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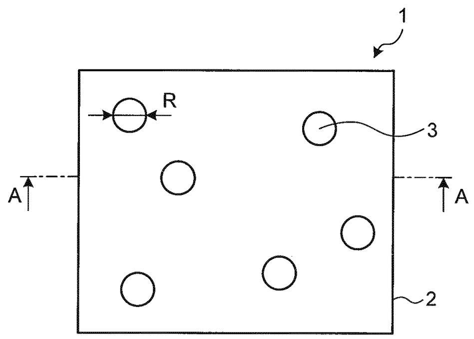
(54) METAL MATERIAL, AND SURFACE TREATMENT METHOD AND DEVICE

(57) A metallic material includes a metal substrate 2 and a modified layer formed on the surface of the metal substrate 2. The modified layer includes three or more protrusions in an area of 10 μm^2 on average protruding from the surface of the metal substrate 2. The protrusions have an average diameter of 1 μm or less when viewed in a direction perpendicular to the surface of the metal substrate. The modified layer may include one or more protrusions in an area of 10 μm^2 on average including a base part protruding from the surface of the metal substrate 2 and a tip part formed on the end of the base part, the protrusions having an average diameter of 1 μm or less when viewed in a direction perpendicular to the surface of the metal substrate 2 and a constricted structure with the outer diameter of the base part being smaller than the outer diameter of the tip part, thereby providing a metallic material having new functions such as hydrophilic properties and luminescence properties.

FIG.1A



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Description

Field

[0001] The present invention relates to a metallic material, a method for a surface treatment of a metallic material, a method for manufacturing a water-repellent material using a metallic material as a base, a surface treatment apparatus for an electroconductive material, and a method for a surface treatment of an electroconductive material.

Background

[0002] Recently, it has been intensely expected to impart new functions to metallic materials. Specifically, in addition to advantageous properties that metallic materials originally have, such as strength, workability, and corrosion resistance, new functions about metallic surfaces such as hydrophilic properties, water-repellency properties and luminescence properties are greatly expected in developing a new field of use of metallic materials. In view of these circumstances, recently, researches have been extensively conducted that form modified layers such as a plated layer, an oxidized layer, a surface-hardened layer, and a modified layer with improved surface roughness on metallic surfaces. For example, there are surface treatment techniques forming microstructures by anodic oxidation (refer to Non Patent Literature 1) and forming surface microstructures by electrochemical machining (refer to Non Patent Literature 2).

Citation List

Non Patent Literature

[0003] Non Patent Literature 1: Hideaki TAKAHASHI; Masatoshi SAKAIRI; Tatsuya KIKUCHI; and Himendra JHA, Hyomen Gijutsu, vol. 60 (2009) No. 3, p. 14

[0004] Non Patent Literature 2: Wataru NATSU, "Application and Theory of Micro Electrochemical Machining," Hyomen Gijutsu, vol. 61 (2010) No. 4, p. 294 Summary

Technical Problem

[0005] In order to impart new functions such as hydrophilic properties, water-repellency properties, and luminescence properties to metallic material surfaces, it is required to design the structure and composition of surface modified layers from a microscopic point of view of 1 μm or less. Conventional researches, however, aiming at improving functions such as workability and corrosion resistance, have designed the structure and composition of surface modified layers on a micron scale, and they have been insufficient for the exhibition of the new functions. As a method for improving surface roughness, for example, a method has been proposed that presses a dull roll against a metallic material surface. However, asperities on the metallic material surface formed by this method have a size on the order of micron or more. Given this situation, although the surface of the metallic material has the effects of improving workability by oil retention, and giving uniform surface appearance, it exhibits no new function. As a method for improving coating adhesion of outer plates for automobiles, a method has been proposed that forms phosphoric crystals on the surface of a metallic material. The particle diameter of the phosphoric crystals formed by this method, however, has a size of a few microns. Given this situation, the metallic material surface exhibits no new function.

[0006] Among the reported techniques for forming microstructures, anodic oxidation of metallic materials disclosed in Non Patent Literature 1 forms microscopic pours on the surface, which limits functions to be imparted. In addition, the surface becomes an oxidized layer, and the surface properties are limited by the type of oxides. Electromechanical machining method disclosed in Non Patent Literature 2 demands to remarkably reduce the distance between a target surface and a counter electrode close as much as possible in order to form surface microstructures, but the control is extremely difficult.

[0007] The present invention has been achieved in view of the above circumstances, and an object thereof is to provide a metallic material having new functions such as hydrophilic properties and luminescence properties.

[0008] Another object of the present invention is to provide a method for a surface treatment of high water-repellency properties of a metallic material and a method for manufacturing the water-repellent material, without requiring much labor and cost.

