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(54) Titre : POUDRE D'ALLIAGE ABSORBANT L'HYDROGENE ET PROCESSUS DE FABRICATION DE CELUI-CI
(54) Title: HYDROGEN ABSORBING ALLOY POWDER AND PROCESS FOR PRODUCING SAME

(57) **Abrégé/Abstract:**

The invention provides a hydrogen absorbing alloy electrode obtained by the step P1 of preparing a hydrogen absorbing alloy powder containing cobalt and nickel, the step P2 of subjecting the surfaces of the alloy particles to a reduction treatment with high-temperature hydrogen by holding the powder in a high-temperature hydrogen atmosphere under the conditions of temperature, pressure and time sufficient to reduce oxides formed in a surface layer portion of each of the alloy particles, not melting the alloy particles and not permitting the alloy particles to absorb hydrogen, the step P3 of treating the resulting powder with an acid or alkali by immersing the powder in an acid or alkaline aqueous solution, followed by suction filtration, washing with water and drying, and the step P4 of applying the resulting power to an electrically conductive substrate and shaping the substrate in the form of the electrode. The electrode thus provided has higher activity than conventionally.



ABSTRACT

The invention provides a hydrogen absorbing alloy electrode obtained by the step P1 of preparing a hydrogen absorbing alloy powder containing cobalt and nickel, the step P2 of subjecting the surfaces of the alloy particles to a reduction treatment with high-temperature hydrogen by holding the powder in a high-temperature hydrogen atmosphere under the conditions of temperature, pressure and time sufficient to reduce oxides formed in a surface layer portion of each of the alloy particles, not melting the alloy particles and not permitting the alloy particles to absorb hydrogen, the step P3 of treating the resulting powder with an acid or alkali by immersing the powder in an acid or alkaline aqueous solution, followed by suction filtration, washing with water and drying, and the step P4 of applying the resulting power to an electrically conductive substrate and shaping the substrate in the form of the electrode. The electrode thus provided has higher activity than conventionally.

DESCRIPTION

HYDROGEN ABSORBING ALLOY POWDER AND
PROCESS FOR PRODUCING SAME

TECHNICAL FIELD

The present invention relates to a hydrogen absorbing alloy powder for use as a material for electrodes (negative electrodes) of metallic oxide-hydrogen batteries such as nickel-hydrogen batteries, and a process for producing the powder, and more particularly to the surface treatment of a hydrogen absorbing alloy powder.

BACKGROUND ART

Hydrogen absorbing alloy electrodes serving as the negative electrodes of nickel-hydrogen batteries are prepared by pulverizing a hydrogen absorbing alloy ingot to obtain a hydrogen absorbing alloy powder, admixing a binder with the powder and shaping the mixture in the form of the electrode. The hydrogen absorbing alloys heretofore developed include those of AB_5 -type rare earths having a crystal structure of the $CaCu_5$ type, such as $Mm-Ni$ alloys, and $TiNi_2$ alloys having a Laves-phase structure of the C14-type or C15-type.

With the nickel-hydrogen batteries having a hydrogen absorbing alloy electrode as the negative electrode, a gas-phase reaction and an electrochemical reaction proceed at the same time on the surface of the hydrogen absorbing alloy owing to the contact of the alloy surface with an alkaline electrolyte. More specifically, in the relationship between the hydrogen pressure and the temperature, hydrogen is absorbed by the alloy, or the alloy desorbs hydrogen (gas-phase reaction). In the voltage-current relationship, on the other hand, application of voltage (charging) permits the alloy to absorb the hydrogen produced by the electrolysis of water, and the delivery of current (discharging) oxidizes hydrogen to form water (electrochemical reaction). The properties of the alloy surface are therefore important in improving the performance of the nickel-hydrogen battery.

Accordingly, to improve the activity of the hydrogen absorbing alloy for use in nickel-hydrogen batteries, it is conventional practice to immerse a hydrogen alloy powder in an aqueous acid solution for surface treatment as disclosed in JP-B-225975/1993, or in an aqueous alkaline solution for surface treatment as disclosed in JP-B-175339/1988. The surface treatment removes an oxide film formed in the surface layer portions of the alloy

particles, permitting rare-earth elements (such as La) to dissolve out and forming a nickel- or cobalt-rich layer in the surface layer portions of the particles, whereby the alloy is given improved electrochemical catalytic activity.

However, we have found that the conventional surface treatment still fails to afford sufficient activity although forming the nickel- or cobalt-rich layer in the surface layer portions of the alloy particles.

An object of the present invention is to provide a hydrogen absorbing alloy powder having higher activity than conventionally, a process for producing the powder, a hydrogen absorbing alloy electrode wherein the powder is used, and a metallic oxide-hydrogen battery comprising the electrode.

DISCLOSURE OF THE INVENTION

In producing a hydrogen absorbing alloy powder of the present invention, a starting hydrogen absorbing alloy powder containing nickel and cobalt is held in a high-temperature hydrogen atmosphere under the conditions of temperature, pressure and time sufficient to reduce oxides formed in a surface layer portion of each of the alloy particles 1, not melting the alloy particles 1 and not permitting the alloy particles to absorb hydrogen, and thereafter surface-treated with an acid or alkaline

treating liquid. In this process, the temperature is in the range of 100°C to 900°C, the pressure is in the range of 1 atm to 3 atm, and the time is in the range of 30 minutes to 10 hours. The acid treating liquid is, for example, a hydrochloric acid solution. The alkaline treating liquid to be used is at least one aqueous solution selected, for example, from among aqueous solution of KOH, aqueous solution of NaOH and aqueous solution of LiOH.

The hydrogen absorbing alloy powder obtained by the above production process is applied to an electrically conductive substrate and shaped in the form of an electrode to prepare a hydrogen absorbing alloy electrode of the invention.

The oxide film formed in the surface layer portions of the alloy particles 1 in the step of preparing the starting hydrogen absorbing alloy powder is reduced by the high-temperature hydrogen atmosphere (reduction treatment with high-temperature hydrogen) of the above process and thereby converted to a first metal-rich layer 3 which is enriched in metals (nickel and cobalt). Since the temperature, pressure and time for the treatment are adjusted to the respective ranges mentioned, the oxide film is fully reduced without the likelihood of the alloy

particles 1 melting or absorbing hydrogen.

