Novel Plating Technology for Metallic Foam

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The nickel foam "CELMET" has such characteristics as the over 98% porosity, large relative surface area and ease of processing, and is widely used for the cathode current collector of Ni-MH batteries, mainly applied for hybrid electric vehicles. CELMET is produced by the following methods: the conductive treatment of urethane, nickel electroplating, and burning away of urethane under reducing atmosphere. From the increasing awareness of environmental issues in recent years, the low emission process of conducting treatment is strongly demanded. We have studied some electroless plating methods for the conducting treatment of urethane foam. The conventional method using hypophosphite as a reducing agent was well known that phosphorus was co-deposited into nickel film derived from a reducing agent. Also there was a problem of waste from plating solution. To this end, we propose the titanium redox process as a pure nickel electroless plating method of zero-emission. In this process, Ti(IV) formed during electroless nickel plating is electrolytically reduced to Ti(III), which is simultaneously recycled as a reductant of plating solution by using a regeneration system. Furthermore, the charge-discharge test of the obtained CELMET cathode using Ni-MH batteries showed that the cycle life of the Ni-MH battery obtained from this process was far longer than that from the nickel electroless plating method using sodium hypophosphite.

Keywords: metallic foams, porous metals, nickel electroless plating, electrodeposition, titanium redox

1. Introduction

With the recent increasing awareness of global environmental issues, ecologically friendly products are needed in various fields, and the demand for rechargeable batteries has been growing rapidly. In the automotive field, in which exhaust fumes and fuels are inextricably linked with environment, actions to tackle environmental issues are very important. Car manufacturers focus on the development of electric and hybrid electric vehicles and fuel-cell automobiles, and hybrid electric vehicles have become commercially available, now comprising part of the market.

Nickel-metal-hydride (Ni-MH) and lithium ion batteries and capacitors or combinations of these are candidate power sources of hybrid electric vehicles. Safety assurance and a competitive price are important considerations regarding lithium-ion batteries, and capacity for capacitors. Hybrid electric car models, in markedly increasing demand, are equipped with Ni-MH batteries using nickel hydroxide, a hydrogen-storing alloy, and alkaline solution for the positive and negative electrodes and electrolyte solution, respectively, and a high capacity and safety are characteristics.

For the electrode current collector of Ni-MH batteries, 2-dimensional metal base materials, such as punching metal, are used for the negative electrode, but Ni foam base materials with a 3-dimensional structure are used for the positive electrode because positive-electrode active materials are inferior in terms of electric conductivity. Sintered positive electrodes are adopted in some models.

2. Metallic Foam

2-1 Manufacturing method

Ni foam base materials used widely are prepared by adding the property of electric conductivity to a urethane foam sheet with communicating pore electroless Ni plating followed by electrolytic Ni plating. The sheet is then heated in an oxidative atmosphere and subsequently under a reducing atmosphere, such as decomposed ammonia gas. Urethane is burned and lost in this heating process. Ni is mostly oxidized to nickel oxide by heating under an oxidative atmosphere, but the inner Ni metal layer is retained, which maintains the foam shape, and the material is reduced to Ni through the following heating process under a reducing atmosphere (firing) (**Fig. 1**).
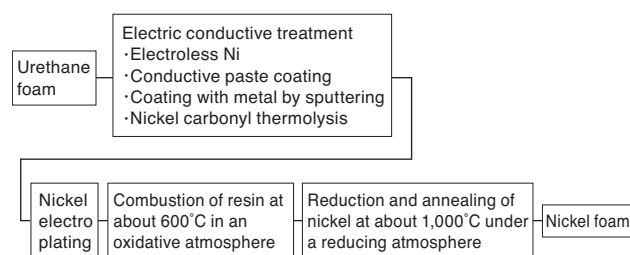

Fig. 1. Manufacturing process of nickel foam base material

To add the property of electric conductivity to urethane resin, an insulator, the following methods are employed on an industrial scale, in addition to electroless Ni plating: 1) In the liquid phase method, natural graphite powder is processed to a paste coating material and applied to the urethane surface. 2) In the gas phase method, urethane is coated with metal by sputtering. 3) In another gas phase method, Ni deposition utilizes the thermolytic reaction of nickel carbonyl. Method 1) tends to involve the thick application of paste on the urethane foam outer