[0009] Still another object of the present invention is to provide method and apparatus for forming nano-level microstructures in a surface specific part or in a surface wide area of an electroconductive material at a low cost and efficiency.

Solution to Problem

[0010] A metallic material according to the present invention includes: a metal substrate; and a modified layer formed on a surface of the metal substrate, wherein the modified layer includes three or more protrusions in an area of 10 μm^2 on average protruding from the surface of the metal substrate, the protrusions having an average diameter of 1 μm or less when viewed in a direction perpendicular to the surface of the metal substrate.

[0011] In the above-described metallic material according to the present invention, the modified layer includes, in an area of 10 μm^2 on average, one or more protrusions including a base part protruding from the surface of the metal substrate and a tip part formed on the end of the base part, the protrusions having an average diameter of 1 μm or less when viewed in a direction perpendicular to the surface of the metal substrate and a constricted structure with the outer diameter of the base part being smaller than the outer diameter of the tip part.

[0012] In the above-described metallic material according to the present invention, the average diameter of the protrusions is 500 nm or less when viewed in a direction perpendicular to the surface of the metal substrate.

[0013] In the above-described metallic material according to the present invention, positions on which the protrusions are formed have no periodicity in the in-plane direction of the metal substrate.

[0014] In the above-described metallic material according to the present invention, the modified layer includes recesses having an average diameter of 500 nm or less when viewed in a direction perpendicular to the surface of the metal substrate.

[0015] In the above-described metallic material according to the present invention, the metal substrate is formed of alloy steel.

[0016] In the above-described metallic material according to the present invention, the metal substrate is formed of a steel material.

[0017] In the above-described metallic material according to the present invention, the metal substrate has a composition different from that of the protrusions.

[0018] In the above-described metallic material according to the present invention, the metal substrate and the protrusions are connected continuously.

[0019] A method for surface treatment of a metallic material according to a first aspect of the present invention includes: immersing a target material as a cathode electrode formed of a metallic material having a target surface and an anode electrode into an electrolytic solution; applying a voltage that is 70 V or more and is in such a range that does not oxidize or melt the target material between the cathode electrode and the anode electrode to form microstructures on the target surface; taking the target material out of the electrolytic solution and washing the target material; and performing a water-repellent treatment on the target surface of the washed target material.

[0020] A method for surface treatment of a metallic material according to a second aspect of the present invention includes: immersing a target material as a cathode electrode formed of a metallic material having a target surface and an anode electrode into an electrolytic solution; applying a voltage of 70 V or more and 200 V or less between the cathode electrode and the anode electrode to form microstructures on the target surface; taking the target material out of the electrolytic solution and washing the target material; and performing a water-repellent treatment on the target surface of the washed target material.

[0021] A method for manufacturing a water-repellent material using a metallic material as a base according to the present invention includes: immersing a metallic material as a target material as a cathode electrode having a target surface and an anode electrode into an electrolytic solution; applying a voltage of 70 V or more and 200 V or less between the cathode electrode and the anode electrode to form microstructures on the surface of the metallic material as the target material; taking the metallic material out of the electrolytic solution and washing the metallic material; and performing a water-repellent treatment on the target surface of the washed metallic material.

[0022] A surface treatment apparatus for an electroconductive material according to the present invention includes: an anode electrode and a cathode electrode formed of an electroconductive material that are immersed into an electrolytic solution spaced apart from each other; a shield that is interposed between the anode electrode and the cathode electrode and has an opening that limits a part to be treated of the cathode electrode; and a power supply that applies a voltage between the anode electrode and the cathode electrode.

[0023] The above-described surface treatment apparatus for an electroconductive material according to the present invention further includes a mechanism that changes the position of the opening and/or the relative positions of the anode electrode and the cathode electrode.

[0024] In the above-described surface treatment apparatus for an electroconductive material according to the present invention, the power supply applies a voltage of 60 V or more and 300 V or less between the anode electrode and the cathode electrode.

[0025] In the above-described surface treatment apparatus for an electroconductive material according to the present invention, the shield is an insulating heat-resistant material provided with the opening that is covered with the surface of the cathode electrode.

[0026] In the above-described surface treatment apparatus for an electroconductive material according to the present invention, the electroconductive material is a metallic material.

[0027] A method for surface treatment of an electroconductive material according to the present invention includes modifying a surface of an electroconductive material using the surface treatment apparatus for an electroconductive material according to the present invention.

Advantageous Effects of Invention

[0028] The metallic material according to the present invention can provide a metallic material having new functions such as hydrophilic properties and luminescence properties.

