(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 686 718 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
05.08.1998 Bulletin 1998/32

(51) Int Cl.[6]: **D04H 1/42**

(21) Application number: **95108312.0**

(22) Date of filing: **30.05.1995**

(54) **Unwoven metal fabric and method of manufacturing the same**

Metall-Vliesstoff und Verfahren zur dessen Herstellung

Tissu non tissé métallique et méthode pour sa fabrication

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **09.06.1994 JP 127508/94**

(43) Date of publication of application:
13.12.1995 Bulletin 1995/50

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Description

This invention relates to an unwoven metal fabric which is a kind of porous metal structure for various uses such as battery electrodes, catalysts and filters and a method of manufacturing the same.

Conventional battery electrodes and filters are formed from ultra-fine metal fibers entangled together. Different materials and various new techniques for forming them have been developed.

For example, Unexamined Japanese Patent Publication 4-11058 discloses a material made of metal fibers that are joined together so that the length of the joint portions will be more than 0.7 time the average fiber diameter, and a method of manufacturing the same. Unexamined Japanese Patent Publication 3-17957 proposes a material made of metal fibers which are subjected to pre-plating treatment using precious metal catalysts to improve the adhesion of plating to the fibers, and a method of manufacturing the same.

Also, Unexamined Japanese Patent Publication 61-76686 proposes to provide a metal coating on a felt member by sputtering under vacuum in order to provide an electrode having a high porosity. But the methods disclosed in these publications require complicated processes such as pre-plating treatment by catalysts and sputtering, so that mass-productivity is low. Also, if the electrodes thus formed contain more than 100 ppm metallic impurities resulting from the catalysts used, their properties will vary so widely that they will not stand practical use.

In order to solve these problems, Unexamined Japanese Patent Publication 4-126859 proposes a metal fiber material formed by electroplating a high-conductivity carbon fiber sheet and removing the substrate. The carbon fiber sheet used here is manufactured by forming a mixture of carbon fibers and a substance for bonding fibers (hereinafter referred to as "binder") into sheet form and drying it.

Ep-A-0 404 961 discloses a method for providing fibers having a smooth surface. In order to obtain this result carbon fibers are made into unwoven fabric, to which a resin is applied and then dried.

The carbon fibers in such a carbon fiber sheet have a resistivity of mere 10^{-3}- $10^{-4}\Omega \cdot cm$. But the binder surrounding the carbon fibers has a very high resistivity because it is an insulating material. It is not an easy job to directly electroplate such a sheet. It would be possible to reduce the content of the binder in order to increase the conductivity of the entire sheet. But this will make it necessary to increase the amount of plating to make up for the reduced adhesion between fibers. The metal fiber product thus obtained would have a porosity of 80-90%, which is too low for use as battery electrodes.

It is possible to reduce the resistivity of the fiber material by increasing its firing temperature to 1000°C or higher to graphitize the fiber. But since the fibers are joined together by the resin binder, it is impossible to electroplate such joint portions. The metallic porous member thus formed tends to be low in mechanical strength and unsatisfactory in its electrical properties. Also, excessive graphitization would make it necessary to increase the temperature to 900°C or higher in removing the substrate by thermal oxidation in the later step. This will in turn result in reduced strength of the unwoven fabric formed.

One solution to these problems is to increase the thickness of plating to 500-1000 g/m^2, because such a thick plating layer provided on the carbon fiber portions overhangs the binder portions. But it is not easy to provide a thick plating having a uniform thickness over the entire area. Also, such a thick plating layer tends to keep a web form because it is difficult to roll. This solution is therefore not suitable for continuous production. Thus, it is an ordinary practice to increase the conductivity of the material by electroless plating and then provide an electroplating layer of a predetermined thickness.

The unwoven fabric formed by this conventional method shows high mechanical strength because plating is provided between fibers. But due to the properties of the plating solution, variations in the distribution of fibers tend to widen. The unwoven fabric thus formed is low in quality stability. If this unwoven fabric is used for batteries, the content of metallic impurities which have been used as catalysts will exceed 100 ppm, so that the variations in the properties of electrodes will increase to such a extent that such electrodes are practically useless. It is therefore desired to provide a method for manufacturing a stable metallic unwoven fabric without reducing the number of joint portions between metal fibers.

An object of the present invention is to provide a method of manufacturing an unwoven metal fabric in which by making possible a direct, stable electroplating of unwoven carbon fiber, the amount of impurities is reduced and the variation in quality is minimized while keeping the mechanical strength and the porosity at high level.

