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(71) Applicant: **SANNO CO., LTD.**
5-8-8 Tsunashima-higashi,
Kouhoku-ku
Yokohama-shi, Kanagawa Prefecture(JP)
Applicant: **NIPPON METAL INDUSTRY CO.,LTD.**
1-1 Nishishinjuku 2-chome
Shinjuku-ku Tokyo(JP)

(72) Inventor: **Saito, Hitoshi**
c/o Sugihara,
1-15-22, Zengyo
Fujisawa-shi, Kanagawa Prefecture(JP)
Inventor: **Yamashita, Tadashi**
Iriyamazu No. 1-226,
2-4-2, Tsurugaoka
Yokosuka-shi, Kanagawa Prefecture(JP)
Inventor: **Nakajima, Hiroo**
4-11-14, Asada,
Kawasaki-ku
Kawasaki-shi, Kanagawa Prefecture(JP)
Inventor: **Inoue, Shougo**
1-9-13, Yokoyamadai
Sagamihara-shi, Kanagawa Prefecture(JP)

(74) Representative: **Dr. Fuchs, Dr. Luderschmidt**
Dr. Mehler, Dipl.-Ing Weiss Patentanwälte
Postfach 46 60
D-65036 Wiesbaden (DE)

(54) Contact material and manufacturing method of the same.

(57) It is an object of the present invention to provide contact materials and manufacturing method of the same; said contact materials possess excellent characteristics in terms of contact resistance, corrosion resistance, bending strength, spring property, and ductility. On a band-shaped nickel-claded stainless steel substrate, there is either partially or entirely plated, at least one type of metal selected from noble metals, tin or tin-based alloys. Various evaluating tests including the contact resistance measurements, salt spray tests, sulfur dioxide tests, mixed gas tests of sulfur dioxide and sulfurized gas, and the bending strength tests are carried out on different samples and the results evaluated which showed that the present materials avoid anti-corrosion post-treatment after the press-forming process and exhibit excellent characteristics, particularly suitable to application for intermediate current and intermediate voltage regimes.

Rank Xerox (UK) Business Services
(3.10/3.09/3.3.4)

Background of the Invention

This invention relates to contact devices which includes connectors, switches or the like. More specifically, this invention is directed to contact materials and the method of manufacturing the same, to provide a material having excellent corrosion resistance, good contact resistance, good bending fracture strength, excellent spring characteristics, and good ductility, making it suitable for use in weak and intermediate current voltage applications.

Conventionally, copper and copper-based alloys including brass, phosphor bronze, beryllium, copper, titanium copper, and oxygen free high conductivity copper have been widely utilized as electrical contact materials in such devices as connectors and switches. Since brass is relatively less expensive than other type of copper-based alloys, it is widely used as a contact material where a specific spring characteristic is not a major concern. Beryllium copper, on the other hand, is utilized where a highly reliable contact material having excellent spring characteristics is needed. However, this material is relatively expensive thus making the device using this material correspondingly expensive. Titanium copper has excellent heat resistance characteristics while oxygen free high conductivity copper exhibits good ductility. Generally speaking, the various types of copper-based alloy noted above are adequate for many proposes as contact materials, however, they all have certain disadvantages which are overcome by the material of the present invention.

For example, if the aforementioned copper-based alloys were utilized as materials for contact means without the benefit of further surface treatment, the surface of these contacts will be vulnerable to sulfidation or oxidation. As a result, these devices can only be utilized where the current is strong enough to fracture the said sulfides or oxides. In weak current applications, noble metals including gold or palladium in addition to tin are sometimes directly plated onto copper-based alloy devices to prevent the devices from being corroded. However, since an inter-diffusion reaction takes place between substrates of the copper-based alloys and the plated films due to the generated heat or secular changes in operating conditions. In normal practices, a nickel plating may also be applied which acts as an intermediate layer between the substrates of copper-based alloys and the aforementioned plated layers. This prevents inter-diffusion action and improves the hardness of the contact device and enhances its wear resistance characteristics.