surface, which causes differences in electric conductivity between the inner and outer surfaces, resulting in thin and thick electric Ni plating on the inner and outer surfaces, respectively, and the subsequently produced Ni foam base material does not have sufficient tensile strength. For Ni-MH batteries of which a high capacity is demanded, base materials are required to have a sufficient tensile strength because these are repeatedly pressed using a roll pressing machine when active materials are added. Ni thicknesses also vary in Ni foam base materials prepared using 2), but the formation of homogeneous electrically conductive film is possible when the urethane foam sheet is thin, because sputtered particles essentially travel in a straight line and reach the inner region of the urethane foam. This method does not negatively influence the characteristics of batteries because the film is composed of pure Ni with a high conductivity. It is also advantageous in that no industrial waste is produced by this electric conductivity-adding process. However, from an industrial viewpoint, the manufacturing capacity and capital expenditure are directly proportional, increasing the ratio of equipment costs in the unit price of the product, because sputtering is a high-vacuum process, and this condition presents a difficulty in reducing the price. Regarding 3), the quality of the produced Ni foam is favorable because the deposited layer as an electrically conductive film is composed of pure Ni, and the metal is deposited at a relatively homogeneous thickness even in the inner surface of urethane foam. However, its material, tetracarbonylnickel gas, is very toxic. Micronized Ni formed in the human bronchus is considered to be more toxic than carbon monoxide contained as a ligand, and fatal when it is aspirated. In Japan, the work environment evaluation criteria specifies the tetracarbonylnickel gas level to be 0.001 ppm or lower under the Air Pollution Control Law Enforcement Ordinance, which prevents its production. The gas is produced only in Canada.

Insufficient strength due to variation of the Ni thickness between the inner and outer surfaces described above is less likely to occur in Ni foam base materials processed by electroless Ni plating to add electric conductivity, and the toxicity of the industrial chemicals used is low. However, problems are present, with the major one being the co-deposition of phosphorus (P) and boron (B) in Ni film. For example, the P content of film processed in a hypophosphite plating bath is pH-dependent, and about 7wt% P is mixed in the deposited film as an impurity after processing in a pH 9 alkaline plating bath[1]-[3]. There are many examples of the industrial application of electroless Ni plating, and a high purity is required for usage considering magnetism in some fields. For example, even though the purity is high in Ni plating using hydrazine as a reducing agent, nitrogen is contained at about 2wt%[4]. Moreover, hydrazine is unstable and hazardous even under normal conditions, and caution is necessary when handling it. The formation of intermetallic compounds, such as Ni_3P, and solid solution in Ni is considered to lead to impurities in Ni foam base materials. Such impurity increases the resistance of Ni due to electron scattering, and, when it is used as an electrode, its efficiency may decrease, particularly in rapid charge-discharge. It was clarified that the battery life was shortened when P-containing Ni foam base materials were used, for which a higher purifi-

cation of electroless Ni plating is needed to prolong the Ni-MH battery life. In addition, although it is not a direct concern of Ni foam materials, environmental consideration is also necessary regarding waste liquids and materials. The following methods to process waste liquids derived from electroless Ni plating are known, and each method has steps to reduce the environmental load[5].

In the neutralization precipitation method in which waste liquid is alkalified to form metal hydroxide, metal hydroxide formation is interfered with due to the presence of inorganic substances increasing the chemical oxygen demand (COD) or organic acids used as a complexing agent in waste liquid at a high level, and the aggregation-precipitation process is not satisfactory.

In the biological oxidation method in which waste liquid is aerated in the presence of microorganisms, organic substances can be processed, but inorganic COD-increasing substances, such as phosphorous acid, and Ni ions cannot.

- Heavy metals can be processed by the electrical oxidative decomposition of waste liquid, but the processing of inorganic COD-increasing substances, such as phosphorous acid, is insufficient, and the COD value of the waste liquid remains high.

The processing of waste liquid from electroless plating has become an important issue due to the recent conclusion of the Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matters and publication of the ISO14000 series[6]. To reduce the amount of waste and waste liquid-processing cost in the production, our company reduces the waste liquid volume by evaporating water using an underwater burner, followed by separation into Ni salt and waste liquid containing other inorganic salts and organic acids employing a waste disposer. Ni salt is re-cast to Ni bare metal, and the residual waste liquid undergoes combustion.

2-2 Characteristics of metal foam[7]

The external appearance of Ni foam is shown in **Photo 1**. Its characteristics are as follows:

(1) Porosity: The porosity is dependent on urethane foam on which Ni is deposited but controllable within the range maintaining the shape in the firing process. At present, about 98% porosity has been achieved.

(2) Open-cell foam: Urethane foam is subjected to vacuum gas replacement with a 2:1 mixture of hydrogen and oxygen in an explosion-proof chamber evacuated to vacuum and then fired. Most cells in the urethane foam are ruptured on firing (membrane removal), and open-cell urethane foam is formed. Accordingly, cells are open in Ni foam using this urethane foam. When this Ni foam is used for the current collector of batteries, all cell spaces can be readily homogenously filled with active materials.

(3) Small flow resistance: The skeleton surrounding cell spaces is a very fine mesh structure with a very low-level resistance to liquid and gas flow. It can be used as a carrier of an effluent gas purification catalyst or filter, and operable with a very low pressure loss. Pressure changes after flowing gas through the Ni foam with 48-52 cells/inch at various flow rates are shown in **Fig. 2**[8].