The alloy powder is thereafter subjected to a surface treatment with the acid or alkaline treating liquid, whereby oxides of rare-earth elements (such as La), or Al, etc. are allowed to dissolve out from a surface layer portion of the first metal-rich layer 3. A second metal-rich layer 4 further enriched in the metals (nickel and cobalt) is formed in the surface layer portion of the first metal-rich layer 3. The first metal-rich layer 3 is internally studded with relatively small clusters 30 of the metals (nickel and cobalt), while the second metal-rich layer 4 is visually found to be internally studded with many relatively large clusters 40 of the metals (nickel and cobalt).

According to the present invention, the first metal-rich layer 3 formed by the reduction treatment with high-temperature hydrogen and enriched in nickel and cobalt is treated with an acid or alkali to form the second metal-rich layer 4 which is further enriched in nickel and cobalt. The invention therefore affords higher activity than the prior art wherein an acid treatment or alkali treatment only is conducted.

The hydrogen absorbing alloys usable according to the invention are those having a crystal structure of the

CaCu₅ type, and alloys having a Laves-phase structure of the C14-type or C15-type. Preferable to use are alloys having a crystal structure of the CaCu₅ type.

Examples of useful alloys having the CaCu₅-type crystal structure are those represented by MmNi₂CoAlMn and obtained by substituting the La of LaNi₅ with Mm (misch metal) which is a mixture of rare-earth elements, i.e., alloys represented by the formula MmNi_xM1_yM2_z (wherein Mm is a mixture of rare-earth elements, M1 is at least one element selected from among Co, Al and Mn, M2 is a transition metal different from M1, x is a positive real number, x, y and z are such that $4.7 \leq x+y+z \leq 5.4$).

Examples of useful alloys having a Laves-phase structure are those represented by AB₂ (wherein A is at least one of Ti and Zr, and B is at least one element selected from among Ni, Co, V, Mn, Fe and Cr). More specifically, TiNi₂ and Ti_{0.5}Zr_{0.5}Ni₂ are useful.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a scheme showing the process of the invention for producing a hydrogen absorbing alloy electrode;

FIG. 2 is a sectional view showing an alkaline battery;

FIG. 3 is a diagram for illustrating the effect of a

reduction treatment of the invention with high-temperature hydrogen;

FIG. 4 is a diagram showing the structure of surface layer portion of a particle of hydrogen absorbing alloy embodying the invention; and

FIG. 5 is a perspective view partly broken away and showing the construction of a test cell.

BEST MODE OF CARRYING OUT THE INVENTION

FIG. 2 shows the construction of a nickel-hydrogen battery (for example, 1000 mAh in battery capacity) of AA size and of the type wherein the positive electrode is dominant, and the present invention is to be practiced. The illustrated battery, which is an alkaline battery, has a closed construction comprising a positive electrode 11, negative electrode 12, separator 13, positive electrode lead 14, negative electrode lead 15, external positive

terminal 16, can 17 serving also as a negative terminal, closure 18, etc. The positive electrode 11 and the negative electrode 12 are accommodated, as rolled up in a spiral form with the separator 13 interposed therebetween, in the can 17. The positive electrode 11 is connected by the lead 14 to the closure 18, and the negative electrode 12 by the lead 15 to the can 17. An insulating packing 20 is provided at the junction of the can 17 and the closure 18 to seal off the battery. A coiled spring 19 is interposed between the external positive terminal 16 and the closure 18. The spring 19 is compressed to release a gas from inside the battery to the atmosphere when the internal pressure of the battery builds up abnormally.

A hydrogen absorbing alloy electrode for use as the negative electrode 12 is produced by the steps shown in FIG. 1.

First, a hydrogen absorbing alloy powder is prepared as specified in composition and particle size (step P1). For example, Mm, Ni, Co, Al and Mn are mixed together in the mole ratio of 1.0:3.1:1.0:0.3:0.6, and the mixture is melted in an arc melting furnace having an argon atmosphere and thereafter allowed to cool spontaneously to obtain an ingot of hydrogen absorbing alloy represented by the formula $MmNi_{3.1}CoAl_{0.3}Mn_{0.6}$. The ingot is mechanically

pulverized in the air to obtain a hydrogen absorbing alloy powder having a mean particle size of 80 micrometers.

Next, the alloy powder is placed into a heat-resistant pressure-resistant container of stainless steel and heated at 300°C after evacuation, hydrogen gas is then introduced into the container to 1.2 atm, and the powder is held in this state for 30 minutes. In this way, the alloy particles are subjected to a surface treatment (reduction treatment with high-temperature hydrogen, step P2).

The temperature, pressure and time for the reduction treatment with high-temperature hydrogen are not limited to the above values but are so determined that the oxide film formed in the surface layer portions of the alloy particles as will be described below can be fully reduced without permitting the particles to melt and to absorb hydrogen. The treatment is conducted, for example, at a temperature in the range of 100 °C to 900 °C and at a pressure in the range of 1.0 atm to 3.0 atm for 30 minutes to 10 hours.

Subsequently, the alloy powder resulting from the reduction treatment is immersed in an acid aqueous solution, for example, in a 0.5N hydrochloric acid solution (room temperature), at a pH of 0.3 for 2 hours,

followed by suction filtration, washing with water and drying, whereby the powder is subjected to an acid treatment (step P3).

The acid aqueous solution is not limited to the hydrochloric acid solution; an aqueous solution having a strong acidity of 0.3 to 2.0 in pH can be used. For example, a sulfuric acid solution or nitric acid solution is usable. In view of the battery characteristics, the hydrochloric acid solution is more preferable than the sulfuric acid solution or nitric acid solution in that the aqueous solution is free from the sulfate radical (SO_4^{2-}) or nitrate radical (NO_3^-).