Methods for fabrication contacts utilizing nickel plated copper-based alloys generally takes two forms. The first includes the entire substrate of band-shaped copper-based alloys plated with nickel, and then entirely or partially plated with a tin or tin-based alloys followed by a press-forming technique to fabricate contacts. The second includes nickel-plating a substrate which is formed as a contact by press-forming an originally band-shaped copper-based alloy, followed by plating the contact entirely or partially with a noble metal, tin, or a tin-based alloy.

Recently, owing to the ever-increasing demands on low-coast contacts, the trend has been to apply a partial plating on the contacts. Accordingly, in the case of a high density application, many of the components of the device are subjected to a solder-plating except the contact portions. However, in the case of a short-pitched or three-dimensional contact or the case of a hoop continuous plating of press-formed component in which side films are forced to be very close, films on both sides of the component can overlap due to meniscus action which takes place when using typical liquid-face control methods.

In order to overcome the aforementioned problems in press-formed components, several forming methods have been employed including a resist-ink, masking methods, tape-masking methods, belt-masking methods, drum-masking methods, brush-plating methods, jig masking methods, and the like. However, it is difficult to control and maintain forming accuracy when utilizing known masking materials or masking jigs. Since the initial cost shares a large portion of the production cost, it is not cost effective to apply these methods in the production of various types of contacts with small quality production. In order to solve the aforementioned problems associated with press-formed products, the trend has been toward fabrication of contact components by applying a plating to the band-shaped substrates which can be easily masked, followed by a press-forming step to fabricate the final contacts.

There are still other types of problems for copper based contact devices which are initially plated on a band-shaped substrate and press-formed; namely, the copper-based alloy will be subject to exposure at fractured points which are usually formed during the press-forming process. The exposed substrate will be further subjected to sulfidation or oxidation contamination. Depending upon the corrosiveness condition of the ambient to which the contacts will be exposed, the copper-based alloy substrate can become severely corroded and the corrosion can thus reach the contacts to contaminate the contact points leading to a contact malfunction.

In order to momentarily overcome these problems, a method is sometimes employed by which the press-formed components are painted with an anti-corrosion agent or a lubricant oil which prevents the corrosion action. However, although these paint films can temporarily prevent corrosion, long-term protection against a hostile environment can not be maintained. Moreover, there is another type of drawback associated with the aforementioned methods; that is, an undesirable organic solvent such as 1.1.1 trichloroethylene must be used to dissolve the anti-corrosion agent or lubricant oil.

Recently, stainless steel substrates have been utilized as an alternative contact material in place of copper or copper-based alloys. After the stainless steel substrate is nickel-plated, contact materials are applied by either entirely or partially plating the nickel plated substrate with a noble metal, tin or tin-based alloys or by direct plating the stainless steel substrates with nickel.

In order to plate a stainless steel substrate with nickel, a Watt bath, which is basically a strong acidity nickel plating bath containing hydrochloric acid, is utilized to partially etch the substrate and cause pitting thereon. It is difficult to completely coat these pits by nickel plating (which has a thickness ranging form 1.0 to 5.0 μm). As evidenced by salt spray tests, the corrosion resistance of these plated products is inferior to that of stainless steel products. Since a strong acidity plating bath containing hydrochloric acid is used for a direct gold plating on stainless steel substrate, similar problems will be recognized as those mentioned above in regard to nickel plating. Although acidity bath containing sulfuric acid which is environmentally more favorable has been recently developed, the corrosion protection on the contact points of most devices is not still satisfied.

Objects and Summary of the Invention

It is an object to provide contact materials which show excellent corrosion resistance, good contact resistance, good bending strength, excellent spring characteristics, good ductility, and does not require a corrosion protection treatment after forming, and manufacturing methods for producing products utilizing these materials.

