

SPECIFICATION

NI PLATED STEEL SHEET FOR POSITIVE ELECTRODE CAN OF
ALKALINE MANGANESE BATTERY AND POSITIVE ELECTRODE CAN OF
5 ALKALINE MANGANESE BATTERY

Field of the Invention

The present invention relates to a plated steel
sheet material used for a positive electrode can for an
10 alkaline manganese battery and, more particularly, to a
plated steel sheet material and a positive electrode can
for an alkaline manganese battery capable of improving
the battery characteristics and the corrosion resistance
of an alkaline manganese battery.

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Background of the Invention

In an alkaline manganese battery, a Ni-plated steel
sheet is generally used as the material for a container
(positive electrode can) which is used for filling a
20 positive electrode material, a negative electrode
material, an electrolyte solution, etc., and which is
also used as a positive electrode terminal.
Conventionally, Ni plating has been performed by so-
called barrel plating method in which plating is
25 performed after the can has been formed. As this method
has problems such as insufficient adherence of the Ni
plating layer to the internal surface of the can, or
instability in the quality of the plating layer, it is
being replaced by a method in which a pre-plated steel
30 sheet is processed into the form of a can. However, this
method using a pre-plated steel sheet has also a problem
in that, as the Ni plating layer has high hardness and
low extensibility, the pre-plated steel sheet has poor
press workability and the plating layer tends to be
35 separated during the processing, leading to deterioration
in corrosion resistance. In order to resolve this
problem, a method is known in which heat treatment is

performed after Ni plating to form a Fe-Ni diffusion layer in the interface between the Ni plating layer and the iron substrate so as to improve the close adherence of the Ni plating layer as well as to improve the
5 extensibility of the Ni plating layer by recrystallization and softening of Ni. This has led to a significant improvement of the press workability and corrosion resistance.

10 In order to attain high capacity in an alkaline manganese battery, it is required to increase the content of manganese dioxide in the positive mix. However, this leads to an increase in contact resistance due to the low electrical conductivity of manganese dioxide itself. As
15 a countermeasure, a conductive film is formed on the internal surface of the positive electrode can. With such an alkaline manganese battery, although the contact resistance is initially low, the contact resistance increases rapidly after prolonged storage at high
20 temperature, leading to degradation of the battery characteristics.

Examples of improvements in the above-mentioned battery characteristics, from the side of the steel sheet material and in prior art, are found in the following patent publications. In Japanese Unexamined Patent
25 Publication (Kokai) No. 05-21044, for example, it is disclosed that, as material for DI drawing and ironing, hard plating such as would produce cracks in Ni plating layer during the processing is effective in causing the surface area in contact with the positive electrode
30 material to be increased by the cracks produced during the processing and permitting the battery characteristics to be thereby improved. Various examples of hard plating are shown such as Ni plating containing organic
35 additives, the aforementioned plating applied via a Fe-Ni diffusion layer, and the like, are mentioned. In Japanese Unexamined Patent Publication (Kokai) Nos. 07-122246 and 07-300695, WO 95/11527, or the like, a method

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for ensuring sufficient contact with the positive electrode material by forming a very hard alloy (such as Ni_3Sn , Ni_3Sn_2 , Ni_3Sn_4 , etc) plating layer on the top layer corresponding to the inner surface of a positive

5 electrode can and producing cracks in the plating layer during press working, is disclosed. Also in Japanese Unexamined Patent Publication (Kokai) No. 08-138636, a method for increasing the surface area in contact with the positive electrode material and thereby improving the

10 battery characteristics is disclosed in which Sn and Ni are plated as dual plating layer, in this order, onto a steel sheet and disposing the plating layer converted into an alloy layer by heat treatment so as to serve as an internal surface of the positive electrode can so that

15 surface cracks are produced during press working due to the difference of extensibility between the upper layer being composed mainly of Ni and the lower layer being composed mainly of Sn. In Japanese Unexamined Patent Publication (Kokai) No. 09-306439, a method is disclosed

20 in which an Ni alloy plating layer having different hardnesses within the plating layer is formed such that the plating layer to be used for the internal surface of a can has higher hardness, for increasing the surface roughness of the internal surface of a can during press