The hydrogen absorbing alloy powder can be treated with an alkaline aqueous solution instead of the acid treatment. The alloy powder is immersed, for example, in a 30 wt. % aqueous solution of potassium hydroxide (80°C), useful as an electrolyte, for 2 hours, followed by suction filtration and drying. The alkaline aqueous solution is not limited to the aqueous solution of potassium hydroxide but can be a strongly alkaline aqueous solution consisting predominantly of potassium hydroxide (KOH), such as an aqueous solution of KOH and LiOH, aqueous solution of KOH and NaOH or aqueous solution of KOH, NaOH and LiOH. An aqueous solution of LiOH and NaOH is also usable.

The hydrogen absorbing alloy powder resulting from the acid treatment is thereafter mixed with a 5 wt. % aqueous solution of a binder such as PEO (polyethylene oxide) in the ratio of 100:20 by weight to prepare a paste, which is applied to opposite surfaces of a substrate of punching metal plated with nickel, followed by drying at room temperature and cutting to a predetermined size, whereby a hydrogen absorbing alloy electrode is produced (step P4).

The electrode thus obtained is incorporated as the negative electrode into the nickel-hydrogen battery shown in FIG. 2. A sintered nickel electrode is usable as the positive electrode, an alkali-resistant nonwoven fabric as the separator, and a 30 wt. % aqueous solution of potassium hydroxide as the electrolyte.

In the process shown in FIG. 1 for producing the hydrogen absorbing alloy electrode, the surfaces of the alloy particles as prepared by step P1 come into contact with the air or the water in the air, with the result that an oxide film 2 of nickel oxide and cobalt oxide is formed in the surface layer portions of the alloy particles 1 as shown in FIG. 3, (a).

The oxide film 2 is thereafter reduced with high-temperature hydrogen in step P2 and thereby converted to a

first metal-rich layer 3 which is enriched in nickel and cobalt as shown in FIG. 3, (b).

Further in step P3, rare-earth elements such as La dissolve out from a surface layer portion of the first metal-rich layer 3, with the result that a second metal-rich layer 4 further enriched in nickel and cobalt is formed in the surface layer portion of the first metalrich layer 3.

FIG. 4 is a diagram schematically showing the surface layer portion of the alloy particle obtained by the above process, as observed under a transmission electron microscope. A sample was prepared by ion etching for the observation of the surface layer portion.

As illustrated, the first metal-rich layer 3 is internally studded with relatively small clusters 30 of nickel and cobalt, while the second metal-rich layer 4 is internally studded with many relatively large clusters 40 of nickel and cobalt. Thus, the second metal-rich layer 4 further enriched in nickel and cobalt is formed in the surface layer portion of the first metal-rich layer 3.

Table I shown below shows the proportions of component elements (proportion, in atm %, of each component element in the entire composition of the layer) in the first metal-rich layer 3 and the second metal-rich layer 4 of the hydrogen

absorbing alloy powder, as determined by energy dispersive X-ray analysis (EDX) using a field emission scanning transmission electron microscope (FESTEM).

Table I

COMPONENT ELEMENT	La	Ce	Pr	Nd	Ni	Co	Al	Mn
SECOND METAL - RICH LAYER (atm %)	0.02	0.04	0.00	0.00	78.93	19.11	0.80	1.10
FIRST METAL - RICH LAYER (atm %)	3.53	5.16	0.31	1.01	65.13	16.05	2.30	6.51

The proportion of nickel (Ni) and the proportion of cobalt (Co) are both greater in the second metal-rich layer 4 than in the first metal-rich layer 3. This indicates that the second metal-rich layer 4 further enriched in nickel and cobalt is formed in the surface layer portion of the first metal-rich layer 3.

Thus, the first metal-rich layer 3 formed by the reduction treatment with high-temperature hydrogen and enriched in nickel and cobalt is treated with an acid to form the second metal-rich layer 4 which is further enriched in nickel and cobalt. The surface treating process of the invention therefore gives higher electrochemical catalytic activity to the hydrogen absorbing alloy electrode than the prior art wherein an acid treatment only is conducted.

Tables II and III shown below show the results of tests conducted to substantiate the advantage of the surface treating process of the present invention.

Table II

ALLOY ELECTRODE	ALLOY PREPARING METHOD	REDUCTION TREATMENT	TREATMENT AFTER REDUCTION TREATMENT	INITIAL DISCHARGE CAPACITY OF TEST CELL (DISCHARGE CAPACITY 1) mAh/g	INITIAL DISCHARGE CAPACITY OF ALKALINE BATTERY (DISCHARGE CAPACITY 2) mAh	RESISTANCE VALUE OF POWDER m Ω / (g $\cdot$ cm ²)
A1	Ar ARC FURNACE	YES	UNTREATED	285	820	0.708
A2	Ar ARC FURNACE	YES	WITH ACID	295	860	0.737
A3	Ar ARC FURNACE	YES	WITH ALKALI	290	855	0.796
A4	ATOMIZING	YES	UNTREATED	292	840	0.767
A5	ATOMIZING	YES	WITH ACID	299	865	0.796
A6	ATOMIZING	YES	WITH ALKALI	296	855	0.885
B1	Ar ARC FURNACE	NO	UNTREATED	222	620	1.003
B2	Ar ARC FURNACE	NO	WITH ACID	246	675	1.032
B3	Ar ARC FURNACE	NO	WITH ALKALI	232	640	1.062
B4	ATOMIZING	NO	UNTREATED	170	580	1.032
B5	ATOMIZING	NO	WITH ACID	221	620	1.062
B6	ATOMIZING	NO	WITH ALKALI	202	610	1.091

Table III

ALLOY PREPARING METHOD	TREATMENT AFTER REDUCTION TREATMENT	TEMPERATURE FOR REDUCTION TREATMENT (°C)	INITIAL DISCHARGE CAPACITY OF TEST CELL (DISCHARGE CAPACITY 1) (mAh/g)	INITIAL DISCHARGE CAPACITY OF ALKALINE BATTERY (DISCHARGE CAPACITY 2) (mAh)
Ar ARC FURNACE	UNTREATED	50	250	680
Ar ARC FURNACE	UNTREATED	100	285	820
Ar ARC FURNACE	UNTREATED	300	285	820
Ar ARC FURNACE	UNTREATED	500	286	825
Ar ARC FURNACE	UNTREATED	700	285	825
Ar ARC FURNACE	UNTREATED	900	284	820
Ar ARC FURNACE	UNTREATED	950	255	675
ATOMIZING	UNTREATED	50	225	630
ATOMIZING	UNTREATED	100	292	835
ATOMIZING	UNTREATED	300	292	840
ATOMIZING	UNTREATED	500	291	840
ATOMIZING	UNTREATED	700	290	840
ATOMIZING	UNTREATED	900	288	835
ATOMIZING	UNTREATED	950	224	625

Described below are preparation of a test device,
test method and test results.