In order to overcome the aforementioned problems and to achieve said objects, a stainless steel substrate is initially clad with nickel or a nickel-based alloy (which is hereinafter called as nickel-claded stainless steel substrate material), and then noble metals, tin or tin-based alloys are plated upon said nickel-claded stainless steel substrate to fabricate contacts. In the first embodiment of the present invention, contacts comprising the nickel-claded stainless steel substrate are entirely or partially plated with at least one type of material composed of various types of noble metals, tin or tin-based alloys. The contacts were further evaluated and found to exhibit excellent characteristics in terms of corrosion resistance, contact resistance, bending strength, spring property, and ductility. The second embodiment of this invention involves a manufacturing method for contacts which possess excellent corrosion resistance, good contact resistance, good ductility and excellent spring characteristics in which a band-shaped nickel-claded stainless steel substrate is entirely or partially plated with at least one type of material which consists of various types of noble metals, tin or tin-based alloys. A third embodiment of the present invention describes a manufacturing method of contacts with excellent corrosion resistance, good contact resistance, good bending strength, and excellent spring characteristics. A press-formed nickel-claded stainless steel substrate is plated with at least one type of material which consists of various types of noble metals, tin or tin-based alloys.

The nickel-claded stainless steel substrate material can be any type of materials produced by well known techniques, including band-shaped or press-formed material. It is preferable to have a thickness of plated nickel within a range from 1.0 to 5.0 μm.

It is preferable to have a thickness of the plated layer of noble metals, tin or tin-based alloys to be in a range from 0.01 to 10 μm. Plating baths for various metals can be employed from normally used baths; namely borofluoric bright bath for tin plating, alkali cyanide silver bath for silver plating, ammonium chloride palladium nickel plating bath for palladium nickel plating and acid hard cobalt gold plating bath of the citric acid salt buffer solution for gold plating.

Since the substrate for the contact materials is a stainless steel claded with nickel-based alloy, corrosion pits caused by etching during the plating process will be of considerably lower severity than for etched copper-based alloy substrates or nickel-plated stainless steel substrates. Hence the nickel-claded substrates exhibit superior corrosion resistance when compared to copper-based alloy or nickel-plated stainless steel substrates. Furthermore, no fractures were produced during the pressing of substrates plated with noble metals, tin or tin-based alloys. Accordingly, there are no exposed portions of the substrate materials, and thus no sulfidation or oxidation thereof which might cause corrosion to form which might contaminate the contacts. Moreover, contacts which are fabricated through the present invention exhibit superior bending strength, spring characteristics and ductility to contacts conventionally manufactured.

Brief Description of the Figures

Figs. 1 (a, b, c) shows microstructures observed by an optical microscope, showing the corrosion appearance of contact surfaces after a salt spray tests;
Figs. 2 (a, b, c) shows microstructures examined under an optical microscope, showing the corrosion appearances of press-fractured surfaces after a salt spray test;
Fig. 3 shows microstructures observed under a scanning electron microscope, showing the bent portions of specimens after a bending strength test.

Detailed Description of the Preferred Embodiments

Embodiment 1

After a band-shaped nickel-claded stainless steel substrate (namely, an AISI Type 304 stainless steel substrate claded with 3 µm thick nickel having dimensions of 15.5 mm width x 50 mm length x 0.2 mm thickness) was electrolytically degreased at a temperature of 50°C in an alkali cyanide degreasing solution at 6 V for 15 seconds, the stainless steel substrate was activated by immersion in 10% sulfuric acid solution at room temperature for 30 seconds and was subjected to 0.2 µm thick gold plating by using an acid hard cobalt gold plating bath of citric acid salt buffer solution. The plated sample was then cut into 30 mm length and further subjected to the following tests.

1) Contact resistance test: A contact resistance meter (KS Component Kenkyusho, MS 800-type) was utilized with an open voltage of 50 mV, measuring direct current of 10 mA and a load of 10 g. The probe for measurements has an 1∅ diameter and the tip portion is K625 alloy (that is 62.5% gold, 29% silver and 8.5% copper alloy) which is formed into 0.5R. All together 50 locations in which each reading was apart by 0.1 mm from each other were subjected to the resistance measurements. The obtained results are listed in Tables 1 and 2.

2) Corrosion tests: (i) salt spray tests: spraying specimen with 5% sodium chloride aqueous solution at a temperature of 35°C for 96 hours, (ii) sulfur dioxide gas test: exposing specimen to an atmosphere containing 25 ppm sulfur dioxide gas at a temperature of 25±2°C and at a relative humidity of 75% for 240 hours, and (iii) mixed gas test: exposing specimen to a mixed gas that consists 10 ppm sulfur dioxide gas and 3 ppm sulfur oxide gas at a temperature of 40±2°C and at relative humidity of 75% for 96 hours. After each test was conducted, the tested specimens were washed in water by the ultrasonic cleaner, immersed in ethyl alcohol and then dried by a drier. Corrosion appearances of contact portions and cross sections were observed under optical and scanning beam electron microscopes. Results are shown in Table 2, and in Figs. 1(a) and 2(a).