Another object of the prevent invention is to provide an unwoven metal fabric which is uniform in quality and low in the content of impurities, has high mechanical strength and porosity and a large surface area of the metal portion, and is highly resistant to thermal stress.

According to this invention, unwoven carbon fabric having carbon fibers bound together by a resin is heated at a temperature of 550-850°C in an inert atmosphere using N_2 gas or Ar gas for one to two hours to impart conductivity to the binder resin by carbonizing it. During this carbonizing process, the fiber surfaces and the resin surface at its joint portion are finely roughened. A metal layer is formed on the surface of the substrate of the unwoven carbon fabric thus heat-treated (i.e. on the surfaces of the fibers and the resin) by electroplating. Then, the unwoven carbon fabric is

removed by roasting (baking for decarbonization), leaving an aggregate of hollow metal fibers connected together and having their voids communicating with each other. The aggregate of hollow metal fibers thus formed is heated in a reducing atmosphere to densify them. The desired unwoven metal fiber, is thus obtained.

The unwoven carbon fiber, which is the substrate of the metal fabric according to this invention, is prepared by forming a mixture of carbon fibers and a binder into sheet form and drying the sheet thus formed so as to have a desired porosity. The carbon fibers used may be mainly carbon fibers, graphite fibers or activated carbon fibers.

The carbon fiber should be obtained by baking at 750 - 900°C. If less than 750°C, the resistivity of the carbon fibers will become too high (10^4-$10^6\Omega \cdot$ cm), so that the resistivity of the sheet will be too high for the sheet to be electroplated. If higher than 900°C, the fabric has to be heated in baking after electroplating to more than 750°C to remove carbon fibers and binder. This lowers the strength of the unwoven metal fabric.

The diameter of the fibers should be 7-20 μm. If less than 7 μm, the fabric formed into sheet will be too limp and thus difficult to handle. If over 20 μm, the sheet formed will be too stiff. The carbon packing density (how much fiber is filled per unit volume) when the carbon fibers are formed into sheet form is determined by the fiber length. The packing density in turn determines the structure of the unwoven metal fabric finally obtained.

Namely, if the fabric formed is used as a filter, the carbon packing density factor will influence its collecting capacity. If it is used as a battery electrode, the carbon packing density will influence the contents of active materials. Also, it influences the strength of the sheet. The fiber length should be determined so that the fiber packing density will be 2-20%. If the fiber length is longer than 20 mm, the packing density will be less than 2%. The sheet formed tends to be too low in strength. If the fiber length is shorter than 3 mm, the fiber packing density will exceed 20%. The fabric formed tends to be too low in porosity.

The amount of resin relative to the amount of carbon fibers should be within a predetermined range. If lower than this range, it will be impossible to form the fibers into sheet form. If higher than the range, the fabric will be clogged with the resin. The amount of resin is adjustable by removing the volatile content by heating it. The structure of the end product is influenced by the amount of resin.

To remove the volatile content of the resin, the fabric should be heated at a temperature between 200°C and 350°C in the atmosphere. At a temperature less than 200 °C, the volatile content would not volatilize sufficiently. The resin may foam when the fiber sheet is later subjected to carbonizing later. If higher than 350°C, the resin would decompose, weakening the structure of the fabric in sheet form. The heating conditions should be controlled so that after this step, the resin content decreases to 5-15 wt%. If less than 5 wt%, it would be difficult for the fabric to retain its sheet form. If more than 15 wt%, the fabric may be clogged with resin and also tend to be stiff and difficult to bend. This step should be carried out for 10-90 minutes in the atmosphere.

Then, the resin is carbonized in a non-oxidizing atmosphere. The non-oxidizing gas used here may be H_2, low-molecular hydrocarbon, argon, N_2 gas. Argon or N_2 gas is preferable. The heat treatment for carbonizing should be carried out once or more than once at 500-850°C. From an economical viewpoint, the duration of this step should be limited within 90 minutes. If the temperature is less than 500°C, the resin will not carbonize sufficiently and thus the fabric will be low in conductivity for electroplating. If higher than 850°C, the resin will carbonize excessively, so that the fabric sheet will be low in flexibility. Under these conditions, the resin at the surface of carbon fibers and at the joint portions between carbon fibers tend to agglomerate upon carbonizing, so that the fabric thus treated will have a surface roughness of 0.5-1.5 μm. It is preferable to treat the fabric for about one hour at 550-700°C.

The carbon unwoven fabric thus formed shows electrical conductivity even at the joint portions. Its surface roughness is 0.5-1.5 μm. It is flexible enough to withstand continuous plating. The surface roughness refers to irregularity in the direction of thickness of carbon fiber.