[0029] The method for treating the surface of a metallic material and the method for manufacturing a water-repellent material using a metallic material as a base according to the present invention can impart high water-repellency properties to a metallic material surface without requiring much labor and cost.

[0030] The surface treatment apparatus and a method for surface treatment of an electroconductive material according to the present invention can manufacture an electroconductive material formed with nano-level microstructures in a surface specific part or in a surface wide area at low cost and efficiently.

Brief Description of Drawings

[0031]

FIG. 1A is a plan view illustrating a structure of a metallic material as an embodiment according to the present invention.

FIG. 1B is A-A line sectional view of FIG. 1A.

FIG. 2 is a scanning electron microscope (SEM) photograph illustrating an example of protrusions formed on the surface of a cold-rolled steel sheet.

FIG. 3 is a schematic diagram for illustrating a method for calculating the outer diameter of a protrusion.

FIG. 4 is a schematic diagram for illustrating a constricted structure of a protrusion.

FIG. 5 is a SEM photograph illustrating an example of a protrusion having a constricted structure formed on a cold-rolled steel sheet.

FIG. 6 is a cross-sectional TEM photograph illustrating an example of a protrusion having a constricted structure formed on a cold-rolled steel sheet.

FIG. 7 is a SEM photograph illustrating an example of recesses formed on the surface of stainless steel.

FIG. 8 is a SEM photograph illustrating an example of recesses formed on the surface of stainless steel.

FIG. 9 is a cross-sectional TEM photograph illustrating an example of a protrusion having a different composition from that of a base.

FIG. 10 is a cross-sectional TEM photograph illustrating that a protrusion is formed on a cold-rolled steel sheet continuously.

FIG. 11 is a flowchart illustrating the flow of a surface treatment on a metallic material as an embodiment according to the present invention.

FIG. 12 is a schematic diagram illustrating an example of the configuration of an apparatus for use in a method for surface treatment of a metallic material as an embodiment according to the present invention.

FIG. 13 is a SEM photograph illustrating the surface of SUS316L stainless steel performed by the surface treatment.

FIG. 14 is a side-view photograph of distilled water dropped on the surface of the stainless steel illustrated in FIG. 13 after being subjected to a water-repellent treatment.

FIG. 15 is a schematic diagram illustrating the configuration of a surface treatment apparatus for an electroconductive material as an embodiment according to the present invention.

FIG. 16 is a schematic diagram illustrating a modification of the surface treatment apparatus for an electroconductive material illustrated in FIG. 15.

FIG. 17 is a schematic diagram illustrating a modification of the surface treatment apparatus for an electroconductive material illustrated in FIG. 15.

FIG. 18 is a diagram illustrating the configuration of an opening.

FIG. 19A are photographs illustrating secondary electron images of the longitudinal left part of an opening when 150 V is applied between an anode electrode and a cathode electrode.

FIG. 19B are photographs illustrating secondary electron images of the longitudinal central part of the opening when 150 V is applied between the anode electrode and the cathode electrode.

FIG. 19C are photographs illustrating secondary electron images of the longitudinal right part of the opening when 150 V is applied between the anode electrode and the cathode electrode.

FIG. 20 is a photograph illustrating the appearance of a cathode electrode after being treated when the dimensions of openings are 5 mm×5 mm and 5 mm in diameter.

FIG. 21 is a photograph illustrating a SEM image of the surface of the cathode electrode after being treated when the dimension of an opening is 5 mm in diameter.

FIG. 22 is a photograph illustrating a SEM image of the surface of the cathode electrode without any surface treatment performed.

Description of Embodiments

Metallic Material

[0032] FIGS. 1A and 1B are a plan view illustrating a structure of a metallic material as an embodiment according to the present invention and A-A line cross-sectional view of FIG. 1A, respectively. As illustrated in FIGS. 1A, 1B, this metallic material 1 as an embodiment according to the present invention includes a base 2 and protrusions 3 as a modified layer formed on the surface of the base 2. The base 2 is formed of a metallic material. Examples of the metallic material may include alloy steel including stainless steel, steel sheets such as cold-rolled steel sheets containing Fe, C, and alloy elements as needed in a minute amount such as 3% by mass or less, mild steel sheets, high-strength steel sheets with a tensile strength of around 2 GPa, and hot-rolled steel sheets. Examples of the shape of the base 2 may include, but not limited to, a sheet shape, a rod shape, a line shape, and a pipe shape. The base 2 may be constructed by welding plural pieces. When the base 2 is a sheet shape, its sheet thickness is not limited; available are from a metallic foil with a thickness of 100 μm or less to a thick steel sheet with a thickness of 3 mm or more.

