
Niihama-shi
Ehime 792-0002 (JP)

- **KOBAYASHI Hiroshi**
Niihama-shi
Ehime 792-0002 (JP)

(74) Representative: **Jones, Nicholas Andrew**
Withers & Rogers LLP
4 More London Riverside
London, SE1 2AU (GB)(54) **CATHODE PLATE FOR METAL ELECTRODEPOSITION AND MANUFACTURING METHOD FOR SAME**

(57) Provided are: a cathode plate for metal electrodeposition which makes it less likely to lose a non-conductive film on a metal plate, which can be used repeatedly, and for which maintenance is easy even if a non-conductive film is lost; and a manufacturing method for such cathode plate. This cathode plate 1 includes a metal plate 2 on which a plurality of disk-shaped protrusions 2a are arranged, and a non-conductive film 3 formed in flat sections 2b which are sections of the metal plate 2 other than the protrusions 2a. The protrusions 2a each have a side face that has a shape formed of a substantially vertical section 2d and an inclined section 2e. A height L1 of each protrusion 2a is 50 μ m to 1000 μ m, and when an intersection of the side face of the protrusion and a vertical line that is vertically lowered from a position X that is 20 μ m outward from the outer peripheral edge of the protrusion is defined as Y, then a length L2 from X to Y is at least 40 μ m but not more than 0.8 \times L1 μ m.

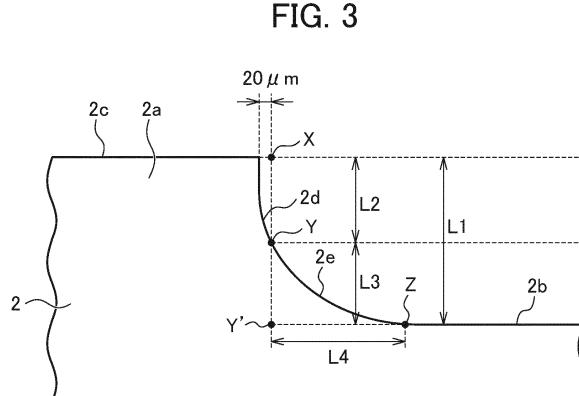


FIG. 3

Description**TECHNICAL FIELD**

5 **[0001]** The present invention relates to a cathode plate for metal electrodeposition and a manufacturing method for the same.

BACKGROUND ART

10 **[0002]** In the related art, electric nickel used as an anode raw material of nickel plating is used by being put into a titanium basket that is an anode retainer, and by being hanged in a nickel plating bath. At this time, as the electric nickel that is the anode raw material, plate-shaped electric nickel that is electrodeposited on a cathode plate is used by being cut into a small piece.

15 **[0003]** However, the small piece-shaped electric nickel has a sharp corner section, and thus, it is difficult to handle the small piece-shaped electric nickel at the time of being put into the titanium basket. In addition, the corner section is caught by the reticulation of the titanium basket after the small piece-shaped electric nickel is put into the titanium basket, and thus, so-called shelf hanging occurs, a filled state in the titanium basket is changed, and there is a case where plating unevenness is caused.

20 Therefore, it has been proposed to use rounded small mass-shaped (button-shaped) electric nickel of which a corner section is chamfered. The small mass-shaped electric nickel, for example, can be manufactured by using a cathode plate on which a plurality of circular conductive sections are arranged at regular intervals, by precipitating nickel on the conductive section with electrolysis, and then, by peeling off electrodeposited nickel from the conductive section. According to such a method, it is possible to effectively manufacture a plurality of small mass-shaped electric nickels from one cathode plate.

25 **[0004]** Fig. 5 is a diagram illustrating an example of a cathode plate of the related art that is used for manufacturing small mass-shaped electric nickel. A cathode plate 11 is masked with a non-conductive film 13 by leaving a portion to be a conductive section 12a on a flat plate-shaped metal plate 12, and in the cathode plate 11, the conductive section 12a is a concave section, and the non-conductive film 13 is a convex section. By using such a cathode plate 11, nickel having a suitable size is electrodeposited on the conductive section 12a, and small mass-shaped electric nickel is manufactured.

30 **[0005]** Examples of a method of forming the non-conductive film 13 on the metal plate 12, as with the cathode plate 11, include a method in which a thermosetting non-conductive resin such as an epoxy resin is applied onto the flat plate-shaped metal plate 12 by a screen printing method, and is heated, and thus, the non-conductive film 13 having a desired pattern is formed, as illustrated in Fig. 6A (refer to Patent Documents 1 and 2). Furthermore, Fig. 6B illustrates a state in which nickel (electric nickel) 14 is electrodeposited on the conductive section 12a by using the cathode plate 11 on which the non-conductive film 13 is formed. In the cathode plate 11, the nickel 14 starts to be electrodeposited from the conductive section 12a, and grows not only in a thickness (vertical) direction but also in a planar (horizontal) direction, and thus, is in a state where the nickel 14 rises to the upper section of the non-conductive film 13.

35 **[0006]** In addition, for example, as illustrated in Fig. 7A, a method has been also proposed in which a photosensitive non-conductive resin is applied onto a metal plate 22, and is exposed and developed, and the non-conductive resin in a portion corresponding to a conductive section 22a is removed, and thus, a non-conductive film 23 having a desired pattern is formed. Furthermore, Fig. 7B illustrates a state in which the nickel (electric nickel) 24 is electrodeposited on the conductive section 22a by using the cathode plate 21 on which the non-conductive film 23 is formed. Even in the cathode plate 21, the nickel 24 starts to be electrodeposited from the conductive section 22a, and grows not only in the thickness direction but also in the planar direction.

40 **[0007]** Further, a method has been also proposed in which the periphery of a metal structure that is incorporated such that a plurality of studs to be a conductive section are arranged at regular intervals is solidified with an insulating resin by an injection molding method, and thus, a cathode plate configuring a non-conductive section is manufactured (refer to Patent Document 3).

50

Patent Document 1: Japanese Examined Patent Application Publication No. S51-036693

Patent Document 2: Japanese Unexamined Patent Application, Publication No. S52-152832

Patent Document 3: Japanese Examined Patent Application Publication No. S56-029960

55

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

5 [0008] In a case where the small mass-shaped electric nickel is manufactured by using the cathode plate as described above, it is required that the lifetime of the non-conductive film formed on the cathode plate (the non-conductive section) is long, and even in a case where the non-conductive film is lost (degraded), the maintenance can be easily performed.

10 [0009] As illustrated in Fig. 6A, in a case where the non-conductive film 13 is formed by applying the non-conductive resin onto the metal plate 12 by screen printing, a film thickness of the non-conductive film 13 gradually decreases as being close to the conductive section 12a, and thus, becomes extremely thin on the boundary with respect to the conductive section 12a. Such a change in the film thickness of the non-conductive film 13 depends on a coating amount of the non-conductive resin, the viscosity of the non-conductive resin, temperature properties of the viscosity, a curing temperature of the non-conductive resin, surface roughness of a metal surface, surface free energy, and the like. For this reason, the film thickness of the non-conductive film 13 becomes extremely thin on the boundary with respect to the conductive section 12a.