(1) Preparation of hydrogen absorbing alloy powders

Mm (a mixture of rare-earth elements), Ni, Co, Al and Mn (elemental metal with a purity of 99.9%) were mixed together in the mole ratio of 1.0:3.1:1.0:0.3:0.6, and the mixture was melted in an arc melting furnace having an argon atmosphere and thereafter allowed to cool spontaneously to obtain an ingot of hydrogen absorbing alloy represented by the formula $\text{MmNi}_{3.1}\text{CoAl}_{0.3}\text{Mn}_{0.6}$. The ingot was mechanically pulverized in the air to obtain a hydrogen absorbing alloy powder (untreated alloy powder 1) adjusted to a mean particle size of 80 micrometers.

A hydrogen absorbing alloy powder (untreated alloy powder 2) was also prepared with the same composition and mean particle size by the gas atomizing process.

(2) Preparation of alloy powders by reduction

Untreated alloy powders 1 and 2 were placed into respective heat-resistant pressure-resistant containers of stainless steel and heated at varying temperatures of 50°C to 950 °C after evacuation, hydrogen gas was then introduced into the containers to 1.2 atm, and the powders were held in this state for 30 minutes to obtain alloy powders reduced with high-temperature hydrogen.

(3) Preparation of alloy powers treated with acid

Untreated alloy powders 1 and 2, and the reduced alloy powders were each immersed in a 0.5N hydrochloric

acid solution (room temperature) at a pH of 0.3 for 2 hours, followed by suction filtration, washing with water and drying to obtain acid-treated alloy powders.

(4) Preparation of alloy powders treated with alkali

Untreated alloy powders 1 and 2, and the reduced alloy powders were each immersed in a 30 wt. % aqueous solution of potassium hydroxide (80 °C), which is for use as an electrolyte, for 2 hours, followed by suction filtration and drying to obtain alkali-treated alloy powders.

(5) Preparation of alloy electrodes

A 0.5 g quantity of each of various hydrogen absorbing alloy powders thus prepared was admixed with 0.1 g of PTFE, the mixture was applied to an expanded nickel porous body serving as a conductive substrate, and the body was then pressed at 1200 kgf/cm² for shaping, whereby a hydrogen absorbing alloy electrode was prepared in the form of a disk with a diameter of 20 mm.

(6) Assembly of test cells

The electrodes thus obtained were used as test electrodes (negative electrodes) to assemble test cells like the one shown in FIG. 5.

As illustrated, the test cell has arranged in an insulating closed container 21 of polypropylene a test

electrode 22 which is the hydrogen absorbing alloy electrode to be tested, a sintered nickel electrode 23 in the form of a hollow cylinder and having a sufficiently greater electrochemical capacity than the test electrode 22, and a sintered nickel reference electrode 24 in the form of a plate. The nickel electrode 23 is supported by the lower end of a positive electrode lead 26 connected to the top wall 25 of the closed container 21. The test electrode 22 is vertically supported by the lower end of a negative electrode lead 27 connected to the top wall 25 of the container 21, and is accommodated inside the nickel electrode 23 centrally thereof.

The positive electrode lead 26 and the negative electrode lead 27 extend through the top wall 25 of the closed container and are exposed to the outside and connected to a positive terminal 28 and a negative terminal 29, respectively. The test electrode 22 and the sintered nickel electrode 23 are held immersed in an alkaline electrolyte (30 wt. % aqueous solution of potassium hydroxide). The closed container 21 is filled with nitrogen gas in a space above the alkaline electrolyte, whereby the test electrode 22 is subjected to a predetermined pressure (5 atm). Connected to the center portion of the top wall 25 of the closed container 21 is a

relief pipe 32 equipped with a pressure gauge 30 and a relief valve 31 for preventing the internal pressure of the container 21 from increasing above a predetermined value.

(7) Assembly of alkaline batteries

Each hydrogen absorbing alloy powder and a 5 wt. % aqueous solution of PEO (polyethylene oxide) were mixed together in the ratio of 100:20 by weight to prepare a paste, which was applied to opposite surfaces of punching metal (conductive substrate) plated with nickel, followed by drying at room temperature and cutting to a predetermined size, to prepare a hydrogen absorbing alloy electrode. A nickel-hydrogen battery (1000 mAh in battery capacity) of AA size and of the type wherein the positive electrode is dominant shown in FIG. 2 was then assembled using the electrode as the negative electrode. A sintered nickel electrode was usable as the positive electrode, an alkali-resistant nonwoven fabric as the separator, and a 30 wt. % aqueous solution of potassium hydroxide as the electrolyte.

(8) Charge-discharge cycle test

At room temperature, each test cell was charged at 50 mA/g for 8 hours, then held at rest for 1 hour, subsequently discharged at 50 mA/g to a final discharge

voltage of 0.9 V and thereafter held at rest for 1 hour. This charge-discharge cycle was repeated, and the discharge capacity (mAh/g) was measured every cycle.

In the case of the alkaline batteries, each battery was charged with current of 0.2 C for 6 hours and thereafter discharged at current of 0.2 C to 1.0 V at room temperature to determine the initial discharge capacity (discharge capacity of the first cycle).

(9) Measurement of electric resistance value

Each hydrogen absorbing alloy powder was checked for electric resistance value under the conditions of mean particle size of 35 micrometers, pressure of 350 kgf/cm², test jig inside diameter of 12 mm and powder weight of 5 g

(10) Test results

Tables II and III show the results of the test.