[0033] The protrusions 3 are formed from microstructures protruding from the surface of the base 2 having an average diameter R of 1 μm and preferably 500 nm or less when viewed in a direction perpendicular to the surface of the base 2. FIG. 2 is a scanning electron microscope (SEM) photograph illustrating an example of protrusions formed on the surface of a cold-rolled steel sheet. In the photograph, the objects indicated by the arrows are the protrusions 3. The protrusions 3 were formed by applying a voltage of 135 V for 30 minutes in an aqueous K_2CO_3 solution with a concentration of 0.3 mol/L between the cold-rolled steel sheet and a platinum electrode as a cathode electrode and an anode electrode, respectively. In this case, as illustrated in FIG. 3, the average diameter R of the protrusions 3 when viewed in a direction perpendicular to the surface of the cold-rolled steel sheet was determined as a diameter R of the imagining circle C, which has the same area as the area surrounded by the contour of the protrusion 3. Three or more such protrusions 3 are formed in an area of 10 μm^2 on average, thereby imparting luminescence properties and hydrophilic properties to the surface of the base 2. By enhancing hydrophilic properties, droplets are hard to form on metallic surfaces, resulting in a cleaning effect that resists adhesion of contamination such as organic substances, and various applications can be expected such as a light reflecting plate whose reflection intensity is less likely to drop. Although the in-plane distribution of the protrusions 3 is not limited, not having specific periodicity is advantageous in manufacture. In order to manufacture a surface on which the protrusions 3 have periodicity in a row manner, for example, excessive processes are required, which is disadvantageous in manufacture.

[0034] As illustrated in FIG. 4, when the protrusions 3 have a structure in which the outer diameter Lrmin of a base part 3a is smaller than the outer diameter Lrmax of a tip part 3b, that is a constricted structure, the specific surface area and internal pours of the base 2 become apparently larger than a structure having no constricted structure. This can further improve hydrophilic properties, which are influenced by the specific surface area. It can be expected that the protrusions 3 having the constricted structure have the effects of imparting chemical reactions on the surface and facilitating functions therefor to the surface of the base 2 and improving adhesion of a thin film layer formed on the surface of the base 2. For this purpose, it is desirable to form one or more protrusions 3 in an area of 10 μm^2 on average. Because a larger specific surface area gives higher hydrophilic properties, it is advantageous to reduce the size of the protrusions and increase the number of the protrusions. Because a surface having constricted protrusion structures has a further larger specific surface area, hydrophilic properties further improve.

[0035] The protrusions 3 having the constricted structure can be verified by (1) preparing a cross-sectional specimen of a metallic material surface by the focused ion beam (FIB) method or other methods and observing the cross-sectional specimen by a SEM or a transmission electron microscope (TEM), (2) tilting a metallic material and observing it by a SEM, or other devices. FIG. 5 is a SEM photograph illustrating an example of the protrusion 3 having the constricted structure formed on a cold-rolled steel sheet. This is an image taken by tilting a specimen by 70 degrees. FIG. 6 is a cross-sectional TEM image illustrating an example of the protrusion 3 having the constricted structure formed on a cold-rolled steel sheet. The protrusion having the constricted structure means a structure in which the outer diameter Lrmin of the base part 3a is 90% or less of the outer diameter Lrmax of the tip part 3b as expressed by Formula (1) below and preferably the outer diameter Lrmin of the base part 3a is 80% or less of the outer diameter Lrmax of the tip part 3b as expressed by Formula (2) below. For the example illustrated in FIG. 5, the value of Lrmin/Lrmax was 0.38, whereas for the example illustrated in FIG. 6, the value of Lrmin/Lrmax was 0.62. The outer diameter Lrmin of the base part 3a is the minimum diameter of the base part 3a when the base part 3a is viewed in a direction perpendicular to the surface of the metal substrate, whereas the outer diameter Lrmax of the tip part 3b is the maximum diameter of the tip part 3b when viewed in a direction perpendicular to the surface of the metal substrate.

$$Lr\ \min/Lr\ \max \leq 0.9 \qquad (1)$$

$$Lr\ \min/Lr\ \max \leq 0.8 \qquad (2)$$

[0036] It is desirable that in addition to the protrusions 3, recesses having an average diameter of 1 μm or less and preferably 500 nm or less be formed on the surface of the base 2 when viewed in a direction perpendicular to the surface of the base 2. By forming the recesses in addition to the protrusions 3, the surface area of the metallic material can be further increased, thereby improving luminescence properties and hydrophilic properties of the metallic material surface. By the presence of the recesses besides the projections, lubricating oil and functional liquid can be held in a larger amount and for the long term, thereby imparting the new functions to the surface of the base 2.