Plating treatment is carried out using the unwoven carbon fiber as a cathode. The metal to be plated may be of any kind provided it can be electroplated. Preferably, a metal should be selected from Ni, Cu, Ag and Fe. As plating baths for Ni, Cu, Ag and Fe, watts type, a copper sulfate solution, a silver cyanide solution, and a ferrous sulfate solution are ordinarily used, respectively.

Plating conditions will be described in detail in the description of Examples. They are determined so that the plating obtained has an average thickness of 3-10 μm. If thinner than 3 μm, the fabric tends to be too low in strength and too flexible to maintain its quality. If thicker than 10 μm, the entire unwoven fabric would become so stiff that it is more likely to develop cracks when bent and also its porosity would be low.

The porosity of the unwoven metal fabric should be controlled to 80 - 98% by adjusting the packing density and the resin content of the unwoven carbon fabric and the thickness of plating.

The metallic unwoven fabric after plating should be roasted in the atmosphere within the temperature range of 600 - 900 C according to the kind of metal used to remove the carbon fiber.

The unwoven fabric made up of metal fibers which has been surface-oxidized and hollowed by roasting is reduced in a reducing atmosphere at a temperature of 600-1000 °C into an end product.

In the aggregate of hollow metal fibers thus obtained, all the fiber are hollow and each fiber has a roughness of 0.5-1.5 μm both on the inner and outer surfaces, with the hollow fibers intersecting each other. The joint portions

between them are wide and joined together due to carbonization of the resin. Namely, the joint portions have at least a width equal to or more than 50% of the diameter of the hollow portion of each fiber (approximate to the original carbon fiber diameter). This prevent the metal at the joint portions from being extremely thick. Such wide joint portions are obtained by adjusting the resin content present in the unwoven carbon fabric to 5-15 wt% by heat treatment in the atmosphere.

According to the method of this invention, the resin binder forming the unwoven carbon fabric is given conductivity by carbonizing it. Thus, it is possible to form a metal layer directly on the surface of the resin, as well as on the carbon fibers, by electroplating. Thus, there is no need to subject the fabric to electroless plating, which is not favorable because it tends to widen quality variation of metal fabrics obtained and also it causes the inclusion of impurities.

Further, by electroplating, the plating layer is deposited uniformly on the unwoven carbon fabric, so that the wall thickness of the metal fibers will be very uniform. Thus, the wall thickness of the hollow metal fibers can be made extremely thin, while keeping a required mechanical strength of the fibers. This makes it possible to increase the porosity of the entire fabric by reducing the wall thickness of the plated layer.

The unwoven metal fabric formed by the method according to this invention is made up of metal fibers having their voids communicating with one another and having their inner and outer surfaces roughened finely. Thus, its surface area is extremely large, so that such metal fabric is especially suited for use as a catalyst or a catalyst carrier. Also, because of its large surface area and high porosity, it shows excellent collecting capacity when it is used as filter.

Moreover, because of its hollow structure and low metal-to-void ratio, the metal fabric according to the present invention is extremely lightweight. Also, since metal fibers are strongly bound together, the fabric as a whole has high mechanical strength. Due to uniform wall thickness of the metal fibers, local stress concentration is less liable to occur. This leads to prolonged life expectancy of the fabric.

Other features and objects of the present invention will become apparent from the following description made with reference to the accompanying drawings, in which:

Figs. 1A to 1C are partially cutaway enlarged perspective views of the unwoven metal fabric according to this invention, showing it after each of the manufacturing steps; and

Figs. 2A to 2C are enlarged perspective views of joint portion of the unwoven metal fabric, showing it after each of the manufacturing steps.

(Example 1)

An unwoven fabric 0.3 mm thick and 40 g/m^2 in weight per unit area was formed from 13 μm-diameter carbon fibers 1, using an epoxy resin as a binder. The content of resin was 20 wt%. Fig. 1A shows an enlarged view of its part. Fig. 2A shows its joint portion.

This unwoven fabric was heated at 300°C in the atmosphere for one hour to remove any low-temperature-volatile content in the binder. As a result, the content of binder decreased to 10.1 wt% of the entire unwoven fabric. Then, the fabric was heated at 650°C for one hour in N_2 gas. Fig. 1B shows its portion. The surface is seen to have irregularities 2. Fig. 2B shows its joint portion.

The fabric obtained was cut to a 200 mm x 400 mm sheet. The sheet was immersed in a nickel plating bath shown in Fig. 1 and plated for 30 minutes while applying a current at a rate of 9.42 A/dm^2 to form a plating layer 3. Fig. 1C shows a portion of the fabric thus obtained.