25 working so as to improve the close adherence to the positive electrode material. As an exemplary method for varying the hardness in an alloy plating layer, varying the type or the amount of the metal to be alloyed with Ni or varying the amount of an organic additive, is

30 disclosed. Also, in Japanese Unexamined Patent Publication (Kokai) Nos. 10-172521 and 10-172522, a method is disclosed in which a Ni-Co alloy plating layer is formed, or Ni-Co alloy plating is applied via a Ni plating layer. As the Ni-Co alloy is very hard, very

35 fine cracks are produced in the plating layer during the press working and a very fine roughness is thereby formed so as to improve the contact with the positive electrode

material, to thereby improve the battery performance. In Japanese Unexamined Patent Publication (Kokai) No. 11-102671, a method is disclosed in which Ni-Ag alloy plating or Ni-Cr alloy plating is applied via a Ni plating layer onto the surface to be used as the internal surface of a positive electrode can. Since both the Ni-Ag alloy plating layer and the Ni-Cr alloy plating layer are very hard, very fine cracks are produced in the plating layer during press working and a very fine roughness is thereby formed so as to improve the contact with the positive electrode material, to thereby improve the battery performance. Also in Japanese Unexamined Patent Publication (Kokai) Nos. 11-329377 and 11-329378, a method is disclosed to utilize a Ni-Bi alloy plating layer and a Ni-In alloy plating layer, respectively, to improve the alkali resistance of the aforementioned Ni-Sn alloy plating layer having low alkali resistance, to thereby improve the battery performance.

The various methods in prior art as described above all aim to form a very fine roughness on the internal surface of a can during press working, and to this end, a steel sheet having a hard plating layer formed thereon is mainly used to produce fine cracks in the plating layer during press working. However, there is a problem associated with the concept of producing cracks in the plating layer during press working that production of cracks in the plating layer varies depending upon the variation of the condition of the press working, and therefore, stable battery characteristics cannot be obtained.

In order to overcome the above-described problem, a method is disclosed in WO 97/44835 for increasing the close adherence to the positive electrode material by applying an electrolytic treatment in acidic solution after Ni plating and thereby roughening the surface. Also in Japanese Unexamined Patent Publication (Kokai) No. 2000-192281, a method is disclosed in which, after

discontinuously forming Ni plated layers, etching is performed in an acidic solution and, further, a Ni plating layer is formed to obtain a surface having many small pits formed thereon. However, these methods
5 require equipment for treatment in an acidic solution, and are therefore undesirable in terms of cost.

It is an object of the present invention to overcome the above-described problems and to provide a plated steel plate material to be used as a positive electrode
10 can for an alkaline manganese battery and a positive electrode can for an alkaline manganese battery having good battery characteristics.

Disclosure of the Invention

15 The present invention can be summarized as follows:

(1) A Ni plated steel sheet to be used for a positive electrode can for an alkaline manganese battery, characterized in that a Ni-based diffusion plating layer having pinholes, as observed by SEM, of diameter in the
20 range of $0.1 \sim 1 \mu\text{m}$ and at density of not less than 30 pcs/ $(10 \mu\text{m} \times 10 \mu\text{m})$ on its surface is formed on the surface of the steel sheet to be used as an internal surface of the can.

(2) A Ni plated steel sheet to be used for a
25 positive electrode can for an alkaline manganese battery according to (1), characterized in that a Fe-Ni diffusion plating layer and a Ni plating layer are formed on the surface of said steel sheet to be used as an external surface of can.

30 (3) A Ni plated steel sheet to be used for a positive electrode can for an alkaline manganese battery according to (2), characterized in that the Ni plating layer, on the surface of said steel sheet to be used as an external surface of the can, has been softened by
35 recrystallization.

(4) A positive electrode can for an alkaline

manganese battery, characterized in that the positive electrode can is composed of a steel sheet which has, on the surface to be used as an internal surface of the can, a Ni-based diffusion plating layer formed with pinholes, as observed by SEM, of diameter in the range of 0.1 ~ 1 μm and at density of not less than 30 pcs/(10 μm $\times$ 10 μm) on the surface.

(5) A positive electrode can for an alkaline manganese battery according to (4), characterized in that the said positive electrode can for the battery is composed of a steel sheet, having a Fe-Ni diffusion plating layer and a Ni plating layer formed on the surface, to be used as an external surface of the can.