(4) Large specific surface: The specific surface per weight is very large because of the porosity. For example, the

specific surface of Ni foam with 48-52 cells/inch is 7,500 m²/m³. Because of this characteristic, Ni foam is used as a catalyst carrier and material of radiation electric heating parts.

(5) Ease of processing: Ni foam can be cut and bent with a small processing force because of its high porosity and low metal rate. It is also used as an electromagnetic shield because it possesses both electric conductivity and magnetism. For example, walls can be readily lined with Ni foam base materials using a tacker (stapler for construction) for the electromagnetic shielding of areas in hospitals.
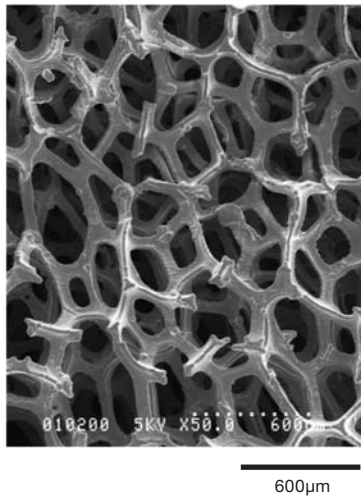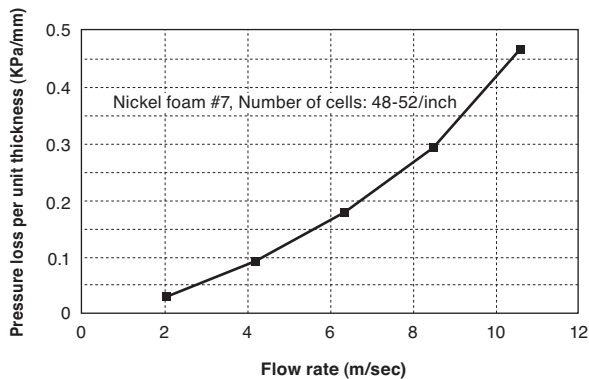

Photo 1. External appearance of Ni foam base material

Fig. 2. Pressure loss of nickel foam

2-3 Use of metallic foam
2-3-1 Application for electrode plates of batteries

Ni foam base materials were initially used as a core material of positive electrodes of nickel-cadmium batteries in 1985[9]. Previously, positive electrodes were manufactured by sintering nickel hydroxide produced by neutralizing nickel nitrate on the Ni-plated iron sheet surface. The maximum porosity of this sintered-type positive electrode was about 80%. To increase the active material-

filling rate to meet the market demand, Ni foam base materials with a higher porosity were adopted. The increased filling rate facilitated the rapid spread of nickel-cadmium batteries in cordless devices, such as video cameras and notebook computers, and increased the demand for compact rechargeable batteries for recycling.

Ni-MH batteries became practically used in the 1990s. Batteries using the sintered-type and Ni foam co-existed at the beginning, but Ni foam base materials became the mainstream as the porosity reached 98%. The method of cobalt metal network formation by cobalt hydroxide, an electric conductivity-assistive agent, and the active material-filling method were also modified, which annually increased the energy density of Ni-MH batteries, as shown in **Fig. 3**[10].
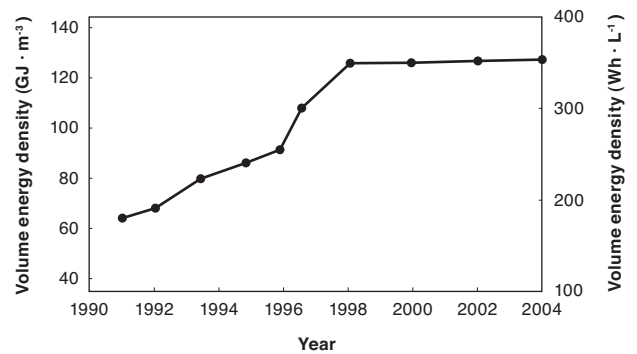

Fig. 3. Change of the energy density of Ni-MH battery

An Ni-MH battery with a capacity density of 126 GJ/m³, comparable to or greater than that of lithium ion batteries, became practically used in 1998[11]. However, Ni foam base materials did not completely substitute the sinter-type, and the sinter-type is still used for some high-power batteries. This is because an Ni-plated iron sheet supporting the sintered body is present in sintered positive electrode core materials, to which a current collector plate can be welded to the entire marginal surface of the support[11], through which the current collection pathway can be set vertically to the current-collecting region, facilitating the ready formation of a structure with a small current collection resistance in the surface direction. Using the sintered-type, a reduction of the internal resistance is achieved, which is essential for high-power batteries, surpassing Ni foam.