Part of the fabric thus obtained was cut off and observed under an optical microscope to measure the thickness of plating and the extent of surface irregularity was observed under a scanning microscope. The results of measurements are shown at No. 1 in Table 1. The gap width at the joint in the table is the value a in Fig. 2C and the gap diameter in the table is the value b in Fig. 2C. This is the case for the other tables.

(Example 2)

Carbon fabrics were prepared in the same manner as in Example 1 with different contents of epoxy resin as shown at Nos. 2-7 of Table 1. They were heated under the same conditions as in Example 1, and then plated with nickel. Table 1 shows the results of observations of these specimens. The specimens had different plating thicknesses from one another. This was accomplished by changing the plating time.

(Example 3)

An unwoven fabric 0.42 mm thick and 30 g/m^2 in weight per unit area was formed from carbon fibers 1 having a diameter of 7 μm, using an unsaturated polyester resin as a binder. The content of resin was 20 wt% of the entire fabric.

This unwoven fabric was heated at 280°C in the atmosphere for 40 minutes to remove any low-temperature-volatile

content in the binder until the content of binder decreases to 9.0 wt%. Then, the fabric was heated at 750°C for 40 minutes in N_2 gas.

The material thus obtained was wound on a 200-mm-diameter roll, and passed through a plating bath for 25 minutes while applying a current at a rate of 11.3 A/dm^2 to form a nickel plating layer 3 shown in Fig. 1C by continuous plating.

The fabric thus obtained was then roasted at 900°C for 10 minutes, and heated at 1000°C in H_2 gas to reduce its surface. An unwoven fabric made up of hollow metal fibers 3 shown in Fig. 2C was obtained. As is apparent from this figure, the interior of one metal fiber 3 communicates with that of another through an opening 5 at the joint portion. The diameter a of the opening 5 (gap width at joint) and the internal diameter b of the metal fibers 3 (gap diameter) are determined to satisfy the relation $a/b > 0.5$.

Part of the metallic unwoven fabric thus obtained was cut off for observation under an optical microscope and to measure its tensile strength. The results of observation and measurement are shown at No. 8 in Table 2

(Example 4)

The same carbon fabrics as used in Example 3 were heated under different heating conditions shown in Table 2 at Nos. 9-20. They were then plated with nickel in the same manner as in Example 3. There were some specimens which could not be wound on rolls. Such specimens were cut to 200 mm x 400 mm sheets and plated in batches. These speciments were plated for 25 minutes while applying a current at a rate of 11.3 A/dm^2. The results are shown at Nos. 9-20 in Table 2.

(Example 5)

The same unwoven carbon fabric as used in Example 1 was heated in the same manner as in Example 1.

The unplated unwoven fabric thus obtained was cut to 200 mm x 400 mm sheets, and the sheets were plated with nickel in the nickel bath shown in Table 1 under different plating conditions.

After plating, the sheets were roasted and reduced under the conditions shown in Table 3.

Part of each sheet was cut off for optical microscopic observation and to measure its tensile strength. The results of observation and measurement are shown at Nos. 21-27 in Table 3.

(Example 6)

The same unwoven carbon fabric as used in Example 1 was heated in the same manner as in Example 1.

The unplated unwoven fabric thus obtained was cut to a 200 mm x 400 mm sheet, and the sheet was plated with Cu in a bath (containing 200 g/l of $CuSO_4 \cdot 5H_2O$ and 52 g/l of H_2SO_4) kept at 30±2°C at a current of 2.0 A/dm^2 for 98 minutes.

After plating, it was roasted at 800°C for five minutes in the atmosphere, and then reduced in an H_2 gas atmosphere at 950°C for 20 minutes. We observed the plating thus formed. The results of observation are shown at No. 28 in Table 4.

(Example 7)

The same unwoven carbon fabric was plated with Ag under the same conditions as in Example 6.

The Ag plating was formed in a bath containing 6 g/liter of AgCN and 110 g/liter of KCN kept at 25 ± 2°C at a current of 5 A/dm^2 for 55 minutes.

After plating, it was roasted at 800°C for three minutes in the atmosphere, and then reduced in an H_2 gas atmosphere at 850°C for 40 minutes. We observed the plating thus formed. The results of observation are shown at No. 29 in Table 4.

(Example 8)

The same unwoven carbon fabric was plated with Fe under the same conditions as in Example 7.