3) Bend test: Using the press specification O-type testing machine (Tsukishima Co. Ltd.,) the sample was placed horizontally on the sample stage and bent 90 degrees by manually rotating the handle. The bent portions of the samples were observed under the scanning electron microscope. Results are shown in Fig. 3(a).

Embodiment 2

The nickel-claded stainless steel substrate, which was the same material as that used for embodiment 1, was 0.5 µm thick pure gold plated by using neutral cyanide pure gold plating bath. Similar tests 1) and 2) as carried out in association with Embodiment 1 were conducted. The obtained results are also listed in Tables 1 and 2.

Embodiment 3

Similarly to Embodiment 1, nickel-claded stainless steel substrates were plated with a 3.0 µm thick tin coating by means of a borofluoric bright bath. Same tests 1) and 2) as performed in association with Embodiment 1 were conducted. The obtained results are shown in Tables 1 and 2.

Embodiment 4

Nickel-claded stainless steel as in Embodiment 1 was plated with a 2.0 µm thick silver coating by use of an alkali cyanide silver plating bath. Similar tests 1) and 2) for Embodiment 1 were conducted and the results are also listed in Tables 1 and 2.

Embodiment 5

Similar nickel-claded stainless steel substrate as in Embodiment 1 was plated with a 0.76 µm thick palladium coating by use of an ammonium chloride palladium nickel plating bath, and plated with a 0.05 µm thick gold coating using a similar plating bath as that used in Embodiment 1. Similar tests 1) and 2) were conducted. The obtained results are shown in Tables 1 and 2.

Embodiment 7

Copper alloys including MX96, MX216, C1720, C5210 and C7250 which are widely utilized as contact materials, nickel-claded AISI Type 304 stainless steel and nickel-claded AISI Type 301 stainless steel were subjected to the spring characteristic tests. The obtained results are listed in Table 3.

Comparison 1

Nickel-claded stainless steel substrate which is a similar material as to that used in Embodiment 1 was subjected to tests 1) and 2) as performed on the material of Embodiment 1. The results of the tests are shown in Tables 1 and 2.

Comparison 2

After AISI Type 304 stainless steel (15.5 mm wide x 50 mm long x 0.2 mm thick) was electrolytically degreased at a temperature of 50°C in an alkali cyanide degreasing solution at 6 V for 15 seconds and the stainless steel substrate was activated by immersion treatment in a 10% sodium chloride aqueous solution for a time of 30 seconds. The activated substrate of stainless steel was then pre-treated for nickel strike plating by using the hydrochloric acid Watt bath. The pre-treated substrate was further plated with 3.0 µm thick nickel using a sulfonamide acid bath and 3.0 µm thick tin be means of employing a borofluoric bright bath. Plated samples were tested by similar tests 1) and 2) as those described for embodiment 1. The obtained results are shown in Tables 1 and 2.

Comparisons 3 ~ 5

After the activating treatment, pre-treating, and 3 µ m thick nickel strike plating an AISI Type 304 stainless steel substrate was similarly prepared as in Comparison 1, 2.0 µm thick silver plated samples prepared as in Embodiment 3 (Comparison 3), 1.0 µm thick palladium nickel plated and 0.05 µm thick gold plated samples as prepared in an Embodiment 4 (Comparison 4), and 0.2 µm thick gold plated samples prepared as in Embodiment 1 (Comparison 5). All samples prepared as noted above were subjected to similar tests 1) and 2) as performed in association with Embodiment 1. The obtained results are shown in Tables 1 and 2. Comparison 5 was, furthermore, subjected to test 3). Results are also shown in Figs 1(b), 2-(b), and 3(b).