In batteries using an Ni foam base material, one long side of the material is molded by pressing to a high-density metal fragment and the current collector plate is welded to this region, through which a current collecting structure equivalent to that of the sinter-type is realized, not by collecting current through a terminal welded to a single site of the margin of the material. The discharge characteristics of high-power batteries prepared by this method are shown in **Fig. 4**.

Ni foam base materials serve as a support of the current collector and active materials, and, basically, they do not contribute to the electrochemical reactions of batter-

ies. However, impurities contained in Ni foam may negatively influence the electrolyte solution because it is a metal ion source. Metals more precious than Ni are dissolved in electrolyte solution and deposit on the separator, establishing a short circuit. Non-precious metals may also deposit and cover the negative electrode, interfering with the battery reaction. Even when impurities in metals are not dissolved as ions, the formation of a solid solution alloy by them leads to an increase in electrical resistance and, subsequently, resistance in the battery. From these viewpoints, in addition to a high porosity and strength, the high-level purification of Ni is necessary for Ni foam base materials.
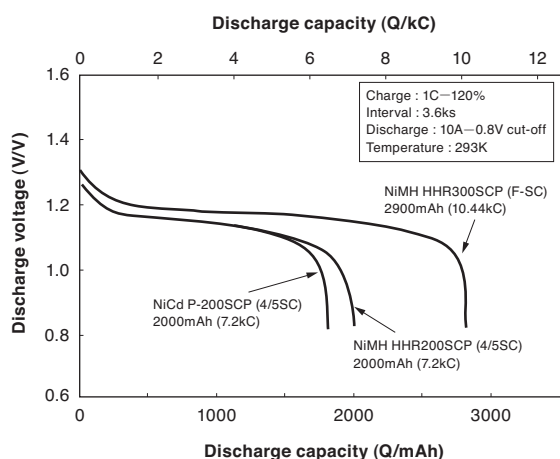

Fig. 4. Discharge characteristics of NiCd and Ni-MH batteries

2-3-2 Usage other than a battery

(1) Kerosene fan heater: Ni foam is widely used for the vaporization of kerosene fan heaters because of its advantages: high porosity and the shape of Ni foam base materials capable of retaining kerosene in cells, and superior resistance to erosion by kerosene. Kerosene retained in Ni foam materials is vaporized when the heat from the burner is instantly transmitted due to the high heat conductivity of Ni.

(2) Purification of exhaust: Ni foam is used as a catalyst carrier because of its high porosity and heat resistance. For example, Ni foam carrying a precious metal catalyst is used as an exhaust-deodorizing catalyst in printers and copy machines. Its application to a filter to reduce soot in exhaust (diesel particulate filter (DPF)) is being investigated as the emission regulation of diesel vehicles has been strengthened. However, application to commercial cars has not been realized due to durability and cost problems.

3. Electroless Nickel Plating Technique

3-1 Characteristics of electroless nickel plating

Electroless plating generally represents an autocatalytic reducing process in which metal film is deposited using a reducing agent without an external power supply, unlike electroplating. Electroless Ni plating was discovered by Brenner and Ridell in 1944 and first reported in 1946[12]. Later, the General American Transportation Corp. investigated complexing agents and patented the technique as the catalytic nickel generation (CANIZEN) method. The history of electroless plating is long and its research and development have matured. Deposited metals have a small crystal diameter and are superior in terms of adhesion to organic materials with an anchor effect as the major adhesion mechanism, such as ABS. Ni plating is most commonly used in industries.

Film produced by electroless Ni plating is frequently co-deposited with elements derived from the reducing agent and forms an alloy containing them in Ni at a few %. There are 3 types of Ni plating: Ni-P using hypophosphite as a reducing agent, Ni-B using a boron compound, such as dimethylaminoborane, and pure Ni using hydrazine. Practically employed electroless Ni plating is mostly Ni-P, and the others are limited to special electronic parts. The use of Ni-P varies depending on the P content. In industries, 1-4, 8-9, and 11-13 wt% P contents are called low-, middle-, and high-P, respectively. Typical practical electroless Ni plating is summarized in **Table 1**[13].

The characteristics of electroless Ni plating using hypophosphite as a reducing agent vary depending on the P content. Widely employed electroless Ni plating adopts about 8-11 wt% P, called middle or middle-high P, which may be most readily applied because of the external appearance and deposition rate. As shown in Table 1, the crystallinity of the deposited film decreases as the P content rises, and vice versa. High-P plating with amorphous deposition is unlikely to develop erosion of the grain boundary and superior in erosion resistance, but a low-level pH should be maintained to form high-P film, for which the deposition rate should also be reduced. Since crystallinity and magnetism are correlated, the high-P type which forms amorphous film is used for the base plating of hard discs requiring non-magnetic film.