The Fe plating was formed in a bath containing 350 g/liter of FeSO4 $(NH_4)_2SO_4 \cdot 6H_2O$ and 120 g/liter of $(NH_4)_2SO_4$ bath kept at 60°C±2°C at a current of 8 A/dm^2 for 35 minutes.

After plating, it was roasted at 800°C for three minutes in the atmosphere, and then reduced in an H_2 gas atmosphere at 850°C for 40 minutes. We observed the plating thus formed. The results of observation are shown at No. 30 in Table 4.

(Example 9)

An unwoven fabric 1.3 mm thick and 50 g/m^2 in weight per unit area was formed from 13-μm-diameter carbon fibers 1, using an epoxy resin as a binder. The content of resin was 20 wt%.

This unwoven fabric was heated at 300°C in the atmosphere for one hour to remove any low-temperature-volatile content in the binder. As a result, the content of binder decreased to 10.1 wt% of the entire unwoven fabric.

Then, the fabric was heated at 650°C for one hour in N_2 gas. The fabric obtained was cut to a 200 mm x 400 mm sheet. The sheet was immersed in a nickel plating bath shown in Table 1 and plated for 38 minutes while applying a current at rate of 9.42 A/dm^2.

Part of the fabric thus obtained was cut off and observed under an optical microscope to measure the thickness of plating and the extent of surface irregularity Its porosity and tensile strength were also measured. The results of measurements are shown at No. 31 in Table 4.

The hollow portions of the metal fibers communicate with each other through openings formed at the joint portions of the fibers, so that the metal layer has a uniform thickness. Such a metal layer shows increased strength and high resistance to thermal stress.

According to the method of the present invention, electrical conductivity is given to the joint portions of the carbon fibers by carbonizing the binder resin. When carbonizing, the carbon fibers and the binder resin are roughened finely. A plating layer can be formed directly on the unwoven carbon fabric thus formed by electroplating. Thus, it is possible to form a sufficiently thin layer without the possibility of inclusion of impurities and wide quality variation. The unwoven metal fabric made up of hollow metal fibers according to the present invention excels conventional metal fabrics of this type in its mechanical strength, porosity, surface area, distribution of fibers and weight.

[Table 1]

No	Amount of binder after volatile removed (wt%)	*1 Electroplating		Gap width a / diameter b of hollow portions	Roughness at surface (μm)
		Average Thickness (μm)	Gap width a at joint portions (μm)		
1	10.1	7	12.1	0.93	1.0
2	5.1	10	6.5	0.5	0.5
3	7.3	9	9.1	0.7	0.8
4	12.2	9	14.3	1.1	1.2
5	14.8	5	17.0	1.3	1.5
6	*2 15.5	7	17.9	1.4	1.8
7	9.0	3	13.0	1.0	0.5

*1 For plating, watt bath (45 g/l of boric acid, 40 g/l of nickel chloride, 330 g/l of nickel sulfide) was used, Ni plate as anode. Used at about 55°C while agitating. Plating conditions; Current constant at 9.42 A/dm^2, plating thickness adjusted by changing the plating time.

*2 This is a control example.

[Table 2]

No	Unwoven Carbon fabric		Heat treatment in atmosphere		Amount of binder after volatile removed (wt%)	Heat treatment in N_2 gas	
	Fiber length (mm)	porosity (%)	Temp. (℃)	Time (min)		Temp. (℃)	Time (min)
8	10	8	280	40	9.0	750	40
9	10	8	250	80	12.0	850	30
10	4	12	300	30	10.0	600	60
11	5	10	350	10	10.0	800	40
12	3	16	200	90	15.0	700	40
13	3.5	12	300	20	11.0	750	35
14	10	8	280	30	12.5	500	70
15	5	12	280	50	8.5	600	50
16	3.5	6	280	60	8.3	700	35
17	15	8	280	70	8.1	800	30
18	10	8	280	80	8.0	650	60
19	5	12	280	90	8.0	550	80
20	10	8	250	30	14.0	600	50