[0037] FIG. 7 and FIG. 8 are SEM photographs illustrating examples of the recesses formed on the surface of stainless steel. FIG. 7 illustrates an observation of the metallic material from immediately above the metallic material surface, whereas FIG. 8 illustrates an observation of the metallic material with the metallic material tilted by 60 degrees. The recesses illustrated in FIG. 7 and FIG. 8 were formed by applying a voltage of 115 V for 30 minutes in an aqueous K_2CO_3 solution with a concentration of 0.1 mol/L between SUS430 stainless steel and a platinum electrode as a cathode electrode and an anode electrode, respectively. The arrows in the photographs indicate the recesses. As is evident from FIG. 7 and FIG. 8, the recesses having a dimension of about from 200 nm to 500 nm are formed everywhere on the stainless steel surface.

[0038] The material forming the protrusions 3 may have the same composition as that of the base 2 or may have a different composition therefrom, which can be used in accordance with a purpose. FIG. 9 is a cross-sectional TEM photograph illustrating an example of the protrusion 3 having a different composition from the composition of the base 2. In the example illustrated in FIG. 9, the base 2 is formed of SUS316 stainless steel, whereas the Cr concentration of the protrusion 3 is lower than the Cr concentration of the base 2. It is expected from such a structure that the catalytic function of Ni can be used more effectively while taking the advantages of the SUS316 stainless steel. As an example, it can be used as a steam reforming catalyst with Ni as an active component as it is. In this case, it is known that Cr reduces the catalytic performance, and it is expected that the influence of Cr can be reduced. The protrusion structure according to the present invention has a large specific surface area, and it is excellent in heat exchangeability. This is also advantageous as a catalytic reaction base.

[0039] It is desirable that the base 2 and the protrusions 3 be continuous to each other. The base 2 and the protrusions 3 being continuous to each other, the strength of the protrusions 3 can be enhanced. FIG. 10 is a cross-sectional TEM photograph illustrating that a protrusion is formed on a cold-rolled steel sheet continuously. Although not illustrated, analysis of crystal orientation on the area R1 of the protrusion 3 and the area R2 of the base 2 revealed that the protrusion 3 was a single crystal and had nearly the same crystal orientation as that of the base 2. Such a continuous structure is stable against mechanical actions and chemical actions, and the protrusions 3 are less likely to drop. In addition, such a continuous structure is also effective when heterogeneous substances or heterogeneous elements are not desired to be used for the protrusions 3. Such a continuous structure can be formed using steel materials or metals containing a smaller amount of easily oxidizable alloy elements (e.g., Cr) as the base 2.

[0040] As a method for manufacturing the metallic material 1 having such a structure, discharge in an electrolytic solution can be used for manufacturing the metallic material 1. Specifically, a DC voltage of about from 60 V to 140 V is applied to electrodes in an electrolytic solution between a target material and inactive metal such as platinum as a cathode electrode and an anode electrode, respectively. The range of the application voltage varies by the target material and can be easily determined while checking the surface structure of the target material with a SEM. By changing the treatment time and the application voltage within appropriate ranges, the average diameter of the protrusions can be controlled. Specifically, for the same material, a higher application voltage, a longer treatment time, and a deeper position from the liquid surface of the electrolytic solution can increase the average diameter of the protrusions.

[0041] However, when the application voltage is a value that gives a perfect plasma state, the surface of iron or stainless steel is excessively melted or oxidized, and the microscopic protrusion structures are difficult to form. In order to impart the constricted structure, it is required to select a condition of high energy density to the extent that the surface is not excessively melted or oxidized. As an example, it is effective to set the application voltage to be higher or to reduce an area to be treated so that an electric field will be concentrated. In this case also, a preferable condition can be determined by comparing SEM observation results of treated surfaces with treatment conditions. The Ni-rich, Cr-poor protrusion structure illustrated in FIG. 9 can be formed by setting a discharge voltage to be higher. In addition, the protrusion structure is prepared in advance, and an element is then supplied in a solution, thereby imparting the new element to the surface. The "perfect plasma state" indicates a state in which luminescence mixed with orange or luminescence mainly consisting of orange covers the cathode electrode surface during discharge.