15 [0010] As described above, in a case where small mass-shaped electric nickel is manufactured by using the cathode plate 11 as illustrated in Fig. 5 and Fig. 6, the nickel 14 starts to be electrodeposited from the conductive section 12a, grows not only in the vertical direction but also in the horizontal direction, and thus, is in a state where the nickel 14 gradually rises to the non-conductive film 13. For this reason, in the portion of the thin non-conductive film 13 that is formed in the vicinity of the boundary with respect to the conductive section 12a, adhesiveness with respect to the metal plate 12 easily decreases due to the permeation of an electrolysis solution, and the non-conductive film is easily lost due to a stress at the time of electrodepositing the nickel 14 or an impact at the time of peeling off the electric nickel. In addition, in a case where the non-conductive film 13 is lost once, the non-conductive film 13 in the vicinity of the lost portion floats from the surface of the metal plate 12, and thus, the electrolysis solution more easily permeates through the gap, and as a result thereof, in the case of continuously electrodepositing nickel, the electrolysis solution is sunk into the gap of the non-conductive film 13 that floats from the surface of the metal plate 12, and thus, the nickel 14 is electrodeposited. Then, in the case of peeling off the nickel 14 that is sunk into the gap and is electrodeposited, the non-conductive film 13 that is bitten by the nickel 14 is further lost.

20 [0011] As described above, in the cathode plate 11 of the related art, in a case where the non-conductive film 13 is lost in a chain reaction, and the lost portion spreads, the nickels 14 grown from the adjacent conductive section 12a are easily joined to each other, and thus, it is not possible to obtain electric nickel having a desired shape, and a defective product is obtained. Therefore, it is necessary to maintain the cathode plate 11 by peeling off the entire non-conductive film 13 before the non-conductive film 13 is lost, and by forming again the non-conductive film 13. However, in practice, it is necessary to maintain the cathode plate 11 in a step where an electrodeposition treatment of nickel is performed several times to less than 10 times at a maximum, and thus, not only does productivity decrease, but also a maintenance cost increases.

25 [0012] On the other hand, as illustrated in Fig. 7A, in the cathode plate 21 on which the non-conductive film 23 is formed by being exposed and developed by using the photosensitive non-conductive resin, it is possible to form the non-conductive film 23 with a uniform film thickness. However, when the nickel 24 is peeled off after the electrodeposition, the nickel 24 is caught by a step of the non-conductive film 23 configuring the convex section, and a large impact is easily applied to the non-conductive film 23, and thus, the non-conductive film 23 is lost.

30 [0013] Furthermore, as with Patent Document 3, in the method of configuring the non-conductive section by injection molding, the lifetime of the non-conductive section to be formed is lengthened, but a manufacturing cost of the cathode plate itself increases, and thus, it is difficult to maintain the cathode plate in a case where the non-conductive section is degraded.

35 [0014] The present invention has been made in consideration of such circumstances of the related art, an object thereof is to provide a cathode plate for metal electrodeposition in which a non-conductive film on a metal plate is less likely to be lost, and thus, can be repeatedly used, and even in a case where the non-conductive film is lost, maintenance becomes easy, and a manufacturing method for the same.

40
50
55 [0015] The present inventors have conducted intensive studies in order to solve the problems described above. As a result thereof, it has been found that a conductive section is formed by providing protrusions on a metal plate, and a non-conductive film is provided on a metal surface other than the protrusion, and thus, the non-conductive film is less likely to be lost. Further, it has been found that a side face of the protrusion has a predetermined shape, and thus, the non-conductive film is more effectively prevented from being lost, and even in a case where the non-conductive film is formed again, and thus, maintenance is necessary, the non-conductive film does not remain at the time of peeling off

the non-conductive film, and the maintenance is easily performed, and the present invention has been completed.

5 (1) A first invention of the present invention is a cathode plate for metal electrodeposition, including: a metal plate in which a plurality of disk-shaped protrusions are arranged on at least one surface; and a non-conductive film formed on a surface of the metal plate other than the protrusion, in which the protrusion has a side face that is in a shape formed of a substantially vertical section and an inclined section, a height L1 of the protrusion is greater than or equal to 50 μm and less than or equal to 1000 μm , and when an intersection between a vertical line vertically lowered from a position X that is 20 μm outward from an outer peripheral edge of the protrusion and the side face is defined as Y, a length L2 from X to Y is greater than or equal to 40 μm and less than or equal to $0.8 \times L1 \mu\text{m}$.

10 (2) A second invention of the present invention is the cathode plate for metal electrodeposition in which the metal plate is formed of titanium or stainless steel, in the first invention.

15 (3) A third invention of the present invention is the cathode plate for metal electrodeposition that is used for manufacturing electric nickel for plating, in the first invention or the second invention.

(4) A fourth invention of the present invention is a manufacturing method of the cathode plate for metal electrodeposition according to any one of the first invention to the third invention, in which the plurality of disk-shaped protrusions are formed on at least one surface of the metal plate by wet etching processing or end mill processing.

20 (5) A fifth invention of the present invention is the manufacturing method of the cathode plate for metal electrodeposition in which in the end mill processing, a radius end mill is used, in the fourth invention.

20 Effects of the Invention

[0016] According to the present invention, it is possible to provide a cathode plate for metal electrodeposition in which a non-conductive film is less likely to be lost, and thus, can be repeatedly used, and even in a case where the non-conductive film is lost, maintenance becomes easy, and a manufacturing method for the same.

25 BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

30 Fig. 1 is a plan view illustrating a configuration of a cathode plate.
 Fig. 2 is an enlarged sectional view of main parts illustrating the configuration of the cathode plate, in which
 Fig. 2A is an enlarged sectional view of main parts describing a state of the cathode plate before nickel electrodeposition, and Fig. 2B is an enlarged sectional view of main parts describing a state of the cathode plate after the nickel electrodeposition.
 35 Fig. 3 is an enlarged sectional view of main parts enlarging an A section in Fig. 2, and is an enlarged sectional view of main parts describing a shape of a side face of a protrusion on a metal plate.
 Fig. 4 is an enlarged sectional view of main parts describing a manufacturing method of the cathode plate, in which
 Fig. 4A is an enlarged sectional view of main parts describing a first step, and Fig. 4B is an enlarged sectional view of main parts describing a second step.
 40 Fig. 5 is a plan view illustrating a configuration of a cathode plate of the related art.
 Fig. 6 is an enlarged sectional view of main parts illustrating the configuration of the cathode plate of the related art, in which Fig. 6A is an enlarged sectional view of main parts describing a state of the cathode plate before the nickel electrodeposition, Fig. 6B is an enlarged sectional view of main parts describing a state of the cathode plate after the nickel electrodeposition.
 45 Fig. 7 is an enlarged sectional view of main parts illustrating the configuration of the cathode plate of the related art, in which Fig. 7A is an enlarged sectional view of main parts describing a state of the cathode plate before the nickel electrodeposition, Fig. 7B is an enlarged sectional view of main parts describing a state of the cathode plate after the nickel electrodeposition.

50 PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0018] Hereinafter, an embodiment in which a cathode plate for metal electrodeposition of the present invention is applied to a cathode plate for metal electrodeposition that is used for manufacturing electric nickel (hereinafter, referred to as "this embodiment") will be described in detail. Furthermore, the present invention is not limited to the following embodiment, but can be suitably changed within a range not departing from the gist of the present invention.