A major difference between electroless and electrical Ni plating is the marked hardness of electroless plating.
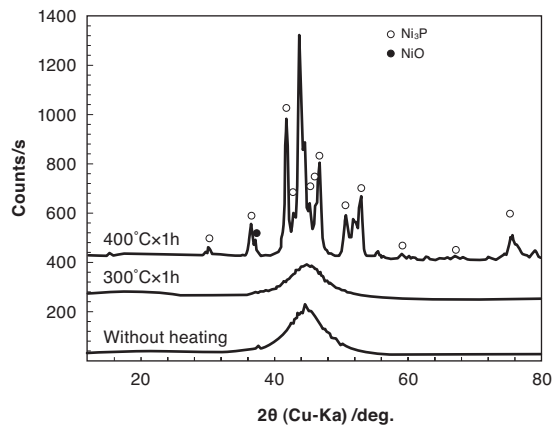

Fig. 5. Heating temperature and thin film X-ray diffraction of electroless nickel plating

Table 1. Functions and characteristics of typical electroless nickel plating

Film characteristics		Ni-P alloy					Ni-B alloy
Reducing agent		Sodium hypophosphite					Dimethylaminoborane
P or B content (wt%)		Low P	Middle-low P	Middle P	Middle-high P	High P	Low B
		1-4	5-7	8-9	10-11	11-13	B: 0.2-1.0
Plating bath		Neutral-ammonia alkali	Weakly acidic	Neutral	Neutral-ammonia alkali	Weakly acidic	Neutral
Function		High-level hardness, electric conductivity, solderability, EMC	Base of displacement gold plating	General-purpose, high-level hardness, corrosion resistance	Corrosion resistance, resistance to chemicals, non-magnetic	Parting layer, resistance to chemicals, free-machining, high-level electrical resistance	High-level hardness, electrical conductivity, solderability
Usage		Sliding part, EMC cabinet, IC header, lead frame	PCB, FPC, BGA base	General-purpose material for corrosion-resistant parts, sliding part	General-purpose material for corrosion-resistant parts, sliding parts, hermetic seal	Molds for injection molding, thin film resistance, clean room floor	Sliding parts, hermetic seal, lead frame
Crystal structure	Without heating	Crystalline	Crystalline-amorphous	Crystalline-amorphous	Amorphous	Amorphous	Crystalline
	300°C 2hr	Crystalline	Crystalline	Crystalline	Crystalline	Amorphous	Crystalline
Density (g·cm^{-3})		8.5	8.1	7.9	7.9	7.6	8.6
Young's modulus (GPa)		50-52	62-66	50-60	50-70	50-70	
Tensile strength (MPa)		150-200	420-700	800-1100	650-900	650-900	
Melting point (°C)		890					1380
Thermal expansion coefficient (µm·m^{-1}·°C)		13	12	12	11	11	12
Magnetism	Without heating	Soft magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Non-magnetic	Soft magnetic
	400°C 2hr	Soft magnetic	Soft magnetic	Soft magnetic	Soft magnetic	Non-magnetic	Soft magnetic
Specific resistance (µΩ·cm)		30-60	60-75			150-200	5-6
TCR(ppm°C^{-1})		1000	300			100	2000
Acid resistance		Poor	Fair			Favorable	Poor
Alkali resistance		Favorable	Fair			Slightly favorable	Poor
Corrosion resistance (SST)		Fair	Favorable-excellent			Favorable	Poor
Solderability		Slightly favorable	Fair				Favorable
Deposition rate (µm·hr^{-1})		15-20	15-25			5-10	3-8
Bath temperature (°C)		70-90	80-95			85-90	60-70
Bath stability		Fair				Favorable	Fair
Bath life		3-6 MTO	5-10 MTO			3-4 MTO	4-6 MTO

The Vickers hardness of electrical Ni plating using no brightening agent is about 100—200 Hv, whereas that of electroless Ni plating is 450 Hv or harder even when no heating process is applied. Appropriate heating process application increases the hardness to 700 Hv or greater. P atoms enter Ni lattices immediately after deposition and thermodynamically form a non-equilibrated sub-stable phase in many cases. However, heating changes the condition to a thermodynamically stable equilibrated state. Heating at about 300°C releases P atoms from the lattices, with which Ni recrystallization progresses. The coarsening of Ni crystals reduces the hardness, but the continuation of heating at a high temperature promotes an Ni-P reaction and produces an intermetallic compound, Ni₃P. The very low level Ni₃P promotes the dispersion-strengthening of Ni. We measured changes in the crystal structure of Ni film by heating in 0.5 mm-thick rolled copperplates with middle-high-P electroless Ni plating. The results are shown in **Fig. 5**.

The middle-high-P electroless Ni film showed a broad peak mainly at about 2θ, 45° immediately after deposition. A diffraction peak derived from the Ni (200) surface is present near this position. A similar tendency was noted after heating at 300°C for 1 hour. A clear diffraction peak appeared after heating at 400°C and surface oxidation and Ni₃P formation occurred.