Example 1

[0042] A mild cold-rolled steel sheet (CRS, dimensions: 2 mmx20 mm×0.7 mm) and Pt as a cathode electrode and an anode electrode, respectively, were immersed into an aqueous K_2CO_3 solution with a concentration of 0.3 mol/L, and different application voltages were applied between the cathode electrode and the anode electrode to prepare specimens. The surface of the mild cold-rolled steel sheet after the voltage application was observed with a SEM, and the average diameter and density of protrusions formed on the surface were measured. During the process, in order to observe how the treatment varied by the depth from the liquid surface of the aqueous solution, for a partial specimen, a sample was cut out of the mild cold-rolled steel sheet at a different depth from the liquid surface, and surface observation was performed therefor. The average diameter of the protrusions is the average value of the diameters of 20 protrusions arbitrarily selected in the range of 12 μm × 9 μm arbitrarily selected, whereas the density is the number of protrusions per 10 μm^2 determined by dividing the number of protrusions existing in the above range by 108 μm^2 (=12 μm×9 μm) and multiplying the result by 10 μm^2. Table 1 lists the measurement results. The specimen of Experiment No. 1-7 listed in Table 1 is a mild cold-rolled steel sheet before the above voltage application in the aqueous solution. As is evident from a comparison between the specimens of Experiment Nos. 1-1 to 1-6 and the specimen of Experiment No. 1-7 listed in Table 1, it has been found out that the voltage application treatment can achieve a modified layer having protrusions according to the present invention. It has been found out that reducing the application voltage can reduce the average diameter of the protrusions and increase the density of the protrusions. It has been found out that reducing the distance from the liquid surface to the target surface such as No. 1-6 can also reduce the average diameter of the protrusions and increase the density of the protrusions.

Table 1

Experiment No.	Voltage (V)*time (minutes)	Depth from liquid surface (mm)	Average protrusion diameter (nm)	Protrusion density (pieces/10 μm^2)	Remarks
1-1	100 V*30 minutes	20	278	50	Inventive example
1-2	115 V*30 minutes	20	315	30	Inventive example
1-3	125 V*30 minutes	20	474	9	Inventive example
1-4	130 V*30 minutes	20	611	6	Inventive example
1-5	130 V*30 minutes	20	729	5	Inventive example
1-6	115 V*30 minutes	10	131	98	Inventive example
1-7	No treatment	-	-	0	Comparative example

Example 2

[0043] SUS316 stainless steel (dimensions: 25 mmx2.5 mm×0.8 mm) and Pt as a cathode electrode and an anode electrode, respectively, were immersed into an aqueous K_2CO_3 solution with a concentration of 0.3 mol/L, and different application voltages were applied between the cathode electrode and the anode electrode to prepare specimens. The surface of the SUS316 stainless steel after the voltage application was observed with a SEM, and the average diameter and density of protrusions formed on the surface were measured in the same manner as Example 1. During the process, in order to observe how the treatment varied by the depth from the liquid surface of the aqueous solution, for partial specimens, a sample was cut out of the mild cold-rolled steel sheet at a different depth from the liquid surface, and surface observation was performed therefor. Photoluminescence of the surface of the SUS316 stainless steel after the voltage application was measured. An apparatus, FP6200, manufactured by JASCO Corporation was used to perform measurement, with a starting wavelength of 350 nm, an ending wavelength of 600 nm, and an excitation wavelength of 435 nm. Specifically, in a photoluminescence spectrum obtained from the stainless steel surface after the voltage application, an emission peak centered around the wavelength of 430 nm, which was not observed for a photoluminescence spectrum obtained from the stainless steel surface before the voltage application, was observed. Given this situation, in the present example, the intensity at this emission peak was measured in the photoluminescence measurement. Evaluation was performed with the height of the emission peak of Experiment No. 2-5 for which the maximum emission intensity was obtained in the present example being 10 and with the height of the emission peak of Experiment No. 2-7 that was untreated and for which no emission peak was observed being 0. Table 2 lists the evaluation results. As listed in Table 2, it has been found out that the stainless steel surface (the specimens of Experiment Nos. 2-1 to 2-5) having the protrusions according to the present invention has higher luminescence properties than that of the stainless steel surface (the specimen of Experiment No. 2-7) having no protrusion or the specimen of Experiment No. 2-6 having protrusions exceeding 1,000 nm by far. A smaller sized protrusion gave higher luminescence properties, and an average diameter of the protrusions of 500 nm or less gave particularly high luminescence properties. It is expected from these results that the stainless steel having the protrusions according to the present invention can be used as a metallic material of display elements or elements utilizing light in the visible light range.

