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(54) A method for preparing metal fiber articles.

(57) A method for preparing metal fiber articles is disclosed. The method comprises forming a metal coating on an organic fiber fabric by plating and firing the thus coated fabric in a reducing gas atmosphere. Also a method for preparing a cadmium electrode with a nickel substrate utilizing said method is disclosed.

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A method for preparing metal fiber articles

Field of the Invention

This invention relates to a method for preparing metal fiber articles used as electrodes, various filters, parabola antennas, and the like.

Background of the Invention

As processes for manufacturing metal fibers, there have been known a method comprising repeatedly drawing metal threads as in the case of production of copper fibers, vibration cutting (lathing) of a metal rod as in the case of the production of nickel fibers, a method comprising extruding a viscoelastic composition comprising powder of a reducible metal compound, a binder, a dispersant, etc. in the form of fibers, and thereafter firing the extruded material in a reducing atmosphere, etc. Metal fiber articles are manufactured by forming the thus produced metal fibers into a fabric (woven, nonwoven or knit fabric) as described in JP-A56-35702, etc. However, all these methods comprise a plurality of complicated process steps, wherein the metal fibers are easily fatigued, and, therefore, working or fabricating thereof is difficult and uniform products cannot be regularly produced.

Also it is known to manufacture foamed metal materials such as foamed nickel by plating a foamed resin body with nickel for instance, firing the plated foamed resin in the atmosphere and reducing the formed nickel oxide. This method is also complicated in the process steps and the products obtained is too hard to be used easily although the products are uniform.

These metal fiber articles are utilized because of their electric conductivity and high porosity (void fraction). However, the porosity is 95% at the highest in the product of JP-A56-35702, which is made by forming a nonwoven fabric of nickel fibers and sintering it with nickel powder. That of the nonwoven fabric of the nickel fibers made by vibration cutting is 91% and that of the foamed nickel is 93%. The metal fiber articles other than the foamed nickel exhibit obvious non-uniformity in the thickness of fibers and in the porosity.

This invention is intended to solve the above-described problems, that is, the complexity of manufacturing process steps, non- uniformity in the product, difficulty of making articles having porosity of higher than 95%, lack of flexibility in the final products (hardness and brittleness) and to provide an improved process for a cadmium electrode with a nickel substrate.

Under the circumstances, we intensively studied in search of measure for solving the problems and have found that the production process steps are simplified, uniform and flexible products having void rate up to about 98% can be obtained by firing in a reducing gas atmosphere organic fiber fabric (woven, nonwoven and knit) plated with a metal. As a result of the study, we have found that an excellent cadmium electrode with nickel substrate can be easily obtained by said process.

Summary of the Invention

This invention provides a method for preparing metal fiber articles comprising forming a metal coating on a piece of an organic fiber fabric by plating and firing the thus coated fabric in a reducing gas atmosphere. Also, this invention provides a process for preparing a process for preparing a cadmium electrode with a nickel substrate.

This process of the present invention is applicable to all metals that can be precipitated from an aqueous solution. Preferred are Cu, Ni, Ag and Co.

In the process of the present invention, the term "fabric" encompasses woven, nonwoven and knit fabrics.

As the method of plating, any of electroless plating, electrolytic plating and vapor deposition plating and any combination thereof can be employed.

The plating step is started with the refining using a surfactant. When only electroless plating is employed, the refined fabric is activated with a Sn/Pd catalyst system, whereafter it is immersed in an electroless plating solution containing a metal salt, a complexing agent, a reducing agent, etc. As a reducing agent, sodium borohydride, dimethylamine, borane, sodium hypophosphite, hydrazine and derivatives

thereof, formalin, etc. can be used. In order to obtain pure metal and from the viewpoint of ease of handling, formalin is preferred in the case of Cu, and hydrazine and derivatives thereof are preferred in the case of Ni and Co.

Usually electrolytic plating is applied after the scouring and vapor deposition or electroless plating. However, sometimes electroless plating is employed after vapor deposition plating.

Commercially available scouring agents, pretreatment agents, electroless plating solutions, brightening agents, additives, etc. can be used.