Comparisons 6 and 7

After the pre-treated surface was gold strike plated using a hydrochloric acid cyanide gold potassium bath, samples were 0.2 µm thick gold plated using a similar plating bath as used for Embodiment 1 (Comparison 6). After activating in 10% sulfuric acid solution and pretreating in sulfuric acid cyanide gold potassium bath the sample was 0.2 µm thick gold strike plated using a similar bath as that which was used for Embodiment 1 (Comparison 7). The thus plated samples were subjected to similar tests 1) and 2) as for Embodiment 1. The obtained results are listed in Tables 1 and 2.

Comparison 8

AISI Type 304 stainless steel was subjected to similar tests 1) and 2) as those described for the Embodiment 1. Results are also listed in Tables 1 and 2.

Comparison 9

After a phosphor bronze sample (having the dimensions of 15.5 mm width x 50.0 mm length x 0.2 mm thickness) was degreased in a similar method as that done for the embodiment 1, and activated in a 10% sulfuric acid solution, the activated phosphor bronze was pre-treated with copper strike plating by means of an alkali cyanide copper plating bath. It was then 3.0 µm thick nickel plated and 3.0 µm thick tin plated according to a similar manner as that done for Comparison 2. Similar tests 1) and 2) as those employed for the Embodiment 1 were conducted. The obtained results are shown in Tables 1 and 2.

Comparison 10 ~ 12

After activating and pretreating a 3.0 µm thick nickel plated sample, similarly done for the Comparison 9, phosphor bronze was 2.0 m thick silver plated thereon using a similar bath to that used for Embodiment 3 (Comparison 10), 1.0 and a µm thick palladium nickel was plated thereon using a similar bath as for Embodiment 4 (Comparison 11), and 0.2 µm thick gold plated by using a similar bath as for Embodiment 1 (Comparison 12). All above plated surfaces were subjected to similar tests 1) and 2) as previously described for the Embodiment 1. The obtained results are listed in Tables 1 and 2.

Comparison 13

After degreasing and activating in 10% sulfuric acid solution, pre-treating for nickel strike plating, and plating with 3.0 µm thick nickel through the same manner done for Comparison 2, a substrate was 0.2 µm gold plated by using a similar bath the one used for Embodiment 1, and subjected to same tests 1) and 2) done for Embodiment 1. The obtained results are shown in Figs. 1(c), 2(c), and 3(c).

Comparison 14

Phosphor bronze was subjected to similar tests 1) and 2) as that described for the Embodiment 1. Results are also listed in Tables 1 and 2.

Table 1

		MAX	MIN	AVE	S. D
embodiments	1	2.6	1.1	1.5	0.01
	2	1.8	0.7	1.2	0.01
	3	24.9	2.1	14.4	0.10
	4	1.4	0.5	0.8	0.01
	5	2.3	0.9	1.4	0.01
	6	2.5	0.8	1.3	0.01
comparisons	1	32.0	6.9	11.3	0.02
	2	131.5	7.4	8.9	0.09
	3	3.6	0.6	1.0	0.01
	4	50.3	3.3	24.8	0.14
	5	9.2	0.7	2.6	0.01
	6	9.4	1.4	3.9	0.01
	7	9.3	1.2	3.7	0.01
	8	1967.2	33.3	371.4	0.45
	9	41.2	2.4	22.1	0.15
	10	1.3	0.4	0.6	0.01
	11	2.2	0.6	1.0	0.01
	12	2.0	0.9	1.2	0.01
	13	2.2	0.8	1.3	0.01
	14	93.1	12.9	30.3	0.04

Table 2

		salt spray test	sulfur dioxide gas	mixed gas
embodiments	1	◎	◎	◎
	2	◎	◎	◎
	3	× tin corroded	◎	◎
	4	◎	× brown, large	× black, large
	5	○	◎	◎
	6	◎	◎	◎
comparisons	1	△ red rust, small	× grey, large	× black, large
	2	× tin corroded	◎	◎
	3	◎	× brown	× black
	4	△ red rust, small	◎	◎
	5	△ red rust, small	◎	◎
	6	× red rust, large	◎	◎
	7	△ red rust, small	◎	◎
	8	× red rust, large	◎	◎
	9	× tin corroded	◎	◎
	10	◎	× brown, large	× black, large
	11	◎	◎	◎
	12	△ green, small	△ brown, small	△ black, small
	13	△ green, small	△ brown, small	△ black, small
	14	× green, large	× brown, large	× black, large

Note: Colors (red, black, green, and brown) indicate the color of corrosion products, and degree of each color's appearance is ranked as small or large.