Figure 6 shows a scanning electron microscope (SEM) observation of changes in the surface after heating. SEM photographs of electrically plated Ni film containing no P are also shown for comparison. In middle-high-P electroless Ni plating, surface tissue masses were coarsened by heating at 400°C, and many cracks were noted on the surface. The findings of X-ray diffraction analysis and surface SEM of the thin film suggests that marked recrystallization of Ni occurred at about 400°C, and a large movement of atoms upon recrystallization caused the destruction and reproduction of surface oxide film.

Figure 7 shows a TEM observation of the surface oxide film prepared by middle-high-P electroless Ni plating. The

oxide film was about 10 nm thick when no heating process was added, but it grew to 50-60 nm after heating at 400°C for 1 hour.
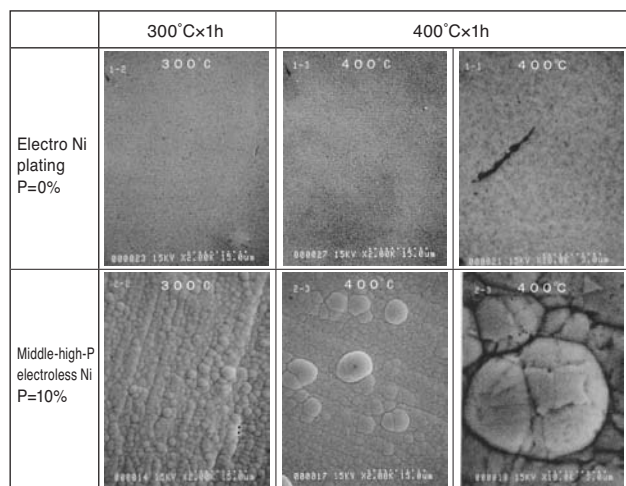

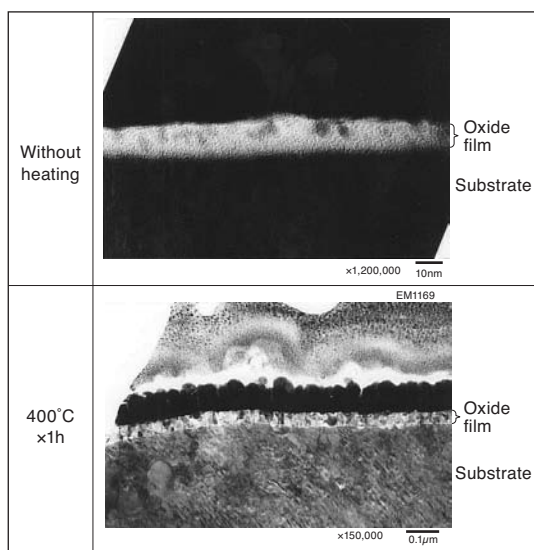**Fig. 6.** Heating and surface condition of electroless nickel plating

Fig. 7. Surface oxide film of middle-high-P (P=10%) electroless nickel plating

3-2 Electroless nickel plating bath[14]

In electrical Ni plating, Ni ions are reduced by electrons supplied by an external power source and deposited on the cathode base plate. Ni ions are also reduced by receiving electrons in electroless Ni plating, but the electron supplier does not employ an external power source. Electrons are released when a reducing agent contained in the bath, such as hypophosphite, is oxidized on the catalyst metal surface. Palladium is frequently used as a catalyst mainly because metal palladium has both a hydrogen-ab-

stracting catalyst function and hydrogen-absorbing capacity.

Table 2 shows the composition of a typical electroless Ni plating bath[15]. Basically, baths are composed of an Ni ion source and reducing, complexing, and stabilizing agents. Nickel sulfate and nickel chloride are used as the Ni ion source, sodium hypophosphite, dimethylaminoborane, sodium boron hydride, and hydrazine as the reducing agent, organic acid and ammonium salts as the complexing agent, and heavy metals, such as lead and thallium, organic sulfur compounds, such as mercaptobenzothiazole and thiourea, and polyethylene glycol as the stabilizing agent.

Table 2. Composition of electroless nickel plating bath

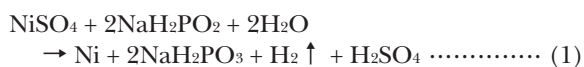| Nickel sulfate	$0.13 \ \mathrm{mol/dm^3}$
Sodium hypophosphite monohydrate	$0.18 \ \mathrm{mol/dm^3}$
Sodium acetate	$0.035 \ \mathrm{mol/dm^3}$
Sodium citrate	$0.12 \ \mathrm{mol/dm^3}$
Stabilizer (Pb)	−
pH-adjusting agent	Ammonia−dilute sulfuric acid

The composition of electroless Ni film depends on the reducing agent. Ni-P and Ni-B alloys are produced when hypophosphite and boron compounds are used, respectively, and pure Ni is formed when hydrazine is used.