Continued

No	Winding on 200mm dia.roll	*1 Plated State			Gap width a / diameter b of hollow portions	Porosity (%)	Tensile strength (kg/mm²)
		Avarage Thickness (μm)	Surface roughnes (μm)	Gap width a at joint portions (μm)			
8	good	7. 0	1. 0	10. 5	1. 50	90. 1	3. 7
9	cracked *2	7. 0	1. 3	13. 5	1. 93	90. 1	3. 2
10	good	10. 0	1. 0	11. 5	1. 64	85. 9	3. 3
11	cracked *2	9. 0	1. 0	11. 5	1. 64	87. 3	3. 8
12	good	10. 0	1. 5	16. 5	2. 36	85. 0	5. 0
13	good	9. 5	1. 2	12. 5	1. 79	86. 6	4. 1
14	good	7. 0	1. 3	14. 0	2. 00	90. 1	3. 5
15	good	9. 0	0. 8	10. 0	1. 43	87. 3	4. 1
16	good	10. 0	0. 8	9. 8	1. 40	85. 0	4. 5
17	good	6. 0	0. 7	9. 6	1. 37	91. 5	3. 0
18	good	7. 0	0. 7	9. 5	1. 36	90. 1	4. 0
19	good	9. 0	0. 8	9. 5	1. 36	87. 3	4. 3
20	good	3. 0	0. 7	14. 0	2. 0	90. 0	3. 2

*1 Plating bath and plating conditions are the same as in Table 1. Only plating time changed.

*2 Cracks observed at edge. Batch treated.

[Table 3]

No	Plating Conditions *1		Roasting Conditions		Reducing Conditions *2		Plated State		Porosity (%)	Tensile Strength (kg/mm²)
	Current (a/dm²)	Time (min)	Temp. (℃)	Time (min)	Temp. (℃)	Time (min)	Average Thickness (μm)	Surface Roughness (μm)		
21	9.42	30	700	40	1000	30	7	1.0	88.0	3.0
22	11.3	25	900	8	1000	60	7	1.0	88.0	3.0
23	11.3	18	1000	3	1000	10	5	0.9	91.4	1.1
24	9.42	38	900	10	900	60	9	1.1	84.6	2.8
25	12.0	40	900	8	900	90	10.0	1.1	81.0	3.5
26	8.07	35	900	10	800	60	7	1.1	88.0	2.5
27	11.3	32	900	12	800	120	9	1.1	84.6	2.8

*1 Plating bath was the same as the one used in Table 1. Voltage varied with bath resistanse.
*2 H_2 gas used.

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[Table 4]

No	Metal plated	Plated State			Gap width a / diameter b of hollow portions	Porosity (%)	Tensile Strength (kg/mm^2)
		Average Thickness (μm)	Roughness at surface (μm)	Gap width a at joint portions (μm)			
28	Cu	7.0	1.1	9.1	0.70	88	1.7
29	Ag	8.2	1.0	12.1	0.93	85	1.5
30	Fe	8.2	1.0	12.1	0.93	85	1.2
31	Ni	7.0	1.0	12.1	0.93	97.0	1.5

Claims

1. An unwoven metal fabric comprising an aggregate of hollow metal fibers, said metal fibers being joined together, the hollow portions of said fibers communicating with each other at joint portions between said metal fibers, characterized in that said metal fibers have a roughness of 0.5-1.5 μm on inner and outer surfaces thereof.

2. An unwoven metal fabric as claimed in claim 1 wherein the portion of the fabric except said joint portions has an average metal thickness of 3-10μm.

3. An unwoven metal fabric as claimed in claim 1 or 2 wherein it has a porosity of 80 to 98%.

4. An unwoven metal fabric as claimed in any of claims 1-3 wherein the minimum width of the opening of said metal fibers at said joint portions is not less than 50% of the diameter of the hollow portions of said metal fibers.

5. An unwoven metal fabric as claimed in any of claims 1-4 wherein said metal fibers are formed from one selected from the group consisting of Ni, Cu, Ag and Fe.

6. A method of manufacturing an unwoven metal fabric comprising the steps of joining a plurality of carbon fibers together by means of a resin to provide an unwoven fabric material, heating said unwoven fabric material to carbonate said resin and impart conductivity to said resin and roughen both the fiber surface and the resin surface, forming a metal layer on the surface of said fabric and said resin by electroplating, roasting the unwoven fabric material to remove the carbon fibers, and reducing said unwoven fabric material in a reducing atmosphere to make dense the metallic structure, characterized in that said heating step comprises heating said unwoven fabric material at 200-350°C in the atmosphere and then heating at 500-850°C in a non-oxidizing atmosphere, said heatings being carried out at least once.

7. A method of manufacturing an unwoven metal fabric as claimed in claim 6 wherein as the carbon fibers forming said unwoven carbon fabric is one obtained by heating carbon fiber to 750-900°C.

8. A method of manufacturing an unwoven metal fabric as claimed in claim 6 or 7 wherein said carbon fibers forming said unwoven carbon fabric have a diameter of 7-20 μm, a fiber length of 3-20 mm and a packing density of 2-20%.