Table 3

		MX 96	MX 216	C 1720	C 5210	C 7250	304-Ni	301-Ni
tensile strength (kg/mm^2)	H grade	73	74	76	66	59	106	152
	HT grade	112	112	140				
elongation (%), H grade		7	6	7	26	10	19	9
spring tolerance (kg/mm^2)		>100	>100	>100	49	51	>100	>100
0.2% offest yield strength (kgf/mm^2)		102	103	120	55	54	97	134
Vicker's hardness (Hv)		355	350	430	210	198	341	469
Young's modulus (kgf/mm^2)		12000	13000	12000	10000	12000	19700	19700
age-hardening conditions		400 °C × 2Hr	450 °C × 2Hr	315 °C × 2Hr				

From the above Tables, it was clearly found that the contact materials prepared through the present invention exhibit superior contact resistance characteristics, corrosion resistance, bending strength, and spring property over the conventional type of contact materials including copper, copper-based alloys, nickel-plated stainless steel when compared to other similar devices. Accordingly, it is suggested that the present contact materials can be applied to highly reliable components to which conventional types of contact materials are not readily adapted.

In the above, the present invention has been described on stainless steel clad with nickel or nickel-based alloys, but stainless steel surface can be vapor-deposited with nickel or nickel-based alloys to perform same functions.

Accordingly, since the nickel-claded stainless steel substrate of the present invention is plated with noble metals, tin or tin-based alloys, the contact materials exhibiting excellent characteristics in terms of corrosion resistance, contact resistance, bending strength, spring property, and ductility can be fabricated easily and inexpensively. AT the same time, anti-corrosion treatment after the press-forming process can be entirely avoided.

While this invention has been described in detail with reference to preferred embodiments disclosed herein, it should be understood that the invention is not limited to that precise embodiments; rather many modifications and variations would present themselves to those of skill in the art without departing from the scope and spirit of this invention, as defined in the appended claims.

Claims

1. A contact material exhibiting excellent properties in terms of corrosion resistance, contact resistance, bending strength, spring characteristics, and ductility; said contact material comprising a nickel-clad stainless steel substrate and at least one other layer at least partially plated thereon which is selected from the group consisting of noble metals, tin, and tin-based alloys.

2. A manufacturing method of a contact material exhibiting excellent properties in terms of corrosion resistance, contact resistance, bending strength, spring characteristics, and ductility; said contact material being at least partially plated with one other material selected from the group consisting of noble metals, tin and tin-based alloys upon a band-shaped nickel-clad stainless steel substrate material.

3. A manufacturing method of a contact material exhibiting excellent properties in terms of corrosion resistance, contact resistance, bending strength, spring characteristics, and ductility; said contact material being at least partially plated with one other material selected from a group consisting of noble metals, tin and tin-based upon a press-formed nickel-claded stainless steel substrate material.