For electroless Ni plating baths used in industries, greater importance is attached to the plating quality, such as the deposition rate, pits, and surface smoothness, in which the complexing agents described above serve as key technology. Since complexing agents stabilize the ionic state by coordinating with Ni ions, the deposition rate markedly varies depending on the type and additive amount of complexing agent. The additive amounts of complexing agents are presented as chelate mole (cM), defined as the molar concentration multiplied by the coordination number. For example, the chelate mole of 1.0 $\mathrm{mol/dm^3}$ acetic acid is the same because the ligand is composed of one carboxyl group, whereas that of 1.0 $\mathrm{mol/dm^3}$ lactic acid is 2.0 $\mathrm{cM/dm^3}$ because lactic acid contains a bidentate ligand. Utilizing cM, the deposition rate in a bath containing two or more complexing agents can be estimated with basic data from single complexing agent-containing baths. When the chelate mole is the same, the deposition rate is rapid and middle-P film with a relatively low P content is formed when carboxylic acid complexing agents: acetate, propionate, and succinate, are used. In contrast, when a hydroxycarboxylic acid complexing agent, citrate, and amino acid complexing agents, glycine and aspartate, are used, the deposition rate is very slow and film with a high P content is formed.

3-3 Deposition mechanism of electroless nickel plating

The basic reaction of electroless plating is the reduction of Ni ions by receiving electrons from the reducing agent being oxidized in solution, but there is no established theory for the detailed mechanism of electron re-

lease from the reducing agent. Proposed mechanisms include atomic hydrogen[15], local battery formation[16], and dehydrogenation[17] theories. The basic reaction of Ni deposition is the reduction of Ni ions by the reducing agent and deposition of P, and these are generally presented by reaction formulas as follows:

$$NiSO_4 + 2NaH_2PO_2 + 2H_2O$$
$$\rightarrow Ni + 2NaH_2PO_3 + H_2\uparrow + H_2SO_4 \cdots\cdots\cdots (1)$$
$$NaH_2PO_2 + 1/2H_2 \rightarrow P + NaOH + H_2O \cdots\cdots\cdots (2)$$
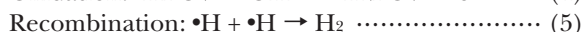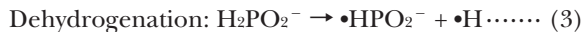
In **Reaction (1)**, atomic Ni produced by the main reaction of Ni deposition promotes deposition as a catalyst, and the main component level and pH decrease. P is deposited and incorporated into film in **Reaction (2)**. The total consumption of the reducing agent is the sum of that used in **Reactions (1)** and **(2)**.
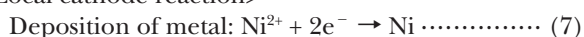
In many previous reports, the H2/Ni ratio did not decrease to below 1 and the co-deposition level of P varied from 1 to 13 wt% in experiments[18]-[20]. **Reaction formulas (1)** and **(2)** are presented as overall oxidation-reduction reactions. Regarding the detailed mechanism of electron release from the reducing agent, dehydrogenation is the most consistent with the experimental results[21].

This mechanism was proposed by van den Meerakker, in which the first reaction step common to all electroless plating regardless of plated metal and reducing agent is basically dehydrogenation of the reduction agent. For example, this mechanism is applied to electroless Ni plating using hypophosphite as follows:
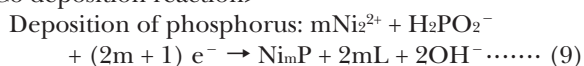
<Local anode reaction>
Dehydrogenation: $H_2PO_2^- \rightarrow \bullet HPO_2^- + \bullet H \cdots\cdots$ (3)
Oxidation: $\bullet HPO_2^- + OH^- \rightarrow H_2PO_2^- + e^- \cdots\cdots$ (4)
Recombination: $\bullet H + \bullet H \rightarrow H_2 \cdots\cdots\cdots\cdots$ (5)
Oxidation: $\bullet H + OH^- \rightarrow H_2O + e^- \cdots\cdots\cdots\cdots$ (6)
<Local cathode reaction>
Deposition of metal: $Ni^{2+} + 2e^- \rightarrow Ni \cdots\cdots\cdots$ (7)
Production of hydrogen:
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \cdots\cdots\cdots\cdots$$ (8)
<Co-deposition reaction>
Deposition of phosphorus: $mNi_2^{2+} + H_2PO_2^-$
$$+ (2m + 1) e^- \rightarrow Ni_mP + 2mL + 2OH^- \cdots\cdots$$ (9)

Local anode reactions **(5)** and **(6)** and local cathode reactions **(7)** and **(8)** are competitive reactions and the priority is determined depending on the types of metal and reducing agent. In electroless Ni plating using hypophosphite, **Reaction (5)** is prioritized to **(6)** and progresses at nearly 100%. Accordingly, the overall anode reaction is presented as **(10)**, and the maximum use efficiency of the reducing agent is 50%.