Table II shows the initial discharge capacity (discharge capacity 1) of each test cell, and the initial discharge capacity (discharge capacity 2) of each alkaline battery. Alloy electrodes A1 to A6 are those prepared from the hydrogen absorbing alloys subjected to the reduction treatment with high-temperature hydrogen at 300°C. Alloy electrodes B1 to B6 are those obtained from the hydrogen absorbing alloys not treated for reduction. Alloy electrodes A1 to A6 which are treated for reduction

are 285 mAh/g to 299 mAh/g in discharge capacity 1 and 820 mAh to 865 mAh in discharge capacity 2, whereas alloy electrodes B1 to B6 which are not treated for reduction are 170 mAh/g to 246 mAh/g in discharge capacity 1 and 580 mAh to 675 mAh in discharge capacity 2. Thus, the alloy electrodes are greater in both discharge capacities and more highly activated initially when treated for reduction than otherwise.

Alloy electrodes A1 to A6 treated for reduction include those acid-treated or alkali-treated after the reduction treatment, and those treated neither with acid nor with alkali after the reduction. Acid-treated alloy electrodes A2 and A5 are 295 mAh/g and 299 mAh/g, respectively, in discharge capacity 1, and 860 mAh and 865 mAh, respectively, in discharge capacity 2. Alkali-treated alloy electrodes A3 and A6 are 290 mAh/g and 296 mAh/g, respectively, in discharge capacity 1, and are both 855 mAh in discharge capacity 2. On the other hand, untreated alloy electrodes A1 and A4 are 285 mAh/g and 292 mAh/g, respectively, in discharge capacity 1, and 820 mAh and 840 mAh, respectively, in discharge capacity 2. Thus, the acid-treated or alkali-treated alloy electrodes are greater in both discharge capacities 1 and 2.

Accordingly, although the reduction treatment with

high-temperature hydrogen, even when singly conducted, results in great discharge capacities as described above, further enhanced effects are available when the acid treatment or alkali treatment, preferably acid treatment, is carried out after the reduction treatment.

Table II reveals that the alloy electrode of the invention (A2 or A3) subjected to the reduction treatment and the acid treatment is given higher activity than the conventional alloy electrode (B2 or B3) which is subjected to the acid treatment only.

Alloy electrodes A1 to A3 and B1 to B3 are prepared from the alloy powder which is obtained by mechanically pulverizing an ingot made by an argon arc furnace, while alloy electrodes A4 to A6 and B4 to B6 are prepared from the alloy powder obtained by the gas atomizing process. These two groups of electrodes will be compared in discharge capacities 1 and 2, as divided in two cases depending on whether the alloy is treated for reduction with high-temperature hydrogen or otherwise. In the case where no reduction treatment is conducted, alloy electrodes B1 to B3 are 222 mAh/g to 246 mAh/g in discharge capacity 1 and 620 mAh to 675 mAh in discharge capacity 2, while alloy electrodes B4 to B6 are 170 mAh/g to 221 mAh/g in discharge capacity 1 and 580 mAh to 620

mAh in discharge capacity 2. Thus, alloy electrodes B1 to B3 prepared with use of the argon arc furnace are greater in both discharge capacities 1 and 2.

In the case where the reduction treatment is conducted, on the other hand, alloy electrodes A1 to A3 are 285 mAh/g to 295 mAh/g in discharge capacity 1 and 820 mAh to 860 mAh in discharge capacity 2, while alloy electrodes A4 to A6 are 292 mAh/g to 299 mAh/g in discharge capacity 1 and 840 mAh to 865 mAh in discharge capacity 2. Thus, alloy electrodes A4 to A6 prepared by the gas atomizing process are greater in both discharge capacities 1 and 2.

Accordingly, it is advantageous to prepare the alloy powder by the gas atomizing process in respect of the initial activity in the case where the reduction treatment is conducted with high-temperature hydrogen.

Furthermore, alloy electrodes A1 to A6 treated for reduction are lower than alloy electrodes B1 to B6 not treated for reduction in the resistance value of the powder as measured under the conditions of particle size of 35 micrometers, pressure of 350 kgf/cm², measuring jig inside diameter of 12 mm and powder weight of 5 g. This substantiates that the alloy particles are formed in their surface layer portions with a metal-rich layer having

higher nickel and cobalt contents than in the alloy electrode not treated for reduction with high-temperature hydrogen.

Table III shows the results obtained by measuring discharge capacities 1 and 2 of alloy electrodes which were prepared from the alloy powder made with use of an argon arc furnace and the alloy powder obtained by the gas atomizing process after subjecting the powders to the reduction treatment with high-temperature hydrogen at varying temperatures of 50°C to 950°C.

The alloy electrodes prepared with use of the argon arc furnace are as great as at least 284 mAh/g in discharge capacity 1 and at least 820 mAh in discharge capacity 2 when the temperature for the reduction treatment is in the range of 100°C to 900°C.

The alloy electrodes prepared by the gas atomizing process are as great as at least 288 mAh/g in discharge capacity 1 and at least 835 mAh in discharge capacity 2 when the temperature for the reduction treatment is in the range of 100°C to 900°C.

For the alloys thus used for testing, it is suitable that the temperature for the reduction treatment be in the range of 100°C to 900°C under the conditions of pressure of 1.2 atm and time period of 30 minutes regardless of

whether the argon arc furnace or the gas atomizing process is used. If the reduction treatment temperature is at least 100 °C , the equilibrium hydrogen pressure of the hydrogen absorbing alloy rises to suppress the absorption of hydrogen by the alloy.

INDUSTRIAL APPLICABILITY

The hydrogen absorbing alloy power embodying the invention is suitable as a material for electrodes of metallic oxide-hydrogen batteries, for example, as a material for the negative electrodes of nickel-hydrogen batteries.

CLAIMS

1. A hydrogen absorbing alloy powder containing nickel and cobalt, the alloy powder comprising:

alloy particles; and

a metal-rich layer formed by enriching a surface layer portion of said alloy particles in metals by a reduction treatment with hydrogen, the metal-rich layer being surface-treated with an acid or alkaline treating liquid.

2. A hydrogen absorbing alloy powder according to claim 1 wherein the acid treating liquid is a hydrochloric acid solution.