F I G. 1

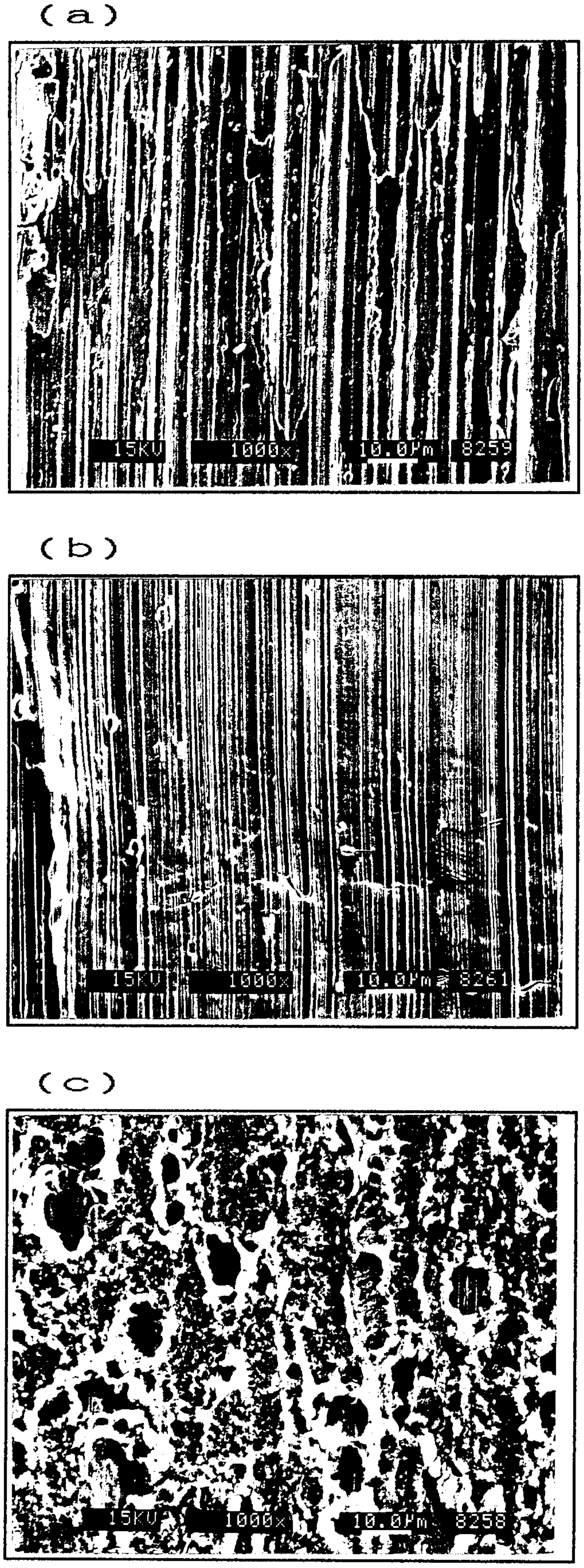
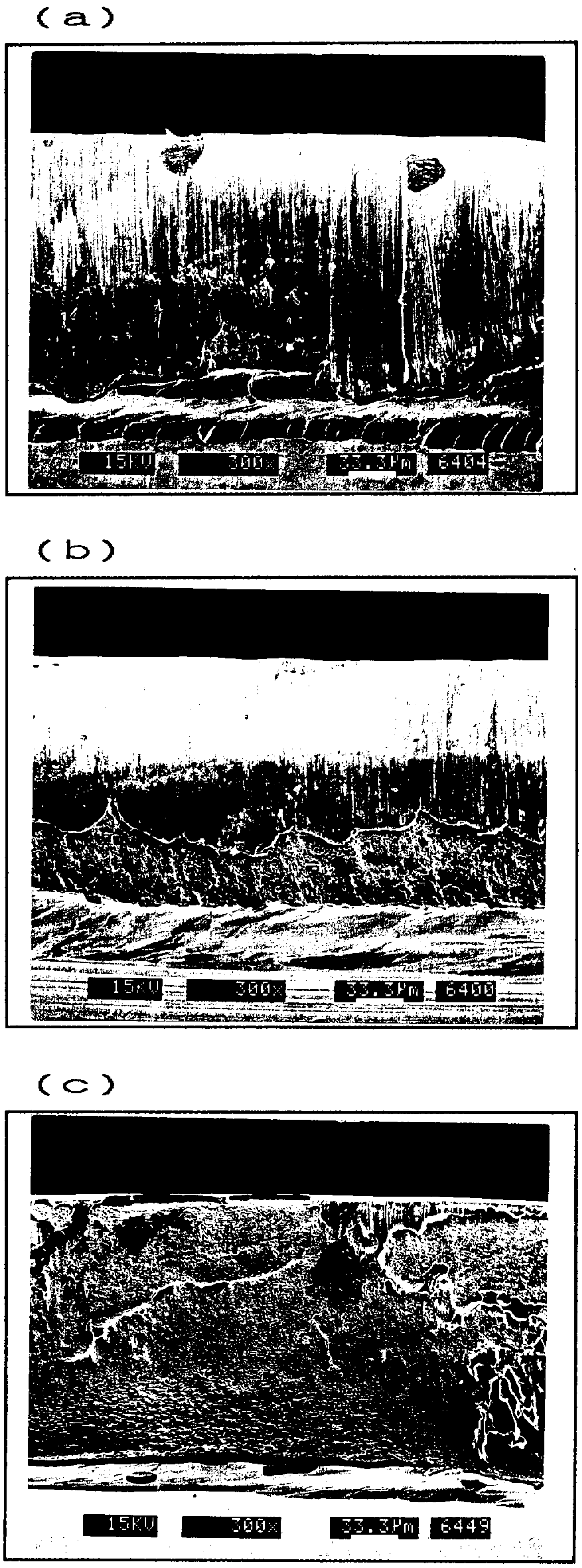