Organic fibers consisting of elements C and H; C, H and O; or C, H, O and N are used. Organic fibers containing other elements are apt to char or leave ash.

Typical fibers constituted of C and H are fibers of polyolefins such as polyethylene, polypropylene, etc. Typical fibers constituted of C and H are polyolefin fibers, those of C, H and O are rayon fibers, acetate fibers, polyvinyl alcohol fibers, polyester fibers, etc., and those of C, H, O and N is polyamide fibers and acrylonitrile fibers.

As a reducing gas, hydrogen gas, ammonia gas, carbon monoxide gas, thermally cracked ammonia gas or any mixture thereof can be used.

The flow rate of the reducing gas must be varied in accordance with the size of the furnace used, firing temperature, etc. and cannot be simply specified. There is a tendency for the firing rate to increase as the gas flow rate increases. For the sake of regulation of reaction rate the reducing as can be diluted with an inert gas such as nitrogen, argon, etc.

Firing is conducted at 250°C - 1200°C, preferably 300°C - 1200°C, and more preferably 500°C - 1000°C. At temperatures below 250°C, too long firing time is required, and yet firing is often incomplete. At temperatures over 1200°C, the material is excessively sintered and loses flexibility.

The firing time depends upon the firing temperature and, therefore, it cannot be specifically defined, but is generally between 15 minutes and 4 hours, preferably 30 minutes and 2 hours.

The electroless plating can be carried out by any known conventional process. For instance, a substrate fiber fabric is scoured, activated with a $SnCl_2/PdCl_2$ catalyst, and thereafter is immersed in an electroless plating solution containing a Ni salt, a complexing agent, a reducing agent, a pH-adjuster, a stabilizer, additives, etc.

The thus produced metal fiber articles can be further plated another metal or metals by processes known per se. Needless to say, the formed metal fiber articles cannot be exposed to a temperature at which the plated metal or metals deteriorate.

When a cadmium electrode with a nickel substrate is prepared, electrolytic plating of Cd can be effected by an ordinary process since Ni has good electric conductivity. That is, Ni coating of the fiber substrate is effected by connecting it to the cathode and immersing it in a plating solution containing cadmium oxide, sodium cyanide, any additives, etc. and applying electric current to the plating bath.

The reducing gas is practically ammonia gas, hydrogen gas, or a mixture thereof or one of these diluted with an inert gas such as argon.

The firing is carried out at a temperature between 250°C - 300°C. At temperatures lower than 250°C, excessively long firing time is required and often firing is incomplete. At temperatures over 300°C, Cd is apt to volatilize. The firing time is 1 - 10 hours, preferably 2 - 5 hours.

Preferred Embodiments of the Invention

The invention will be explained specifically by way of preferred working examples.

Example 1

A piece of nonwoven fabric (50x50x3mm) made of 3d rayon fibers and weighing 1.42g was scoured and immersed in 500ml of a solution containing 10g/ℓ $SnCl_2$ and 10mℓ/ℓ HCl for 10 minutes. The thus treated fabric was activated by immersion in 500mℓ of an aqueous solution containing 1g/ℓ $PdCl_2$ and 1mℓ/ℓ HCl for 10 minutes, thereafter it was immersed in 500mℓ of an electroless nickel plating solution of the following composition at 80°C for deposition of Ni.

Nickel sulfate	18g/ℓ
Sodium citrate	10g/ℓ
Hydrated hydrazine	50mℓ/ℓ
Ammoniacal water (25%)	100mℓ/ℓ

After the treated fabric was rinsed with water and dried, it weighed 3.38g, which proved that 1.96g of Ni was deposited. The plated fabric was placed in a furnace and fired at 800°C for 1 hour as hydrogen gas was passed through the furnace at the rate of 2ℓ/min. After cooling, it weighed 1.93g and consisted of Ni only in the state of flexible nonwoven fabric. The size was 41x43x2.8mm and the porosity was 97.7%.