<1. Cathode Plate for Metal Electrodeposition>

(1) Configuration of Cathode Plate

5 [0019] As illustrated in Fig. 1, a cathode plate 1 according to this embodiment includes a metal plate 2 on which a plurality of disk-shaped protrusions 2a are arranged and a non-conductive film 3 that is formed on a surface of the metal plate 2 other than the protrusion 2a. As described below, for example, the cathode plate 1 is used by being hung in an electrolysis bath in which an electrolysis solution containing nickel or an anode is contained by a hanging member 5, and nickel is electrodeposited on the surface into a desired shape.

10 [Metal Plate]

15 [0020] As illustrated in Fig. 1 and Fig. 2A, the metal plate 2 is a flat plate-shaped metal plate, and includes the plurality of disk-shaped protrusions 2a. Here, in the metal plate 2, the surface other than the protrusion 2a is referred to as a "flat section 2b" with respect to the protrusion 2a. In addition, a "height L1 of the protrusion" is a protruding height from the surface of the flat section 2b in the metal plate 2.

20 [0021] Furthermore, in Fig. 2, an example in which the protrusions 2a are provided on one face of the metal plate 2 is illustrated, and the protrusions 2a may be provided on both faces.

25 [0022] The size of the metal plate 2 is not particularly limited, and may be suitably set in accordance with a desired size or the number of electric nickels to be manufactured. For example, the size of the metal plate 2 can be a rectangular size in which one side is greater than or equal to 100 mm and less than or equal to 2000 mm. In addition, in a case where the protrusions 2a are provided on one surface, for example, it is preferable that the thickness of the metal plate 2 is approximately greater than 1.5 mm and less than or equal to 5 mm, and in a case where the protrusions 2a are provided on both surfaces, for example, it is preferable that the thickness of the metal plate is approximately greater than or equal to 3 mm and less than or equal to 10 mm. In a case where the thickness of the metal plate 2 is excessively small, there is a tendency that warpage easily occurs by the protrusion 2a and the flat section 2b. On the other hand, in a case where the thickness of the metal plate 2 is excessively large, the weight of the metal plate 2 increases, and thus, it is difficult to handle the metal plate 2.

30 [0023] The material of the metal plate 2 is not particularly limited insofar as the material is a metal that is less corrosive with respect to an electrolysis solution to be used, and forms only loose adhesion with respect to an electrodeposition such as nickel, and examples of the material preferably include titanium and stainless steel.

35 [0024] In the metal plate 2, the plurality of disk-shaped protrusions 2a have a function as a conductive section by exposing the upper face from the non-conductive film 3 described below, and the adjacent protrusions 2a form a concave step such that the non-conductive film 3 is formed to have a predetermined thickness. Hereinafter, in the protrusions 2a, the upper face exposed from the non-conductive film 3 may be referred to as a "conductive section 2c". In the conductive section 2c, nickel 4 is electrodeposited by an electrolysis treatment.

40 [0025] The size of the disk-shaped protrusion 2a may be suitably set in accordance with the size of desired electric nickel, and the diameter of the disk-shaped protrusion 2a, for example, can be greater than or equal to 5 mm and less than or equal to 30 mm. In addition, the height L1 of the protrusion 2a is preferably greater than or equal to 50 μm and less than or equal to 1000 μm , and is more preferably greater than or equal to 100 μm and less than or equal to 500 μm . In a case where the height L1 of the protrusion 2a is excessively small, a film thickness of the non-conductive film 3 that is formed on the flat section 2b of the metal plate 2 becomes insufficient, and thus, the non-conductive film 3 is easily lost due to a stress at the time of electrodepositing the nickel 4 or an impact at the time of peeling off the electric nickel. On the other hand, in a case where the height L1 of the protrusion 2a is excessively large, for example, when the non-conductive film is formed by screen printing, the number of times of performing coating increases, and thus, productivity decreases. In addition, in a case where the height L1 is excessively large, the distortion of the metal plate 2 easily occurs at the time of processing the protrusion 2a, and the metal plate 2 is easily warped, and thus, it is difficult to form the non-conductive film 3. Furthermore, in order to decrease the influence of the distortion of the metal plate 2, it is also possible to increase the thickness of the metal plate 2, but the weight of the metal plate 2 increases, and thus, it is difficult to handle the metal plate 2.

45 [0026] Here, Fig. 3 is an enlarged sectional view of main parts enlarging an A section in Fig. 2, and is an enlarged sectional view of main parts describing the shape of the side face of the protrusion on the metal plate. As illustrated in Fig. 3, in the metal plate 2, the side face of the protrusion 2a is in a shape formed of a substantially vertical section 2d and an inclined section 2e. Specifically, the substantially vertical section 2d is a portion that is substantially vertically formed with respect to the upper face formed of the conductive section 2c of the protrusion 2a. In addition, the inclined section 2e is a portion that is formed by being inclined towards flat section 2c from the substantially vertical section 2d.

50 [0027] As described above, the side face of the protrusion 2a is configured to be in the shape formed of the substantially vertical section 2d and the inclined section 2e, and thus, even in a case where the electrodeposition treatment is repeatedly

performed, it is possible to more effectively prevent the non-conductive film 3 from being lost, and to repeatedly use the non-conductive film 3. In addition, even in a case where the non-conductive film 3 is formed again due to degradation such as the loss of the non-conductive film 3, and thus, the maintenance is necessary, a phenomenon that the non-conductive film 3 remains on the side face of the protrusion 2a at the time of peeling off the non-conductive film 3 from the metal plate 2, a so-called peeling residue is less likely to be generated, and thus, the maintenance becomes easy.

[0028] For example, in a case where the side face of the protrusion is in a shape formed only of the substantially vertical section without the inclined section, the non-conductive film easily remains on the corner of the side face of the protrusion that is formed at an approximately right angle, even in the case of peeling off the non-conductive film from the metal plate. On the other hand, in a case where the side face of the protrusion is in a shape formed only of the inclined section without the substantially vertical section, the non-conductive film in the vicinity of the conductive section becomes thin, and the degradation of the non-conductive film is accelerated, for example, the non-conductive film is easily lost by the electrodeposition treatment.

[0029] More specifically, as illustrated in Fig. 3, in the shape of the side face of the protrusion 2a, when an intersection between a vertically lowered line from a position X 20 μm outward from an outer peripheral edge of the protrusion 2a and the side face of the protrusion 2a is defined as Y, a length L2 from X to Y is greater than or equal to 40 μm , and is preferably greater than or equal to 100 μm . By setting the length L2 to be greater than or equal to 40 μm , even in a case where the non-conductive film 3 that is formed on the metal plate 2 (the flat section 2b) is repeatedly subjected to the electrolysis treatment, the non-conductive film 3 is less likely to be lost. Furthermore, here, the outer peripheral edge of the protrusion 2a is an outer peripheral edge (an edge portion) of an upper face that is the conductive section 2c of the protrusion 2a.

[0030] In addition, the length L2 is less than or equal to 0.8 times the height L1 of the protrusion 2a ($L1 \times 0.8 \mu\text{m}$). By setting the length L2 to be less than or equal to $L1 \times 0.8 \mu\text{m}$, it is possible to effectively ensure the inclined section 2e, and as described above, the peeling residue of the non-conductive film 3 is less likely to be generated on the side face of the protrusion 2a, at the time of peeling off the non-conductive film 3 from the metal plate 2.