(6) A positive electrode can for an alkaline manganese battery according to (5), characterized in that the Ni plating layer on the surface to be used as an external surface of said positive electrode can for the battery has been softened by recrystallization.

Brief Description of the Drawings

Fig. 1 is a SEM photograph ($\times 1000$) showing a surface of a Ni plated steel sheet having many sub-micron sized pinholes according to the present invention;

Fig. 2 is a SEM photograph ($\times 5000$) showing a surface of a Ni plated steel sheet having many sub-micron sized pinholes according to the present invention; and

Fig. 3 is a SEM photograph ($\times 5000$) showing a surface of a Ni plated steel sheet according to a prior

art.

Best Embodiments for Implementing the Invention

5 First, constructive requirements of the surface of a steel sheet corresponding to the internal surface of a positive electrode can for an alkaline manganese battery in accordance with the present invention will be described. A Ni based diffusion plating layer is formed on the surface to be used as an internal surface of the can, and it is required the surface of the plating layer have many pinholes of diameter not greater than 1 μm (hereinafter referred to as sub-micron pinholes). Examples of SEM (Scanning Electron Microscope) photograph of the steel sheet surface having a plating layer containing submicron pinholes are shown in Figs. 1 and 2. Magnification is $\times 1000$ in Fig. 1, and $\times 5000$ in Fig. 2. It will be seen that the pinholes can be hardly discerned in magnification of $\times 1000$ (Fig. 1), but that many pinholes of diameter not greater than 1 μm can be observed as dark shadows at a magnification of $\times 5000$ (Fig. 2). Small pits formed in accordance with the conventional method as disclosed in Japanese Unexamined Patent Publication (Kokai) No. 2000-192281 are of larger diameter of about 10 μm , and are present at density of less than about 1 pcs/(10 $\mu\text{m} \times 10 \mu\text{m}$), and therefore are clearly distinct from the submicron pinholes in accordance with the present invention. For comparison, a typical surface condition of Ni plated steel sheet for a positive electrode can in prior art which has much fewer sub-micron pinholes and which has inferior battery performance is shown in Fig. 3 (magnification, $\times 5000$).

Although the reason has not been clarified in detail, it is surmised that, by providing the surface of the Ni based diffusion plating layer with many minute pinholes of diameter not greater than 1 μm , a certain

close chemical adherence is produced between the Ni based diffusion plating layer on the internal surface of the formed positive electrode can and a conductive coating applied on the internal surface of the formed positive electrode can, leading to improvement of battery characteristics. The Ni based diffusion plating layer is also effective in ensuring adequate primary rust-preventing capability, after being formed into a can, and corrosion resistance in strongly alkaline electrolyte solution.

A Ni based diffusion plating layer refers to a layer in which Ni based plating such as Ni plating(bright, semi-bright, dull), Ni-Co alloy plating, Ni-Fe alloy plating is applied, followed by heat treatment to convert a part or all of the Ni based plating layer into a diffusion layer. It is surmised that, if strain has been introduced into the plating layer during plating process, many sub-micron pinholes are formed when diffusion takes place in the heat treatment process. Specific methods for introducing strain include, for example, plating applied at high current density within the range that does not give rise to a burnt deposit, plating applied at extremely low plating efficiency (for example, using plating bath free of boric acid), and the like. It is desirable in order to obtain good battery performance that sub-micron pinholes have, as observed by SEM, diameter of $0.1 \sim 1 \mu\text{m}$, and are present at density of 30 pcs/($10 \mu\text{m} \times 10 \mu\text{m}$). Pinholes having diameter of $0.1 \mu\text{m}$ can be distinctly recognized in an image of SEM at magnification of $\times 5000$.

Next, constructive requirements of the surface corresponding to an external surface of a positive electrode can will be described below. As the influence of an external surface of a positive electrode can is negligibly small as regards improvement of the battery characteristics which is the object of the present

invention, the following requirements are not particularly crucial as long as only the battery characteristics are concerned. However, since more stringent and higher corrosion resistance is typically required for an external surface of a positive electrode can, composition of plating layer that meets this requirement will be described below. It is desirable that the surface to be used as an external surface have a Fe-Ni diffusion plating layer with a Ni plating layer on top of it. This permits good corrosion resistance to be obtained for the terminal portion of the positive electrode which is subjected to particularly severe processing. More preferably, in view of corrosion resistance, the above-mentioned Ni plating layer is softened by recrystallization. The above-mentioned plating layer having composite structure may be formed, for example, by adopting a method in which an Fe-Ni diffusion layer is formed in a portion of a Ni plating layer by heat treatment after Ni plating, such that Ni is left as it is in the uppermost layer.