Example 2

A piece of nonwoven fabric (50x50x3mm) made of 1.5d polyethylene fibers and weighing 1.27g was scoured in the same manner as in Example 1, activated with a Sn/Pd catalyst system. This fabric was immersed in 500mℓ of an electroless copper-plating solution of the following composition at 30°C for deposition of copper.

Copper sulfate	12g/ℓ
Rochelle salt	50g/ℓ
Sodium hydroxide	30g/ℓ
Formalin	50ml/ℓ

After rinsing and drying, the treated fabric weighed 2.76g, which means that 1.49g of copper deposited. The plated fabric was placed in a furnace and fired at 500°C for 2 hours as NH_3gas was passed at the rate of 2ℓ/min. After cooling, it weighed 1.48g and consisted of copper only in the state of a flexible nonwoven fabric. The size was 37x39x2.7mm and the porosity was 95.7%.

Example 3

A piece of woven fabric (50x50x1.5mm) made of 2d polypropylene fibers and weighing 1.32g was scoured and activated with a Sn/Pd catalyst system in the same manner as in Example 1. The thus treated fabric was immersed in 200ml of an electroless cobalt-plating solution of the following composition which was warmed to 80°C for deposition of cobalt.

Cobalt chloride	23.5g/ℓ
Rochelle salt	100g/ℓ
Hydrated hydrazine	50mℓ/ℓ
Sodium hydroxide	50g/ℓ

After rinsing and drying, it weighed 2.17g, which means that 0.85g of cobalt deposited. The thus plated fabric was placed in a furnace, and fired at 700°C for an hour as a gas obtained by thermal cracking of ammonia gas was passed through the furnace at the rate of 2ℓ/min. After cooling, it weighed 0.85g and consisted of cobalt only in the state of a flexible woven fabric. The size was 46x47x1.4mm and the porosity was 96.8%.

Example 4

A piece of nonwoven fabric (50x50x2mm) made of 1.5d rayon fibers and weighing 1.87g was scoured, activated with a Sn/Pd catalyst system in the same manner as in Example 1. The thus treated fabric was immersed in 250ml of an elctcroless silver-plating solution of the following composition at 25°C for deposition of silver.

Silver nitrate	7.9g/ℓ
EDTA disodium salt	50g/ℓ
Ammonia water	50mℓ/ℓ
Formalin	50g/ℓ

After rinsing and drying, the treated fabaric weighed 3.10g, which means that 1.23g of silver deposited. The thus plated fabric was placed in a furnace and fired at 600°C for 2 hours as hydrogen gas passed through the furnace at the rate of 2ℓ/min. After cooling, it weighed 1.23g and consisted of silver only in the state of a flexible nonwoven fabric. The size was 43x44x1.8mm and the porosity was 96.6%.

The porosity, electric resistivity, uniformity and flexibility of the products of the above Examples 1 - 4 and those of foamed nickel, nonwoven fabric of nickel fiber which was prepared by vibration lathing and nonwoven fabric of nickel fiber which was chemically prepared by the process disclosed in JP-A56-35702-(1981) are shown in the following table for comparison.

TABLE

Product	Porosity	El. Resist'y	Uniformity	Flexib'y
Example 1	97.7%	$1.5\times10^{-3}\Omega\bullet$cm	○	○
" 2	97.7%	$7.8\times10^{-3}\Omega\bullet$cm	○	○
" 3	96.8%	$1.9\times10^{-3}\Omega\bullet$cm	○	○
" 4	96.6%	$2.7\times10^{-5}\Omega\bullet$cm	○	○
Foamed Ni	93.0%	$4.3\times10^{-4}\Omega\bullet$cm	○	×(hard)
Vibr'n cutting[1]	91.0%	$4.3\times10^{-4}\Omega\bullet$cm	×	○
JP-A59-35702[2]	95.0%	$1.5\times10^{-3}\Omega\bullet$cm	×	×(brittle)

[1]nonwoven fabric of nickel fiber which was prepared by vibration cutting
[2]nonwoven fabric of nickel fiber which was chemically prepared by the process disclosed in JP-A56-35702
Uniformity: ○ No apparent non-uniformity of pores is observed by the naked eye.
× Apparent non-uniformity of pores is observed by the naked eye.
Flexibility:○ Flexibility is retained even after repeated bending.
:× Crumbles when bent repeatedly.