[0031] Furthermore, the length L2 from X to Y corresponds to the height of the substantially vertical section 2d, but it is not necessary that the intersection Y is a branch point from which the shape of the side face of the protrusion 2a is obviously divided into the substantially vertical section 2d and the inclined section 2e. Hereinafter, there will be a case where the length L2 is referred to as the "height L2 of the substantially vertical section 2d".

[0032] In addition, a length L3 that is a difference between the height L1 of the protrusion 2a and the length L2 is preferably greater than or equal to 10 μm , is more preferably greater than or equal to 25 μm and less than or equal to $0.7 \times L1 \mu\text{m}$. Hereinafter, there will be a case where the length L3 is referred to as the "height of the inclined section 2e". Further, when an intersection between a vertically lowered line from the intersection Y and a virtual face that is formed by extending the surface of the flat section 2b in a horizontal direction is defined as Y', a boundary position between the protrusion 2a and the flat section 2b is defined as Z, and a length from Y' to Z is defined as L4, it is preferable that $L3/L4$ is greater than or equal to 0.2 and less than or equal to 1. Hereinafter, there will be a case where the length L4 is referred to as the "length L4 of the inclined section 2e". L3/L4 corresponds to an inclined angle of the inclined section 2e.

[0033] By setting the length L3 or L3/L4 to be in the range described above, even in a case where the non-conductive film 3 is formed again, and thus, the maintenance is necessary, the peeling residue of the non-conductive film 3 is less likely to be generated on the side face of the protrusion 2a, at the time of peeling off the non-conductive film 3 from the metal plate 2, and the maintenance becomes easy.

[0034] In addition, fine roughness may be provided on the surface of the metal plate 2, that is, the upper face of the disk-shaped protrusion 2a in the metal plate 2 by sandblasting or etching. Accordingly, the nickel 4 that is electrodeposited on the protrusion 2a can be peeled off by a suitable impact without dropping out during the electrolysis treatment. In this case, it is preferable that the film thickness of the non-conductive film 3 described below is greater than or equal to twice maximum surface roughness Rz of the metal plate 2. In a case where the film thickness of the non-conductive film 3 is less than twice the maximum surface roughness Rz of the metal plate 2, there is a concern that a pinhole or an insulation failure portion is generated in the non-conductive film 3.

50 [Non-Conductive Film]

[0035] As illustrated in Fig. 2, the non-conductive film 3 is formed on the flat section 2b that is the surface of the metal plate 2 other than the protrusion 2a, and thus, is in a state where the upper face of the plurality of protrusions 2a arranged on the metal plate 2, that is, the conductive section 2c is exposed. Then, the nickel 4 is electrodeposited in such a conductive section 2c of the metal plate 2, and thus, the nickel 4 is formed by being divided into each small mass.

[0036] The non-conductive film 3 is formed on the flat section 2b on which the concave step formed by the adjacent protrusions 2a is provided. For this reason, in the non-conductive film 3, the film thickness of the end section is less likely to be thin as with the non-conductive film 13 of the related art illustrated in Fig. 6, and thus, the non-conductive

film 3 is less likely to be lost due to a stress at the time of electrodepositing the nickel 4 or an impact at the time of peeling off the nickel 4 after the electrodeposition. In addition, the non-conductive film 3 does not concavely protrude as with the non-conductive film 23 of the related art illustrated in Fig. 7, and thus, the end section is protected from the concave step. Accordingly, the impact of the nickel 4 that is applied to the end section of the non-conductive film 3 is small even at the time of peeling off the nickel 4 from the cathode plate 1, and thus, the non-conductive film 3 is less likely to be lost. As described above, in the cathode plate 1, the non-conductive film 3 is less likely to be lost, and thus, it is possible to repeatedly use the non-conductive film 3 in the electrodeposition without replacing the non-conductive film 3, and it is possible to reduce a maintenance cost and to improve the productivity.

[0037] Furthermore, in a case where the non-conductive film 3 is formed in the flat section 2b on the metal plate 2 by a screen printing method, the material of the non-conductive film 3 is also applied onto the upper face of the protrusion 2a, and thus, a surface area of the conductive section 2c may decrease, and an initial current density may increase, but there is no problem insofar as the properties of the electrodeposited nickel 4 are not degraded. In addition, the film thickness of the non-conductive film 3 attached onto the upper face of the protrusion 2a is extremely thin, and thus, the non-conductive film 3 is easily lost, but the film thickness of the non-conductive film 3 that is formed on the flat section 2b is thick, and thus, the non-conductive film 3 is prevented from being lost, and therefore, there is no problem.

[0038] The non-conductive film 3 is not particularly limited insofar as the non-conductive film has non-conductivity, and is formed of a material that is less corrosive with respect to an electrolysis solution to be used. For example, it is preferable that the non-conductive film 3 is configured of a thermosetting resin or a photocurable resin (an ultraviolet curable resin or the like), from the viewpoint of easy film formation. Specifically, an insulating resin such as an epoxy-based resin, a phenolic resin, a polyamide-based resin, a polyimide-based resin is exemplified.

(2) Manufacturing of Electric Nickel Using Cathode Plate

[0039] In the cathode plate 1 configured as described above, as illustrated in Fig. 2B, the upper face of the protrusion 2a that is exposed from the non-conductive film 3 is the conductive section 2c, and the nickel 4 is electrodeposited. In the cathode plate 1, the nickel 4 grows not only in a thickness direction but also in a planar direction, and thus, is in a state where the nickel 4 rises to the upper section of the non-conductive film 3. For this reason, it is preferable that the electrodeposition is ended before the nickels 4 grown from the conductive section 2c are in contact with each other in the adjacent protrusions 2a.

[0040] Then, the nickel 4 is peeled off from the cathode plate 1 after the electrodeposition of the nickel 4 is ended, and thus, a plurality of small mass-shaped electric nickels can be obtained by one cathode plate 1. As described above, in the cathode plate 1 according to this embodiment, the non-conductive film 3 is less likely to be lost, and thus, it is possible to repeatedly use the non-conductive film 3 in the electrodeposition without replacing the non-conductive film 3, and it is possible to reduce the maintenance cost and to improve the productivity.

[0041] Furthermore, in the cathode plate 1 according to this embodiment, the nickel 4 is electrodeposited, but the present invention is not limited to nickel, and silver, gold, zinc, tin, chromium, cobalt, or an alloy thereof may be electrodeposited.

<2. Manufacturing Method of Cathode Plate for Metal Electrodeposition>

[0042] As illustrated in Fig. 4, a manufacturing method of the cathode plate 1 according to this embodiment includes a first step of forming the plurality of disk-shaped protrusions 2a on at least one surface of the metal plate 2 (Fig. 4A), and a second step of forming the non-conductive film 3 on the surface of the metal plate 2 other than the protrusion 2a (Fig. 4B).

[First Step]

[0043] In the first step, the plurality of disk-shaped protrusions 2a are formed on the surface of the metal plate 2. For example, a portion other than the protrusions 2a is removed from the flat plate-shaped metal plate 2 to leave the protrusions 2a having the height L1, and thus, the flat section 2b is formed. As a processing method, wet etching processing or end mill processing is preferable, and the wet etching processing is more preferable in order to process a large area.