3. A hydrogen absorbing alloy powder according to claim 1 wherein the alkaline treating liquid is at least one aqueous solution selected from among an aqueous solution of KOH, aqueous solution of NaOH and aqueous solution of LiOH.

4. A process for producing a hydrogen absorbing alloy powder characterized in that a starting hydrogen absorbing alloy powder containing nickel and cobalt and comprised of particles is held in a high-temperature hydrogen atmosphere under the conditions of temperature, pressure and time sufficient to reduce oxides formed in a surface layer portion of each of the alloy particles, maintaining the alloy particles below a melting point of the

particles, preventing the alloy particles from absorbing hydrogen, and thereafter surface-treated with an acid or alkaline treating liquid; and

wherein the temperature is in the range of about 100°C to 900°C;

wherein the pressure is in the range of 1 atm to 3 atm;

wherein the time is in the range of 30 minutes to 10 hours.

5. A process for producing a hydrogen absorbing alloy powder according to claim 4 wherein the starting hydrogen absorbing alloy powder is prepared by the gas atomizing process.

6. A process for producing a hydrogen absorbing alloy powder according to claims 4 and 5 wherein the acid treating liquid is a hydrochloric acid solution.

7. A process for producing a hydrogen absorbing alloy powder according to any one of claims 4 to 6 wherein the alkaline treating liquid is at least one aqueous solution selected from among an aqueous solution of KOH, aqueous solution of NaOH and aqueous solution of LiOH.

8. A hydrogen absorbing alloy electrode comprising an electrically conductive substrate having applied thereto a hydrogen absorbing alloy powder, the electrode being characterized in that the hydrogen absorbing alloy powder

contains nickel and cobalt, the alloy particles (1) being formed each in a surface layer portion thereof with a metal-rich layer (3) enriched in metals by a reduction treatment with hydrogen, the metal-rich layer (3) being surface-treated with an acid or alkaline treating liquid.

9. A hydrogen absorbing alloy electrode according to claim 8 wherein the acid treating liquid is a hydrochloric acid solution.

10. A hydrogen absorbing alloy electrode according to claim 8 wherein the alkaline treating liquid is at least one aqueous solution selected from among an aqueous solution of KOH, aqueous solution of NaOH and aqueous solution of LiOH.

11. A metallic oxide-hydrogen battery wherein a hydrogen absorbing alloy electrode is used which comprises an electrically conductive substrate having applied thereto a hydrogen absorbing alloy powder, the metallic oxide-hydrogen battery being characterized in that the hydrogen absorbing alloy powder contains nickel and cobalt, the alloy particles (1) being formed each in a surface layer portion thereof with a metal-rich layer (3) enriched in metals by a reduction treatment with hydrogen, the metal-rich layer (3) being surface-treated with an acid or alkaline treating liquid.

12. A metallic oxide-hydrogen battery according to claim 11 wherein the acid treating liquid is a hydrochloric acid solution.

13. A metallic oxide-hydrogen battery according to claim 11 wherein the alkaline treating liquid is at least one aqueous solution selected from among an aqueous solution of KOH, aqueous solution of NaOH and aqueous solution of LiOH.