Patentansprüche

1. Metall-Vliesstoff, bestehend aus einer Anhäufung von hohlen Metallfasern, die miteinander verbunden sind, wobei die hohlen Bereiche der Fasern an Verbindungsbereichen zwischen den Metallfasern miteinander in Verbindung stehen, dadurch gekennzeichnet, dass die Metallfasern auf ihren inneren und äußeren Oberflächen eine Rauheit von 0,5-1,5 μm haben.

2. Metall-Vliesstoff nach Anspruch 1, bei dem der Bereich des Stoffes außer den Verbindungsbereichen eine durchschnittliche Metalldicke von 3-10 µm hat.

3. Metall-Vliesstoff nach Anspruch 1 oder 2, bei dem er eine Porosität von 80 bis 98% hat.

4. Metall-Vliesstoff nach einem der Ansprüche 1-3, bei dem die minimale Breite der Öffnung der Metallfasern an den Verbindungsbereichen nicht geringer ist als 50% des Durchmessers der hohlen Bereiche der Metallfasern.

5. Metall-Vliesstoff nach einem der Ansprüche 1-4, bei dem die Metallfasern aus einem Element bestehen, welches auszuwählen ist aus einer Gruppe aus Ni, Cu, Ag und Fe.

6. Verfahren zur Herstellung eines Metall-Vliesstoffes, bei welchem eine Vielzahl von Kohlenstoff-Fasern mittels eines Harzes miteinander verbunden werden, so dass ein Vliesstoff entsteht, bei welchem der Vliesstoff erwärmt wird, um das Harz zu karbonisieren und dem Harz Leitfähigkeit zu verleihen und sowohl die Oberfläche der Faser als auch die Oberfläche des Harzes aufzurauen, durch Elektroplattieren eine Metallschicht auf der Oberfläche des Stoffes und des Harzes gebildet wird, der Vliesstoff gebrannt wird, um die Kohlenstoff-Fasern zu entfernen, und der Vliesstoff in einer reduzierenden Atmosphäre reduziert wird, um die metallische Struktur zu verdichten, dadurch gekennzeichnet, dass bei dem Schritt des Erwärmens der Vliesstoff bei 200-350°C in der Atmosphäre erwärmt wird und dann in einer nichtoxidierenden Atmosphäre bei 500-850°C erwärmt wird, wobei das Erwärmen jeweils mindestens einmal stattfindet.

7. Verfahren zur Herstellung eines Metall-Vliesstoffes nach Anspruch 6, bei dem die Kohlenstoff-Fasern, die den Kohlenstoff-Vliesstoff bilden, Fasern sind, die gebildet werden, indem Kohlenstoff-Fasern auf 750-900°C erwärmt werden.

8. Verfahren zur Herstellung eines Metall-Vliesstoffes nach Anspruch 6 oder 7, bei dem die Kohlenstoff-Fasern, die den Kohlenstoff-Vliesstoff bilden, einen Durchmesser von 7-20 µm, eine Faserlänge von 3-20 mm und eine Pakkungsdichte von 2-20% haben.

Revendications

1. Tissu métallique non tissé comprenant un agrégat de fibres métalliques creuses, lesdites fibres métalliques étant liées ensemble, les parties creuses desdites fibres étant en communication les unes avec les autres à des parties de liaison entre lesdites fibres métalliques, caractérisé en ce que lesdites fibres métalliques présentent une rugosité de 0,5 à 1,5 µm sur leurs surfaces interne et externe.

2. Tissu métallique non tissé tel que revendiqué dans la revendication 1 dans lequel la partie du tissu à l'exception des parties de liaison a une épaisseur de métal moyenne de 3 à 10 µm.

3. Tissu métallique non tissé tel que revendiqué dans la revendication 1 ou 2, caractérisé par une porosité de 80 à 98 %.

4. Tissu métallique non tissé tel que revendiqué dans l'une quelconque des revendications 1 à 3, dans lequel la largeur minimum de l'ouverture desdites fibres métalliques auxdites parties de liaison n'est pas inférieure à 50 % du diamètre des parties creuses desdites fibres métalliques.

5. Tissu métallique non tissé tel que revendiqué selon l'une quelconque des revendications 1 à 4, dans lequel lesdites fibres métalliques _sont formées à partir d'un membre choisi parmi le groupe constitué du nickel, du cuivre, de l'argent et du fer.