(a)
15KV
1000x
10.0µm
8259
(b)
15KV
1000x
10.0µm
8261
(c)
15KV
1000x
10.0µm
8258

FIG. 2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15KV
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6400
(c)
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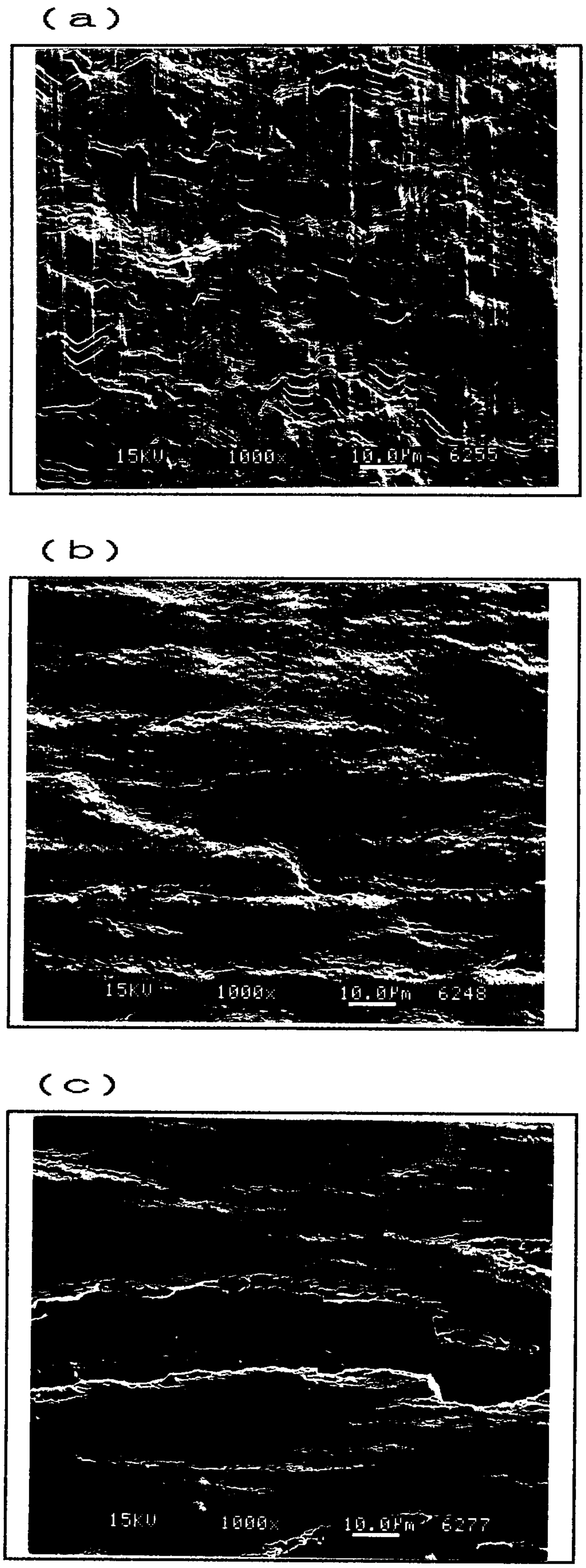
300x
33.3μm
6449

FIG. 3


(a)
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(b)
15KV 1000x 10.0μm 6248
(c)
15KV 1000x 10.0μm 6277