[0044] For example, in a case where the flat plate-shaped stainless steel plate is processed by wet etching, a photo-sensitive etching resist is applied onto a surface of a stainless steel plate, and then, is exposed through a film or glass on which desired pattern is drawn, the etching resist on a portion to be etched is removed by a development treatment. Then, the stainless steel plate subjected to the development treatment is applied to an etching solution (for example, a ferric chloride solution), a part of the stainless steel plate from which the etching resist is removed is removed, and finally, the etching resist is peeled off, and thus, the plurality of disk-shaped protrusions 2a corresponding to a desired pattern

can be formed. In the case of the wet etching, an etching rate with respect to stainless steel in a portion in the vicinity of the resist is slower than an etching rate with respect to stainless steel in a portion separated from a resist end section, and thus, a sectional shape of the protrusion 2a is a shape formed of the substantially vertical section 2d and the inclined section 2e. In addition, it is possible to process a large area at one time, and thus, it is possible to perform the production for a short period of time.

[0045] On the other hand, in the case of the end mill processing, the metal plate 2 is processed by a radius end mill having a desired shape in which a tip end of a blade of a drill is rounded, and thus, the substantially vertical section 2d and the inclined section 2e can be more precisely formed.

[0046] Furthermore, the protrusion 2a may be formed on only one surface of the metal plate 2, or may be formed on both surfaces of the metal plate 2.

[Second Step]

[0047] In the second step, the non-conductive film 3 is formed on the flat section 2b that is the surface of the metal plate 2 other than the protrusion 2a. A formation method of the non-conductive film 3 is not particularly limited, and the non-conductive film 3 can be formed by screen printing. In a case where the material of the non-conductive film 3 is a thermosetting resin or a photocurable resin, as necessary, thermal curing or photo curing may be performed.

[0048] According to the manufacturing method of the cathode plate according to this embodiment, it is possible to obtain the cathode plate 1 in which the non-conductive film 3 on the metal plate 2 is less likely to be lost, and thus, can be repeatedly used, by a simple method described above. In addition, even in a case where the non-conductive film 3 is formed again due to degradation such as the loss of the non-conductive film 3, and thus, the maintenance is necessary, the peeling residue of the non-conductive film 3 is less likely to be generated on the side face of the protrusion 2a, at the time of peeling off the non-conductive film 3, and the maintenance is easy.

EXAMPLES

[0049] Hereinafter, examples of the present invention will be described in more detail, but the present invention is not limited to the examples. Furthermore, for the sake of convenience, the description will be given by applying the same reference numerals to members having the same functions as those of the members illustrated in Fig. 1 to Fig. 6.

<<Preparation of Cathode Plate>>

[Example 1]

[0050] The cathode plate 1 as illustrated in Fig. 1 and Fig. 2 was prepared. Specifically, first, the metal plate 2 of stainless steel (a cold rolling material) having a size of 200 mm × 100 mm × 4 mm was subjected to wet etching, and thus, the (18) disk-shaped protrusions 2a were formed. At this time, in the size of the protrusion 2a, the diameter was 14 mm, the height L1 was 300 µm, and a minimum distance between centers of the adjacent protrusions 2a was 21 mm. The shape was measured by a laser displacement meter, and thus, the height L2 of the substantially vertical section 2d was 120 µm on average, the height L3 of the inclined section 2e was 180 µm on average, and the length L4 of the inclined section 2e was 420 µm on average.

[0051] Next, a thermosetting epoxy resin was applied onto the flat section 2b of the metal plate 2 by a screen printing method, and was cured by being heated at 150°C for 60 minutes, and thus, the non-conductive film 3 was formed.

[Example 2]

[0052] The cathode plate 1 was prepared as with Example 1, except that the height L1 of the protrusion 2a of the metal plate 2 was 500 µm. In the cathode plate 1 prepared as described above, the height L2 of the substantially vertical section 2d was measured by the laser displacement meter, and thus, was 200 µm on average, the height L3 of the inclined section 2e was 300 µm on average, and the length L4 of the inclined section 2e was 650 µm on average.

[Example 3]

[0053] The cathode plate 1 was prepared as with Example 1, except that the height L1 of the protrusion 2a of the metal plate 2 was 60 µm. In the cathode plate 1 prepared as described above, the height L2 of the substantially vertical section 2d was measured by the laser displacement meter, and thus, was 45 µm on average, the height L3 of the inclined section 2e was 15 µm on average, and the length L4 of the inclined section 2e was 20 µm on average.

[Example 4]

[0054] The cathode plate 1 was prepared as with Example 1, except that the height L1 of the protrusion 2a of the metal plate 2 was 200 μm . In the cathode plate 1 prepared as described above, the height L2 of the substantially vertical section 2d was measured by the laser displacement meter, and thus, was 90 μm on average, the height L3 of the inclined section 2e was 110 μm on average, and the length L4 of the inclined section 2e was 240 μm on average.

[Example 5]

[0055] The cathode plate 1 was prepared as with Example 1, except that the disk-shaped protrusion was formed by using a radius end mill drill. In the cathode plate 1 prepared as described above, the height L2 of the substantially vertical section 2d was measured by the laser displacement meter, and thus, was 100 μm on average, the height L3 of the inclined section 2e was 200 μm on average, and the length L4 of the inclined section 2e was 220 μm on average.

[Comparative Example 1]

[0056] In Comparative Example 1, the cathode plate 11 of the related art as illustrated in Fig. 5 and Fig. 6 was prepared. Specifically, a thermosetting epoxy resin was applied onto the flat plate-shaped metal plate 12 of stainless steel (a cold rolling material) having a size of 200 mm \times 100 mm \times 4 mm by a screen printing method while leaving the (18) conductive sections 12a having a diameter of 14 mm, and was cured by being heated at 150°C for 60 minutes, and thus, the non-conductive film 13 was formed, and the cathode plate 11 was prepared.

[Comparative Example 2]

[0057] The cathode plate 1 was prepared as with Example 1, except that the height L1 of the protrusion 2a of the metal plate 2 was 40 μm . In the cathode plate 1 prepared as described above, the height L2 of the substantially vertical section 2d was measured by the laser displacement meter, and thus, was 30 μm on average, the height L3 of the inclined section 2e was 10 μm on average, and the length L4 of the inclined section 2e was 50 μm on average.

[Comparative Example 3]

[0058] The cathode plate 1 was prepared as with Example 4, except that the metal plate 2 of stainless steel (a hot rolling material) having a size of 200 mm \times 100 mm \times 4 mm was used. In the cathode plate 1 prepared as described above, the height L2 of the substantially vertical section 2d was measured by the laser displacement meter, and thus, a part thereof was approximately 20 μm , the height L3 of the inclined section 2e was 180 μm on average, and the length L4 of the inclined section 2e was 300 μm on average. Such a portion in which the height L2 of the substantially vertical section 2d is low is formed by a concave section of surface roughness that is formed in the manufacturing step of the hot rolling material.

[Comparative Example 4]

[0059] The cathode plate 1 was prepared as with Example 4, except that the disk-shaped protrusion 2a was formed by using a flat end mill drill. In the cathode plate 1 prepared as described above, the height L2 of the substantially vertical section 2d was measured by the laser displacement meter, and thus, was 200 μm , and there was no inclined section.

[Comparative Example 5]

[0060] As with Example 1, the metal plate was subjected to the wet etching, and protrusions of which the height L1 was 2000 μm were formed. However, the warpage of the metal plate was large, and it was difficult to form the non-conductive film by screen printing.