6. Procédé de fabrication d'un tissu métallique non tissé comprenant les étapes consistant à lier une pluralité de fibres de carbone ensemble au moyen d'une résine pour fournir un matériau du type tissu non tissé, chauffer ledit matériau du type tissu non tissé pour carboniser ladite résine et conférer une conductibivité à ladite résine et rendre rugueux à la fois la surface des fibres et la surface de la résine, former une couche métallique sur la surface dudit tissu et de ladite résine par électrodéposition, calciner ledit matériau du type tissu non tissé pour éliminer les fibres de carbone, et réduire ledit matériau du type tissu non tissé dans une atmosphère réductrice pour densifier la structure métallique, caractérisé en ce que ladite étape de chauffage comprend le fait de chauffer ledit matériau

du type tissu non tissé à 200-350°C à l'atmosphère puis chauffer à 500-850°C dans une atmosphère non oxydante, lesdits chauffages étant effectués au moins une fois.

7. Procédé de fabrication d'un tissu métallique non tissé tel que revendiqué dans la revendication 6, selon lequel la fibre de carbone formant ledit tissu de carbone non tissé est une fibre obtenue par chauffage d'une fibre de carbone à 750-900°C.

8. Procédé de fabrication d'un tissu métallique non tissé tel que revendiqué dans la revendication 6 ou 7, selon lequel lesdites fibres de carbone formant ledit tissu de carbone non tissé ont un diamètre de 7 à 20 pm, une longueur de fibre de 3 à 20 mm et une densité de tassement de 2 à 20 %.

FIG. 1A

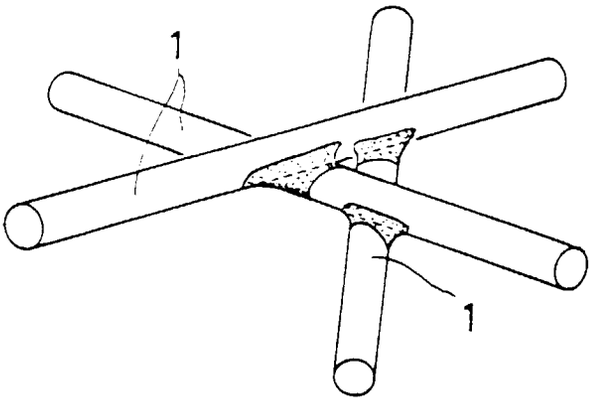


FIG. 1B

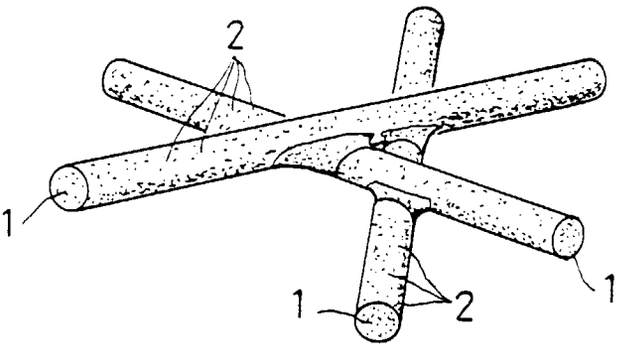


FIG. 1C

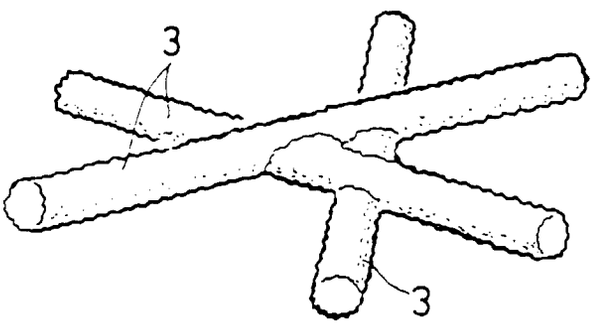


FIG. 2A

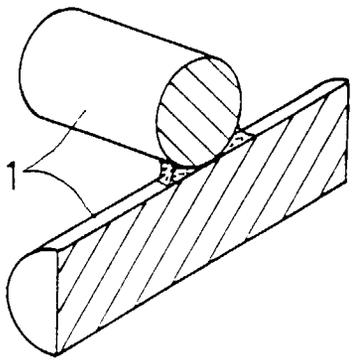


FIG. 2B

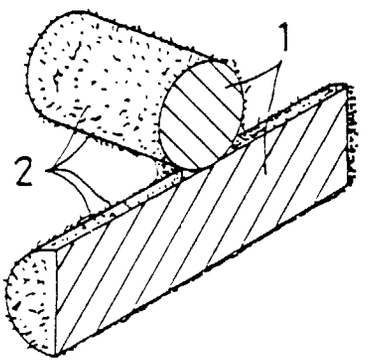


FIG. 2C