Example 5

A 25cm² (5x5cm) piece of nonwoven fabric made of 3d rayon fibers and weighing 1.51g was scoured and immersed in 500ml of an aqueous solution containing 10g/ℓ $SnCl_2$ and 10mℓ/ℓ HCl for 10 minutes. The thus treated fabric was activated by immersing in 500mℓ of an aqueous solution containing 1g/ℓ $PdCl_2$ and 1mℓ/ℓ HCl for 10 minutes, whereafter it was immersed in 500mℓ of an electroless plating solution of the following composition at 80°C for deposition of Ni.

Nickel sulfate	18g/ℓ
Sodium citrate	10g/ℓ
Hydrated hydrazine	50mℓ/ℓ
Lead acetate	1mg/ℓ
Ammonia water	100mℓ/ℓ

After the fabric had been kept in the solution for reaction until the Ni in the solution was consumed, it was taken out and washed with water and applied on a stainless steel plate. The stainless steel plate bearing the treated fabric was immersed in a solution of the following composition

Cadmium oxide	25g/ℓ
Sodium cyanide	120g/ℓ
Dextrin	1g/ℓ

and subjected to electrolysis with 5A/dm^2 electric current density at room temperature for 20 minutes.

The resulting product was rinsed with water and dried. It weighed 5.29g. The product was fired in a furnace through which ammonia gas was passed at the rate of 3ℓ/min at 290°C for 2 hours. After cooling, a metal fabric in the exact same shape as the original nonwoven fabric weighing 3.76g remained. Chemical analysis revealed that it consisted of 1.97g Ni and 1.79g Cd.

Example 6

A 25cm^2 (5x5cm) piece of nonwoven fabric made of 1.5d acryl fibers and weighing 1.33g was scoured and activated with a $SnCl_2/PdCl_2$ catalyst system in the same manner as in Example 5, and was further plated with nickel and cadmium under the same conditions.

The resulting product weighed 5.17g after washing with water and drying. This was fired in a furnace through which hydrogen gas was flown at the rate of 3ℓ/min at 290°C for 5 hours. After cooling, a metal fabric in the exact same shape as the original nonwoven fabric weighing 3.81g remained. Chemical analysis revealed that it consists of 1.92g Ni and 1.89g Cd.

Claims

1. A method for preparing metal fiber articles comprising forming a metal coating on a piece of organic fiber fabric by a plating process known per se and firing the thus coated fabric in a reducing gas atmosphere.

2. The method as recited in Claim 1, wherein the procedure of the plating is:
   i) electroless plating
   ii) electroless plating followed by electrolytic plating
   iii) vapor deposition plating followed by electroless plating, or
   iv) vapor deposition plating followed by electrolytic plating.

3. The method as recited in Claim 1, wherein at least one of Cu, Ni, Ag, and Co is plated.

4. The method as recited in Claim 1, wherein the organic fiber consists of the elements C and H; the elements C, H and O or the elements C, H, O and N.

5. The method as recited in Claim 4, wherein the organic fiber consists of the elements C and H or the elements C, H and O.

6. The method as recited in Claim 4, wherein the organic fiber is selected from polyethylene, polypropylene and acrylic fiber.

7. A method for preparing a Cd-electrode with Ni-substrate comprising forming a Ni coating on a piece of an organic fiber fabric by eletroless plating, forming a Cd coating on the thus formed Ni coating by electrolytic plating and firing the thus treated fabric in a reducing gas atmosphere.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 11 6953

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	FR-A-1 510 317 (UNION CARBIDE) * Page 13, left-hand column, lines 14-17,29-30; page 3, left-hand column, line 41 *	1,4,5,6	C 23 C 18/08 D 06 Q 1/04
A	US-A-3 914 471 (COBB)		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 23 C
D 06 Q
C 25 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-12-1988	NGUYEN THE NGHIEP

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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