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FIG. 1

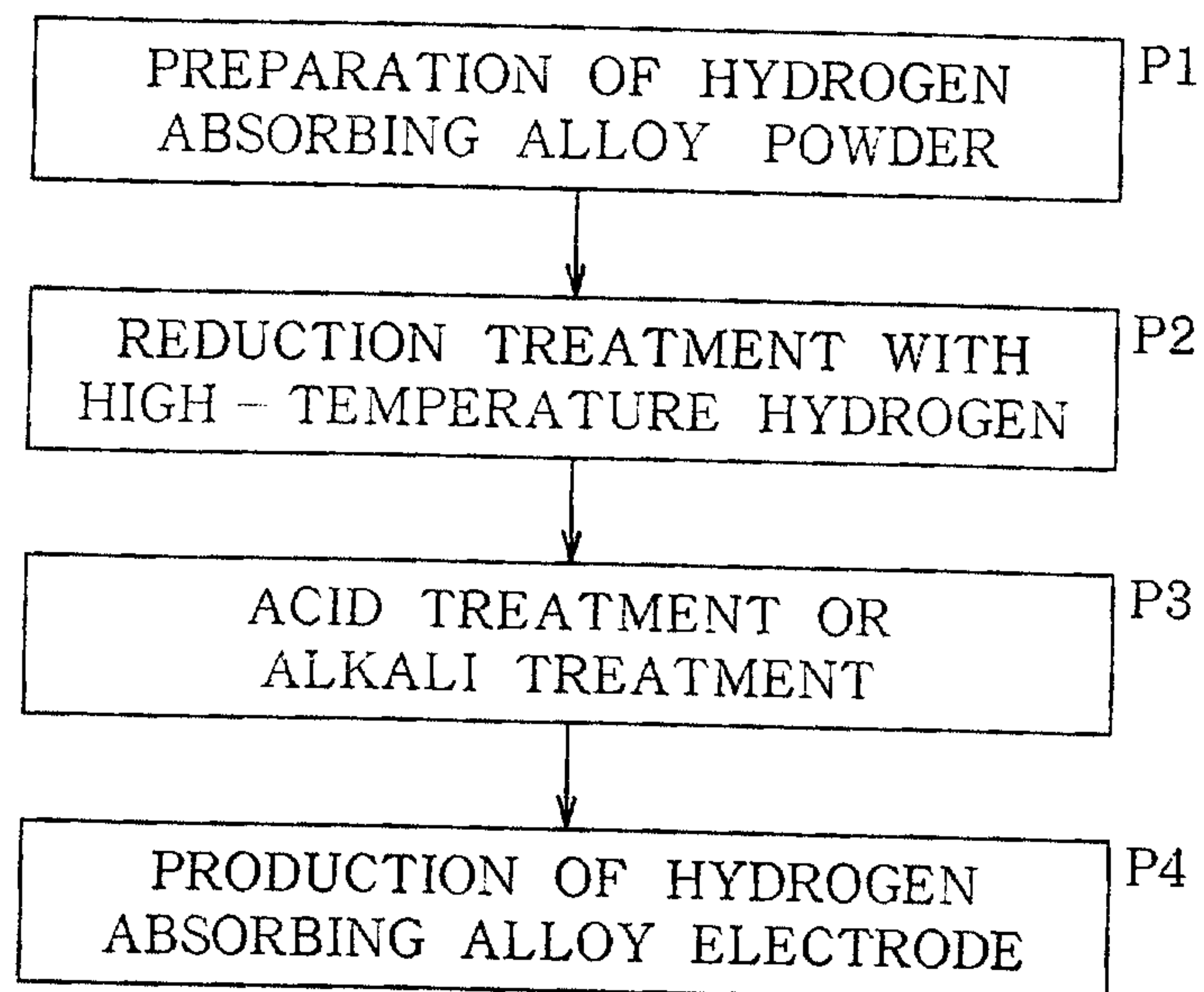
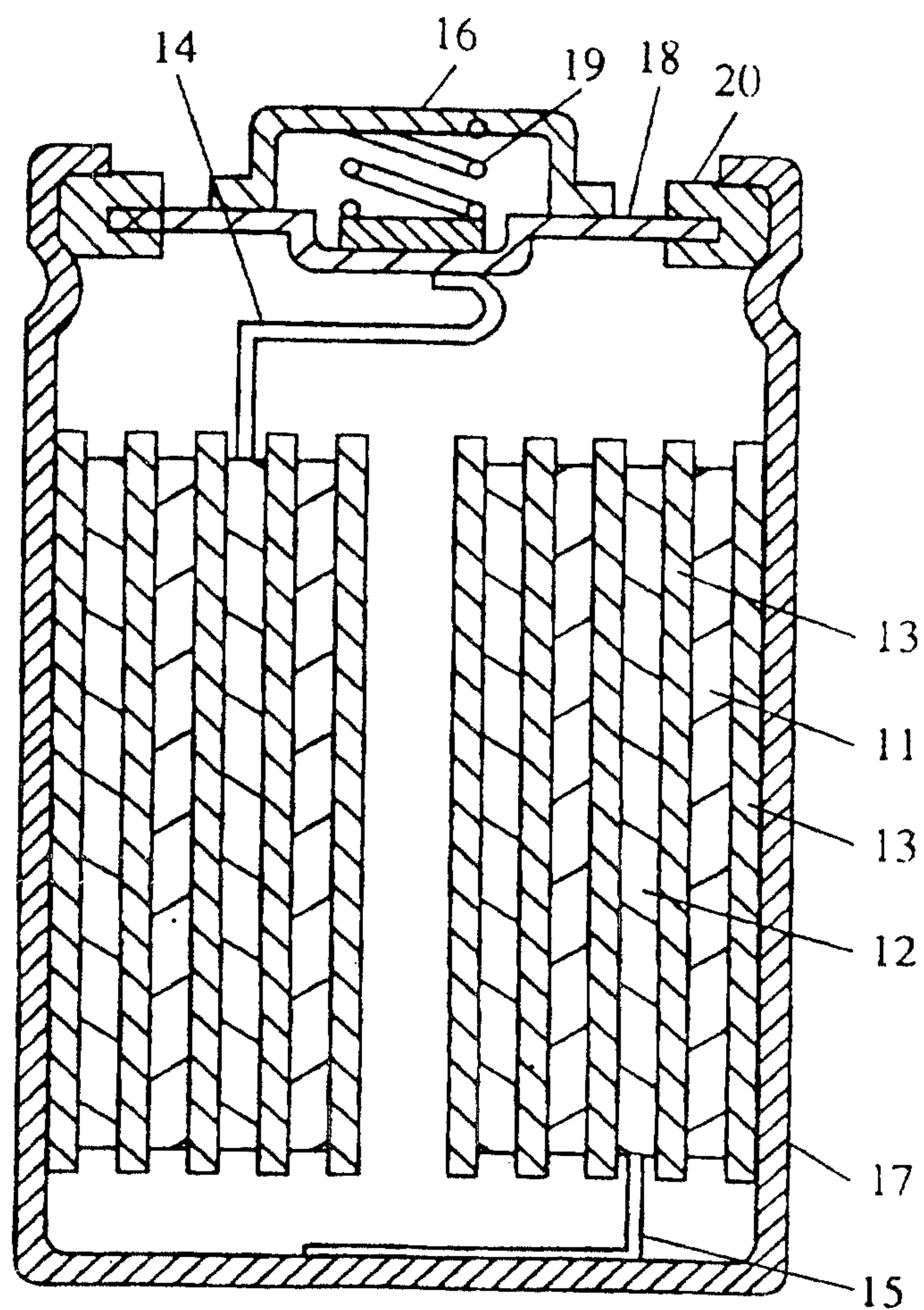
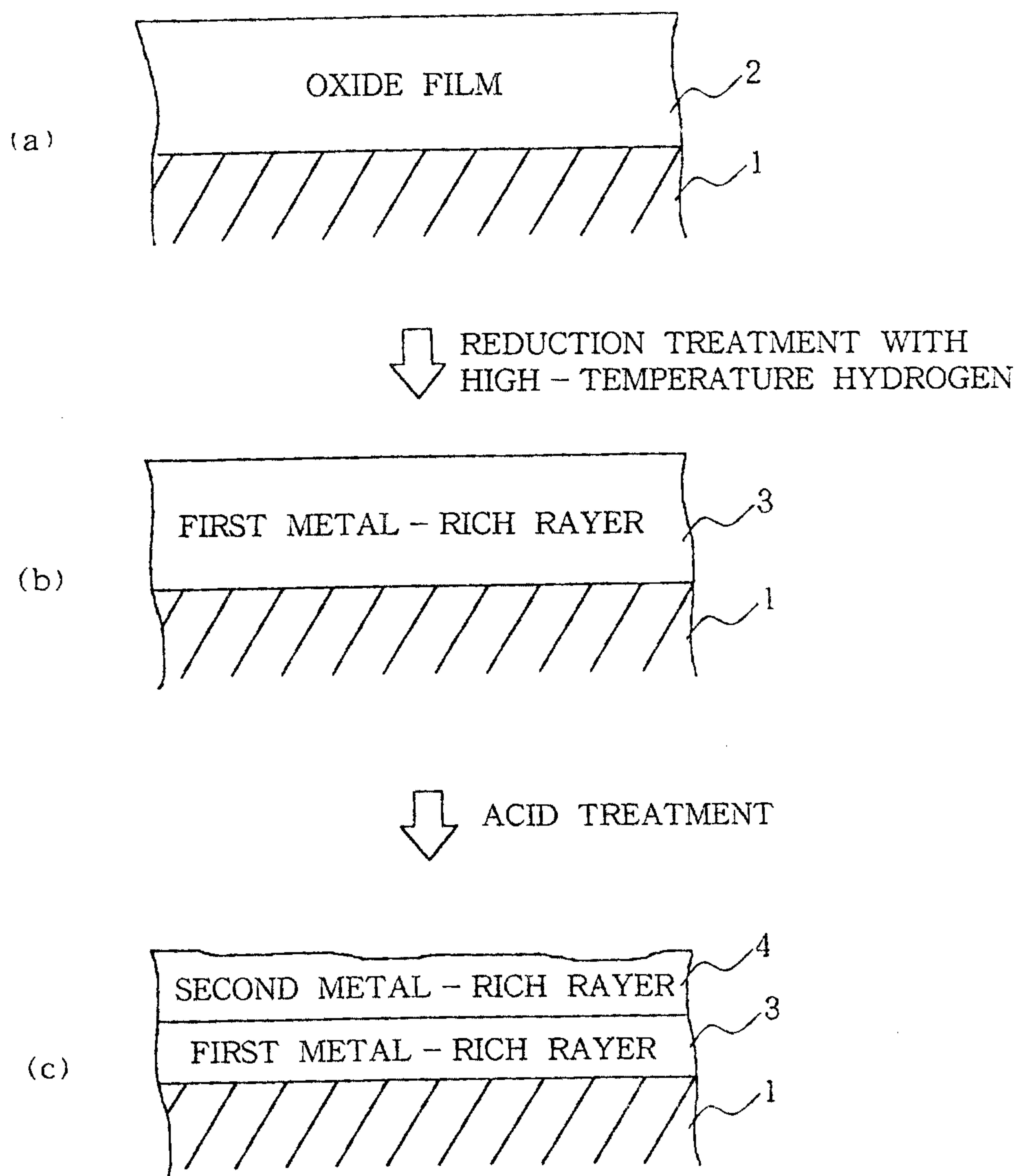