As the steel sheet material for the Ni plated steel sheet for a positive electrode can for an alkaline manganese battery of the present invention, ultra-low carbon steel with Ti and Nb added alone or in combination, low carbon Al killed steel, B added low carbon steel, or the like, may be preferably used.

The Ni plated steel sheet for a positive electrode can for an alkaline manganese battery of the present invention can be manufactured by degreasing and acid pickling of steel sheets followed by Ni plating applied to the steel sheets in a Ni plating bath with current density adjusted to obtain a plating layer of desired thickness, and by subjecting the steel sheet after plating process to heat treatment in an oxygen-free atmosphere at about 800°C. In Ni plating, it is desirable to use a plating bath of low plating efficiency or to use high current density, within the range that

does not give rise to a burnt deposit, in order to introduce strain into the plating layer. Preferably, temper rolling is performed after the heat treatment, as required.

5 By above-mentioned heat treatment, a Ni diffusion layer is formed between the steel sheet and the plating layer, and at the same time, sub-micron pinholes are formed in the Ni plating layer and/or Ni diffusion layer.

10 Using presses such as a DI press or a transfer press, a positive electrode can for an alkaline manganese battery of the present invention can be obtained from the Ni plated steel sheet thus obtained by a shaping and forming process.

15 Examples

 Samples in Examples were fabricated starting from an unannealed Nb-Ti-Sul. C (Ti and Nb containing super low carbon) steel sheet of 0.3 mm in sheet thickness as a sheet material, and after degreasing and acid pickling, Ni based plating was applied under varied plating condition in 2 passes of down-pass and up-pass in a vertical plating cell, followed by heat treatment in an oxygen free atmosphere under varied heat treatment conditions, and then by temper rolling, to obtain samples used in Examples.

 Plating conditions such as type of plating bath, current density, plated amount of Ni plating, etc., and conditions for the heat treatment after plating are as shown in Table 1. For comparison, samples for Comparative examples were fabricated in a method similar that in the Examples. Plating conditions such as type of plating bath, current density, plated amount, etc., and conditions for the heat treatment after plating are as shown in Table 1. Each of the samples was evaluated in observation of surface condition, evaluation of the battery performance, evaluation of corrosion resistance of the can internal surface, and evaluation corrosion

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resistance of the can external surface, using methods as described below.

Table 1 Conditions for Ni plating and for heat treatment

Classification	No.	Steel sheet		Ni plating condition			Heat treatment condition
		Material	Thickness (mm)	Plating bath	Current density (A/dm ²)	Ni plated amount (g/ m ²) Internal surface External surface	
Example	1	Nb-Ti-Sul.C	0.3	Dull Watt bath ⁽¹⁾	75	12	800°C x 20 sec
	2					4	
	3			Boric acid free bath ⁽²⁾	10	27	790°C x 40 sec
Comparative example	1	Nb-Ti-Sul.C	0.3	Dull Watt bath ⁽¹⁾	10	18	800°C x 20 sec
						18	
						18	780°C x 20 sec

⁽¹⁾ Dull Watt bath: Ni sulfate: 340 g/l: Ni chloride: 70 g/l: boric acid: 45 g/l

⁽²⁾ Boric acid free bath: Ni sulfate: 200 g/l: sulfuric acid: 10 g/l

(Observation of surface condition)

The surface corresponding to the can internal surface was observed using SEM (accelerating voltage 15 KV, magnification $\times 5000$). Number of pinholes of $0.1 \sim 1$ μm in diameter was counted, and was reported as number per $10 \mu\text{m} \times 10 \mu\text{m}$.

(Method for evaluating battery performance)

A positive electrode can formed from the above-mentioned steel sheet samples by press working was used to fabricate an ordinary LR6 type alkaline manganese battery, and the fabricated battery was stored for 40 days at 60°C and 70% RH. Internal resistance was measured with an AC resistance meter. An internal resistance of $120 \text{ m}\Omega$ or less was evaluated as $\odot$, $121 \sim 150 \text{ m}\Omega$ as $\bigcirc$, $151 \sim 200 \text{ m}\Omega$ as $\triangle$, and $201 \text{ m}\Omega \sim$ as $\times$.