<<Manufacturing of Electric Nickel>>

[0061] The electric nickel was manufactured by an electrolysis treatment, by using the cathode plate prepared in each of the examples and each of the comparative examples. Specifically, the cathode plate, and an anode plate of electric nickel having a size of 200 mm \times 100 mm \times 10 mm were immersed in an electrolysis bath containing a nickel chloride electrolysis solution to face each other. Then, nickel was electrodeposited on the surface of the cathode plate, in a condition of an initial current density of 710 A/m² and an electrolysis time for 3 days. The electric nickel precipitated on

the cathode plate was peeled off after the electrolysis, and thus, small mass-shaped electric nickel for plating was obtained.

<< Evaluation>>

5 [0062] The number of times that the cathode plate used in the electrolysis treatment can be directly repeatedly used was evaluated. In a case where the loss of the non-conductive film spreads, the adjacent protrusions, and the nickels electrodeposited on the conductive section are joined to each to each other, and thus, electric nickel having desired shape may not be obtained. Therefore, in a case where the non-conductive film was lost over greater than or equal to 1 mm from the boundary with respect to the protrusion in a flat section direction, the use was stopped, and the number of repeating times up to that time point was evaluated. In addition, the electrodeposition and the peeling of nickel were repeated up to 20 times. In addition, even in a case where the non-conductive film was lost and the diameter of the conductive section was enlarged by greater than or equal to 1 mm, the use was stopped, and the number of repeating times up to that time point was evaluated.

10 [0063] The non-conductive film of the cathode plate of which the number of repeating times was evaluated was peeled off by a waterjet, and peeling properties of the non-conductive film were evaluated. Specifically, a rotary nozzle of which a hole diameter was 0.4 mm and the number of holes was 3 was used as the waterjet, and the non-conductive film was peeled off at a hydraulic pressure of 200 MPa, the quantity of water of 10 L/minute, and an effective width of 30 mm, while moving the nozzle at 2 m/minute. In the peeling properties of the non-conductive film, a case where the non-conductive film was capable of being approximately completely removed within approximately 20 seconds per one cathode plate (200 mm × 100 mm) was evaluated as "Excellent" and a case where the non-conductive film was not capable of being removed even after 20 seconds was evaluated as "Peeling Residue Occurs".

15 [0064] In Table 1, an evaluation result is shown along with the configuration of the cathode plate.

25

30

35

40

45

50

55

[Table 1]

	Cathode plate material	Processing method	Shape of cathode plate	L1 (μm)	L2 (μm)	L3 (μm)	L4 (μm)	L3/L4	Number of repeating times	Peeling properties of non-conductive film
Example 1	Cold rolling material	Wet etching	With projection	300	120	180	420	0.43	>20	Excellent
Example 2	Cold rolling material	Wet etching	With projection	500	200	300	650	0.46	>20	Excellent
Example 3	Cold rolling material	Wet etching	With projection	60	45	15	20	0.75	16	Excellent
Example 4	Cold rolling material	Wet etching	With projection	200	90	110	240	0.46	>20	Excellent
Example 5	Cold rolling material	End mill	With projection	300	100	200	220	0.91	>20	Excellent
Comparative Example 1	Cold rolling material	-	Plate shape	-	-	-	-	-	7	Excellent
Comparative Example 2	Cold rolling material	Wet etching	With projection	40	30	10	50	0.2	9	Excellent
Comparative Example 3	Hot rolling material	Wet etching	With projection	200	20	180	300	0.6	10	Excellent
Comparative Example 4	Cold rolling material	End mill	With projection	200	200	-	-	-	>20	Peeling residue
Comparative Example 5	Cold rolling material	Wet etching	With projection	2000	-	-	-	-	(Difficult to print non-conductive film due to large warpage)	

[0065] As shown in Table 1, in Examples 1 to 5 using the cathode plate 1 in which the non-conductive film 3 was formed on the flat section 2b of the metal plate 2, and the height L1 of the protrusion 2a was greater than or equal to 60 μm and less than or equal to 500 μm , the loss of the non-conductive film 3 was suppressed, and thus, was capable of being sufficiently repeatedly used. In particular, in Examples 1, 2, 4, and 5 in which the height L1 of the protrusion 2a was greater than or equal to 100 μm , the number of times that the non-conductive film 3 was capable of being repeatedly used was greater than 20 times. In addition, in Examples 1 to 5 in which the height L2 of the substantially vertical section 2d was greater than or equal to 40 μm and less than or equal to $0.8 \times L1 \mu\text{m}$, when the non-conductive film 3 was peeled off by the waterjet, the non-conductive film 3 was capable of being excellently peeled off without generating a peeling residue or the like.

[0066] On the other hand, in Comparative Example 1 in which the non-conductive film 13 was formed on the flat plate-shaped metal plate 12, the non-conductive film 14 was lost, and thus, was not capable of being sufficiently repeatedly used. In addition, in Comparative Example 2 in which the height L1 of the protrusion 2a was low, the non-conductive film 3 was lost, and thus, was not capable of being sufficiently repeatedly used. In addition, in Comparative Example 3, the non-conductive film 3 is lost from a portion in which the height L2 of the substantially vertical section 2d was as low as 20 μm , in the shape of the side face of the protrusion 2a, and thus, was not capable of being sufficiently repeatedly used. In Comparative Example 4, there was no inclined section in the shape of the side face of the protrusion 2a, and thus, when the non-conductive film 3 was peeled off by the waterjet, a peeling residue was generated on the corner of the side face of the protrusion 2a that was formed at an approximately right angle. Further, in Comparative Example 5, the height L1 of the protrusion 2a was excessively high, and thus, warpage of the metal plate 2 was large, it was difficult to perform coating with respect to the non-conductive film, and thus, it was not possible to configure the cathode plate.

EXPLANATION OF REFERENCE NUMERALS

[0067]

1	CATHODE PLATE
2	METAL PLATE
2a	PROTRUSION
2b	FLAT SECTION
30	2c CONDUCTIVE SECTION
2d	SUBSTANTIALLY VERTICAL SECTION
2e	INCLINED SECTION
3	NON-CONDUCTIVE FILM
4	NICKEL

Claims

1. A cathode plate for metal electrodeposition, comprising:

a metal plate in which a plurality of disk-shaped protrusions are arranged on at least one surface; and a non-conductive film formed on a surface of the metal plate other than the protrusion, wherein the protrusion has a side face that is in a shape formed of a substantially vertical section and an inclined section, a height L1 of the protrusion is greater than or equal to 50 μm and less than or equal to 1000 μm , and when an intersection between a vertical line vertically lowered from a position X that is 20 μm outward from an outer peripheral edge of the protrusion and the side face is defined as Y, a length L2 from X to Y is greater than or equal to 40 μm and less than or equal to $0.8 \times L1 \mu\text{m}$.

2. The cathode plate for metal electrodeposition according to claim 1, wherein the metal plate is formed of titanium or stainless steel.

3. The cathode plate for metal electrodeposition according to claim 1 or 2, wherein the cathode plate for metal electrodeposition is used for manufacturing electric nickel for plating.

4. A manufacturing method of the cathode plate for metal electrodeposition according to any one of claims 1 to 3, wherein the plurality of disk-shaped protrusions are formed on at least one surface of the metal plate by wet etching processing or end mill processing.