FIG. 2



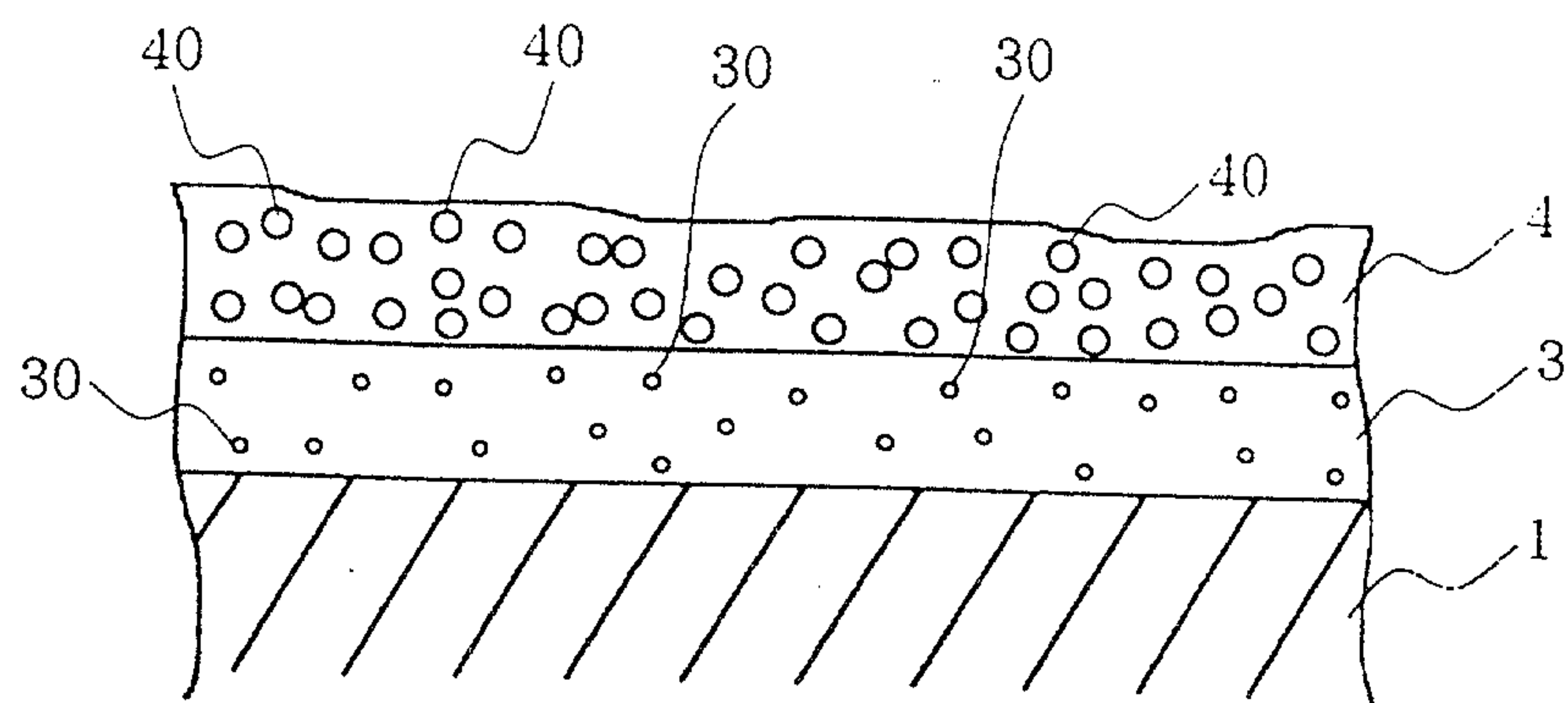
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FIG. 3



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FIG. 4



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FIG. 5