Table 2

Experiment No.	Voltage (V)*time (minutes)	Depth from liquid surface (mm)	Average protrusion diameter (nm)	Protrusion density (pieces/10 μm^2)	Luminous intensity	Remarks
2-1	115 V*30 minutes	20	980	3	2.5	Inventive example
2-2	115 V*30 minutes	15	211	50	5.25	Inventive example
2-3	115 V*30 minutes	10	137	120	7.3	Inventive example
2-4	100 V*30 minutes	20	450	12	4.5	Inventive example
2-5	100 V*30 minutes	10	50	260	10	Inventive example
2-6	150 V*30 minutes	20	2,000	1.5	0.2	Comparative example
2-7	No treatment	-	-	0	0	Comparative example

Example 3

[0044] SUS316 stainless steel (1 mm thickx2.5 mm widex30 mm long) was used. The surface was mirror-polished with Dia-Lap ML-150P. This stainless steel and Pt as a cathode electrode and an anode electrode, respectively, were immersed into an aqueous K_2CO_3 solution with a concentration of 0.1 mol/L, and different application voltages were applied between the cathode electrode and the anode electrode for 15 minutes to prepare specimens. The electrode (SUS316 stainless steel) after the experiment was thoroughly rinsed with distilled water and thoroughly dried. A contact angle measurement experiment was performed for the surface at three parts with a depth from the liquid surface of 30 mm, 28 mm, and 26 mm. One microliter of distilled water (manufactured by Wako Pure Chemical Industries, Ltd.) was dropped on the surface with a micropipette, and each of the droplets was photographed with a camera (EOS Kiss X2 manufactured by Canon Inc.) from just beside. Height (h) and contact length (1) of the droplets were measured from the photograph. The contact angle (θ_R) of each of the droplets was determined from $\theta_R=2\tan^{-1}(2h/l)$, and the average value thereof was calculated, which was determined as the contact angle of the part with a depth from the liquid surface of 30 mm.

[0045] After the contact angle measurement experiment finished, the specimen was thoroughly dried, and the average diameter and measured of the protrusions formed on the surface were evaluated in the same manner as Example 1. In order to evaluate to what extent the surface area of the obtained specimen increased with respect to a flat surface, the surface area of the specimen when the surface area of the flat surface was set to be 1 was calculated as a specific surface area based on the following assumption. Specifically, with the assumption that semispherical protrusions having the average diameter determined as above exist on the flat surface with the density determined as above, it was calculated what multiple the surface area was with respect to the flat surface. Table 3 lists the results. As listed in Table 3, it has been found out that the inventive examples within the range of the present invention result in smaller contact angles and improved hydrophilic properties compared with a specimen (Experiment No. 3-1) that is untreated and does not have the modified layer according to the present invention or a specimen (Experiment No. 3-6) whose properties of the modified layer are out of the range of the present invention.

Table 3

Experiment No.	Voltage (V)*time (minutes)	Depth from liquid surface (mm)	Average protrusion diameter (nm)	Protrusion density (pieces/ 10μm^2)	Specific surface area	Contact angle (°)	Remarks
3-1	No treatment	-	-	0	1.00	77.2	Comparative example
3-2	110 V*15 minutes	30	340	49	2.22	51.6	Inventive example
3-3	125 V*15 minutes	30	350	27	1.79	62.5	Inventive example
3-4	130 V*15 minutes	30	550	13	1.98	58.9	Inventive example
3-5	140 V*15 minutes	30	780	3	1.04	73	Inventive example
3-6	165V*315 minutes	30	1,500	1	1.01	76.8	Comparative example

Example 4

[0046] A mild cold-rolled steel sheet (dimensions: 1.5 mm×20 mm×0.7 mm) and Pt as a cathode electrode and an anode electrode, respectively, were immersed in to an aqueous K_2CO_3 solution with a concentration of 0.3 mol/L, and an application voltage of 110 V was applied between the cathode electrode and the anode electrode for 30 minutes to prepare a specimen. In the present example, the width of the specimen was 1.0 mm, which was different from that of Examples 1 and 2 in order to concentrate an electric field. After the voltage application, a contact angle of one place for a part of 15 mm depth from the liquid surface was measured in the same manner as Example 3. The result of the contact angle was 45°. After the measurement of the contact angle, the specimen was dried, the surface of the same part was observed with a SEM, and the average diameter and density of the protrusions formed on the surface were measured in the same manner as Example 1. FIG. 5 illustrates a representative SEM photograph. The evaluation revealed that the average diameter of the protrusions in a plan view was 350 nm. The density of the protrusions having the constricted structure was measured. The density of the protrusions having the constricted structure was determined by counting the number of the protrusions having the constricted structure existing in the same part (range) as the part in which the average diameter and density of the protrusions have been measured and calculating an average number per 10 μm^2 in the same manner as the density of the protrusions. It has been found out that three protrusions having the constricted structure on average exist.