(Method for evaluating corrosion resistance of the can internal surface)

A positive electrode can formed from the above-mentioned steel sheet samples by press working was degreased, and after the end surface was sealed with wax, was allowed to be left in an atmosphere at 60°C and 90% RH for 3 days. Thereafter, the internal surface was inspected carefully using a loupe ($\times 10$) to check for the occurrence of rust. No rust was evaluated as " $\bigcirc$ ", and occurrence of rust was evaluated as " $\times$ ".

(Method for evaluating corrosion resistance of the can external surface)

Corrosion resistance: A positive electrode can formed from the above-mentioned steel sheet samples by press working was degreased, and after the end surface was sealed with wax, was placed in a salt spray tester (in accordance with JIS - Z - 2371) with the external

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surface of the positive electrode terminal facing upwards. After testing for 3 hours, the positive electrode can was removed from the tester, and after being washed with water and dried, was inspected for the presence or absence of red rust. No rust was evaluated as "○", and occurrence of rust was evaluated as "X".

The result is shown in Table 2. As is evident from Table 2, good characteristics were obtained with the Examples of the present invention.

Table 2 Result of performance evaluation

	Condition of surface to be used as can internal surface		Battery performance	Corrosion resistance of internal surface	Corrosion resistance of external surface
	Condition of surface	Number of Submicron pinholes (pcs/10 μ m $\times$ 10 μ m)			
Example	1 As Fig. 2	120	⊙	○	○
	2 As Fig. 2	170	⊙	○	○
	3 As Fig. 2	60	⊙	○	○
Comparative example	1 As Fig. 3	10	X	○	○

Industrial Applicability

The present invention provides a plated steel sheet used for a positive electrode can for an alkaline manganese battery and a positive electrode can for an alkaline manganese battery wherein, by forming a Ni-based diffusion plating layer on the surface to be used as an internal surface of the can, such that many sub-micron pinholes are formed on the surface, good battery characteristics can be obtained and, while eliminating the problems associated with the prior art battery, an increase in contact resistance can be prevented even after being stored at high temperature for a long period.

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CLAIMS

What is claimed is:

1. (deleted)

2. (after amendment) A Ni plated steel sheet to
5 be used for a positive electrode can for an alkaline
manganese battery, characterized in that, on the surface
of the steel sheet to be used as an internal surface of
the can, a Ni based diffusion plating layer is formed
with pinholes, as observed by SEM, of diameter in the
10 range of 0.1 ~ 1 μm and at density not less than 30
pcs/(10 μm $\times$ 10 μm) on the surface.

3. (after amendment) A Ni plated steel sheet to
be used for a positive electrode can for an alkaline
manganese battery according to claim 2, wherein a Fe-Ni
15 diffusion plating layer and a Ni plating layer are formed
on the surface of said steel sheet to be used as an
external surface of the can.

4. (after amendment) A Ni plated steel sheet to
be used for a positive electrode can for an alkaline
20 manganese battery according to claim 3, wherein the Ni
plating layer on the surface of said steel sheet to be
used as an external surface of the can has been softened
by recrystallization.

5. (deleted)

25 6. (after amendment) A positive electrode can for
an alkaline manganese battery, characterized in that the
positive electrode can is composed of a steel sheet which
has, on the surface of the steel sheet to be used as an
internal surface of the can, a Ni based diffusion plating
30 layer having on its surface pinholes, as observed by SEM,
of diameter in the range of 0.1 ~ 1 μm and at density not
less than 30 pcs/(10 μm $\times$ 10 μm) formed.

7. (after amendment) A positive electrode can for
an alkaline manganese battery according to claim 6,
35 wherein said positive electrode can of a battery is
composed of a steel sheet having a Fe-Ni diffusion

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plating layer and a Ni plating layer formed on the surface to be used as an external surface of the can.

- 5 8. A positive electrode can for an alkaline manganese battery according to claim 7, wherein the Ni plating layer on the surface to be used as an external surface of the can has been softened by recrystallization.