$$2H_2PO_2^- + 2OH^- \rightarrow 2H_2PO_3^- + H_2 + 2e^- \cdots\cdots (10)$$

In electroless copper plating using formaldehyde, **Reaction (6)** is prioritized to **(5)**, and the overall anode reaction is presented as **(11)**. Accordingly, the maximum use efficiency of the reducing agent is 100%.

$$H_2PO_2^- + 2OH^- \rightarrow H_2PO_3^- + H_2O + 2e^- \cdots\cdots (11)$$
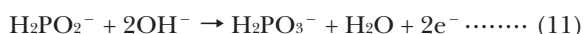
It is considered that the deposition mechanism of all electroless plating can be explained by applying this reaction mechanism: dehydrogenation of the reducing agent occurs as the first step, followed by electron production through the oxidation of hydrogen in **Reaction (6)**.

3-4 Novel plating technique
In the current electroless plating technique, P and B contained in the reducing agent co-deposit in plating film and influence the electrical, mechanical, or chemical characteristics of film. Ni alloy film co-deposited with P and B is preferable for uses requiring mechanical strength and non-magnetism, but pure Ni film is needed for Ni foam used as a current collector of batteries and usage requiring the magnetism of Ni. A new electroless plating technique, called the titanium redox method, has been investigated[22], in which titanium ions are used as a reducing agent. **Table 3** shows a typical plating bath composition employing this method. Since this titanium redox method does not use a reducing agent containing P or B, pure metal plating film containing no co-deposit is formed. Its application is considered in fields in which electroless Ni plating could not previously be employed because of the co-deposition of P and B. Titanium redox is also being investigated for a zero-emission process in which the accumulation of by-products of plating reactions is avoided by reproducing titanium ions through electroreduction[23]. In another example, titanium redox is employed for the process of adding electrical conductivity to urethane in Ni foam[24]. **Figure 8** shows the results of a high-temperature cycle life test at 50°C of Ni-MH batteries using Ni foam as a

Table 3. Composition and conditions of plating bath using titanium ions

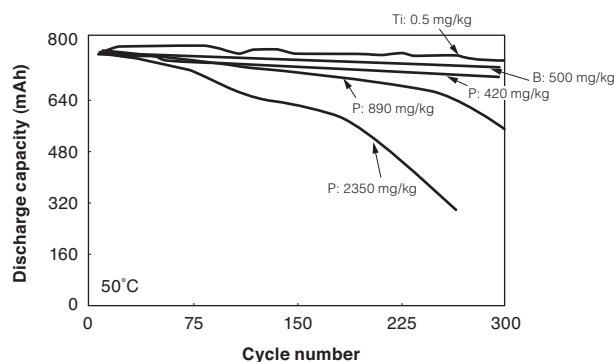| Nickel sulfate	0.04 mol/dm³
Titanium chloride (TiCl₃ and TiCl₄)	0.08 mol/dm³
Trisodium citrate (Na-Cit.)	0.24 mol/dm³
Nitrilotriacetic acid (NTA)	0.04 mol/dm³
Amino acid	100-500 ppm
pH	8-9 (adjusted by NH₃ aq)
Bath temp.	323 K

Fig. 8. High-temperature cycle life test of Ni-MH batteries

positive electrode current collector. The discharge capacity of samples containing P at a high level decreased to about 80% of the initial capacity after about 100 cycles, and the cycle life tended to prolong as the P level decreased. Although the tendency of samples containing B was unclear because the B content was not altered in the experiment, a slightly favorable life characteristic was noted at a level similar to the P level. Samples prepared by the titanium redox process showed a capacity retention rate of 95% after 300 cycles, exhibiting the longest life. Regarding the mechanism, it is considered that interface resistance between the current collector and electrolyte solution increases due to the layer containing a residual insoluble phosphorus compound produced with the dissolution of Ni, which promotes the electrolysis of electrolyte solution with temperature elevation on the collector surface.

4. Conclusion

This report summarized the new electroless Ni plating method employed for the production of Ni foam base materials used as a positive electrode of Ni-MH and NiCd batteries, increasingly in demand as rechargeable batteries. The titanium redox method was also introduced as a novel plating technique capable of: 1) preparing film basically containing no impurities other than Ni, and 2) repeating Ni deposition by reusing the electrolytic bath, aiming at an environment-conscious electroless Ni plating bath. The results of a high-temperature cycle life test of Ni-MH batteries which adopted metal foam prepared by the titanium redox method were presented, in which reduction of the discharge capacity from the initial capacity was very small until 300 charge-discharge cycles.

* CELMET is a trademark or registered trademark of Sumitomo Electric industries, Ltd.

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