EP 3 633 074 A1

5. The manufacturing method of the cathode plate for metal electrodeposition according to claim 4, wherein in the end mill processing, a radius end mill is used.

5

10

15

20

25

30

35

40

45

50

55

FIG. 1

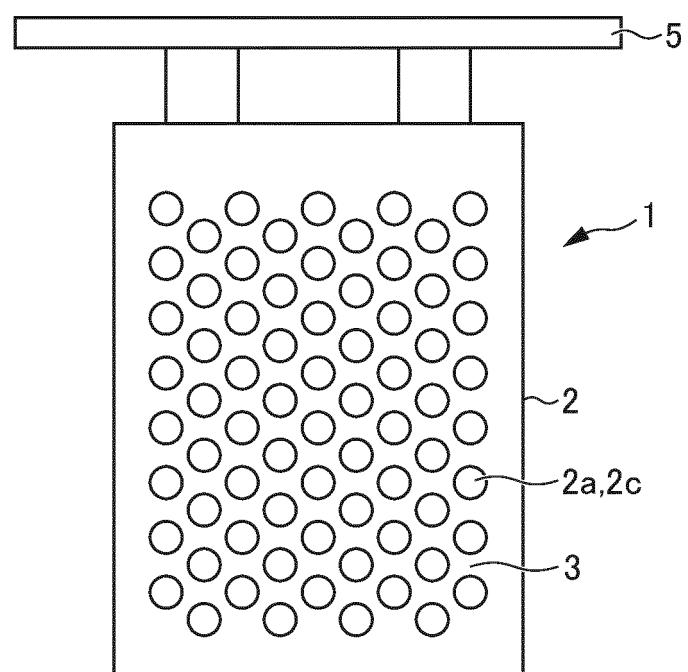


FIG. 2A

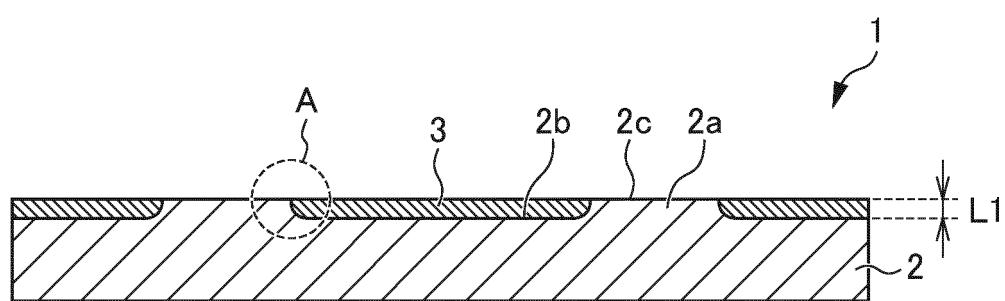


FIG. 2B

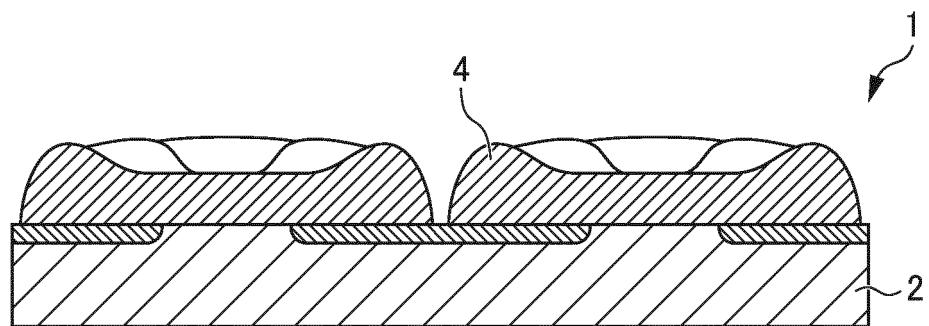


FIG. 3

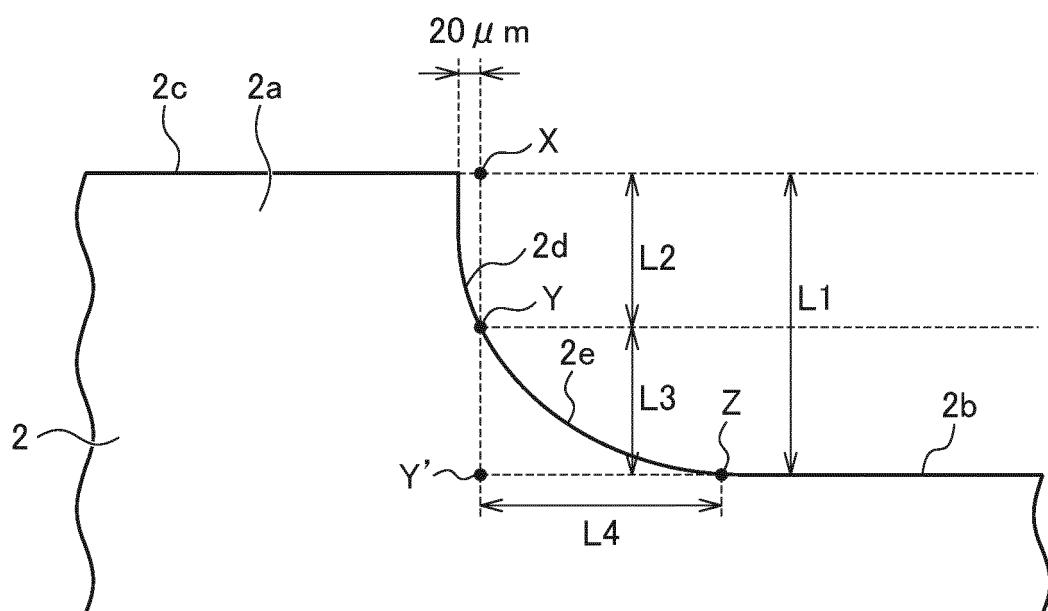


FIG. 4A

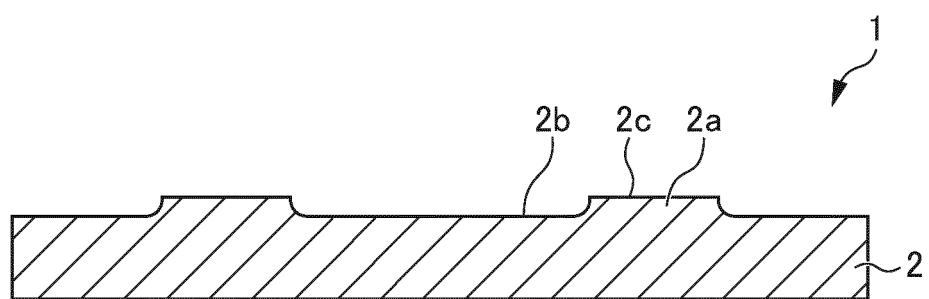


FIG. 4B

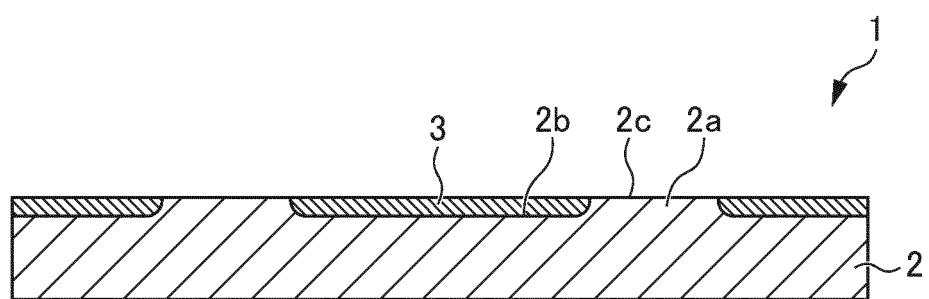


FIG. 5

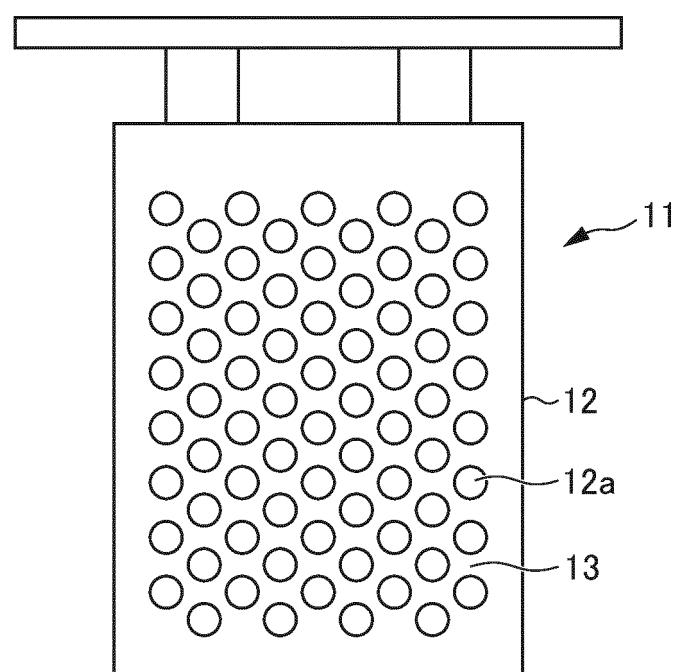


FIG. 6A

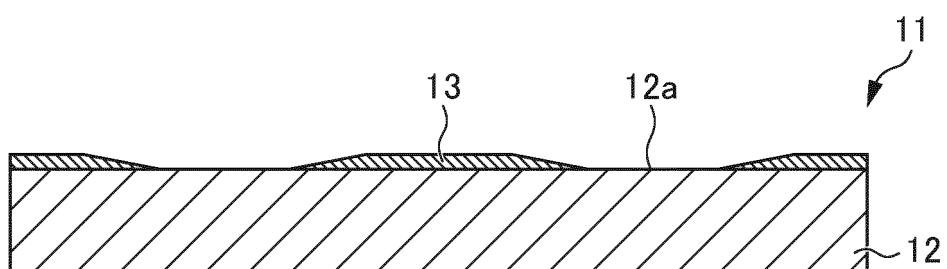


FIG. 6B

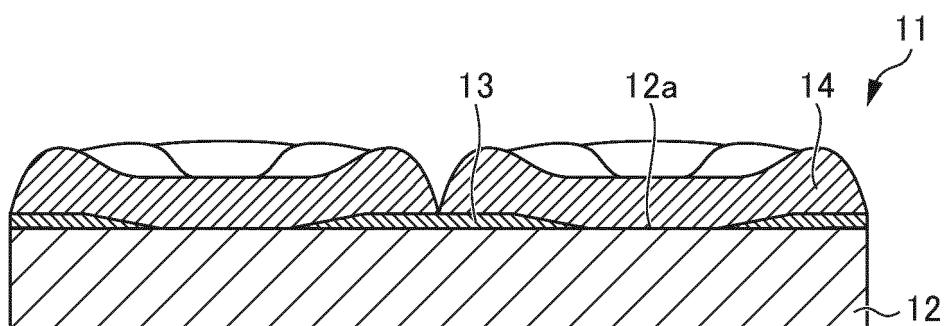


FIG. 7A

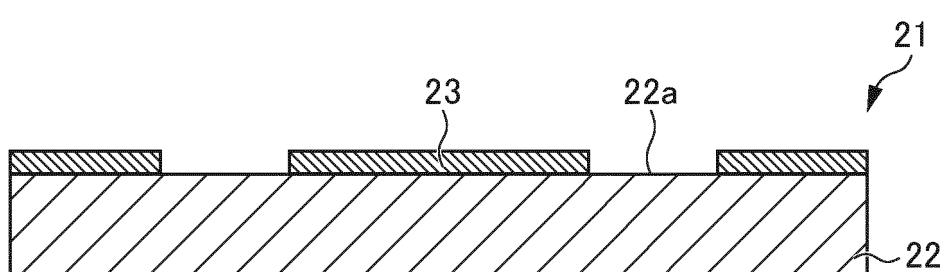
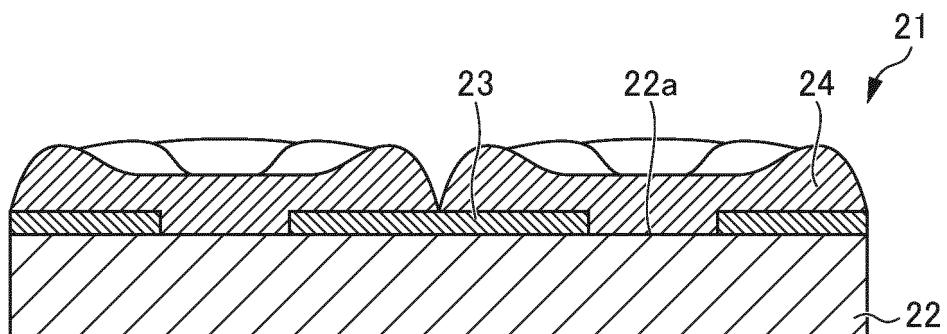


FIG. 7B



INTERNATIONAL SEARCH REPORT		International application No. PCT/JP2018/013187	
5	A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. C25C7/02(2006.01)i, C23F1/02(2006.01)i, C25C1/08(2006.01)i, C25D17/12(2006.01)i		
	According to International Patent Classification (IPC) or to both national classification and IPC		
10	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. C25C7/02, C23F1/02, C25C1/08, C25D17/12		
15	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2018 Registered utility model specifications of Japan 1996-2018 Published registered utility model applications of Japan 1994-2018		
20	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
25	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	X	US 2011/0233055 A1 (STEELMORE HOLDING PTY LTD.) 29 September 2011, fig. 1-3B, 6A-D, paragraphs [0001]-[0042], [0045]-[0051] & WO 2010/028428 A1 & AU 2009291494 A & CN 102149854 A & CN 104611730 A	1-5
30	A	JP 2015-196905 A (OCI COMPANY LTD.) 09 November 2015 & US 2015/0284870 A1 & KR 10-2015-0115084 A	1-5
	A	JP 10-317197 A (SUMITOMO METAL MINING CO., LTD.) 02 December 1998, paragraph [0018], fig. 2 (Family: none)	1-5
35	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "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 "&" document member of the same patent family		
40	Date of the actual completion of the international search 06.06.2018	Date of mailing of the international search report 19.06.2018	
	Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.	
55	Form PCT/ISA/210 (second sheet) (January 2015)		

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP S51036693 B [0007]
- JP S52152832 B [0007]
- JP S56029960 B [0007]