Example 5

[0047] A mild cold-rolled steel sheet (dimensions: 1.5 mm×20 mm×0.7 mm) and Pt as a cathode electrode and an anode electrode, respectively, were immersed in to an aqueous K_2CO_3 solution with a concentration of 0.3 mol/L, and an application voltage of 95 V was applied between the cathode electrode and the anode electrode for 10 minutes to prepare a specimen. After the voltage application, a contact angle of one place for a part of 15 mm depth from the liquid surface was measured in the same manner as Example 3. The result of the contact angle was 60°. After the measurement of the contact angle, the specimen was dried, the surface of the same part was observed with a SEM, and the average diameter and density of the protrusions and the density of the protrusions having the constricted structure formed on the surface were measured in the same manner as Example 1. It has been found out from the evaluation that the average diameter of the protrusions in a plan view is 350 nm and that one protrusion having the constricted structure on average exists within an area of 10 μm^2.

Example 6

[0048] Steel containing 6% by mass of C, 2% by mass of Si, and 2% by mass of Cr was subjected to hot rolling, and the Vickers hardness at 25 g of its section was evaluated to be 900, which was found to be ultrahigh strength steel of around 2 GPa. This steel material cut into the dimensions of 1 mm×20 mm×0.7 mm and Pt as a cathode electrode and an anode electrode, respectively, were immersed in to an aqueous K_2CO_3 solution with a concentration of 0.1 mol/L, and an application voltage of 110 V was applied between the cathode electrode and the anode electrode for 30 minutes. After the voltage application, the surface of the mild cold-rolled steel sheet at a part of 18 mm depth from the liquid surface was observed with a SEM, and the average diameter and density of the protrusions and the density of the protrusions having the constricted structure formed on the surface were measured. It has been found out from the result that the average diameter of the protrusions in a plan view is 400 nm and two protrusions having the constricted structure on average exist within an area of 10 μm^2.

Method for Surface Treatment of Metallic Material

[0049] FIG. 11 is a flowchart illustrating the flow of a surface treatment on a metallic material as an embodiment according to the present invention. FIG. 12 is a schematic diagram illustrating an example of the configuration of an apparatus for use in a method for surface treatment of a metallic material as an embodiment according to the present invention. As illustrated in FIG. 11, in the surface treatment on a metallic material as an embodiment according to the present invention, firstly a metallic material that is a target material is immersed and served as a cathode electrode into an electrolytic solution with an anode electrode, and a voltage is applied between the cathode electrode and the anode electrode, thereby forming microstructures on the surface of the target material (Step S1). Specifically, as illustrated in FIG. 12, an anode electrode 13 and a target material 14 are immersed into an electrolytic solution 12 in a container 11, and a voltage is applied between the anode electrode 13 and the target material 14 from a power supply 16 through a conducting wire 15 such as a copper wire, thereby forming the microstructures on the surface of the target material 14.

[0050] The electrolytic solution 12 is, but not limited to, a solution that has electroconductivity and, during the surface treatment on the surface of the target material 14, hardly etches the surface of the target material 14 excessively, adheres to or precipitates on the surface of the anode electrode 13 and the target material 14, and forms a sediment. Examples of the electrolyte of the electrolytic solution 12 may include potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), sodium hydrogencarbonate ($NaHCO_3$), ammonium carbonate ($(NH_4)_2CO_3$), lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide (NH_4OH), sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride (NH_4Cl), sodium salts of sulfuric acid, potassium salts of sulfuric acid, ammonium salts of sulfuric acid, sodium salts of nitric acid, potassium salts of nitric acid, ammonium salts of nitric acid, sodium salts of citric acid such as sodium citrate ($NaH_2(C_3H_5O(COO)_3)$), potassium salts of citric acid, ammonium salts of citric acid, nitric acid, and hydrochloric acid.

[0051] The electrolytic solution 12 may have any pH and concentration so long as it can modify the surface of the target material 14. When an aqueous potassium carbonate solution is used as the electrolytic solution 12, for example, its concentration may be, but not limited to, 0.001 mol/L or more and more preferably 0.005 mol/L or more. This is because when the concentration of the electrolytic solution 12 is too low, it may be difficult to maintain a favorable discharge state when a voltage is applied between the anode electrode 13 and the target material 14. The upper limit of the concentration of the electrolytic solution 12 may be, but not limited to, 0.5 mol/L or less, for example. The pH of the electrolytic solution 12 may be any value so long as excessive corrosion or etching of the electrodes does not occur and may be from 10 to 12, for example.

[0052] The anode electrode 13 is formed of a material that is thermally and chemically stable on discharge. Examples of the anode electrode 13 may include Pt, Ir, and graphite.

[0053] The target material 14 is not limited so long as it is a metallic material. When it is a steel material, examples of the steel material may include cold-rolled materials, hot-rolled materials, cast materials, and machined (including welded) objects thereof. The type of the steel is not limited; examples of the steel may include carbon steel, low-alloy steel, and stainless steel. Other examples may include plated steel sheets such as electrogalvanized steel sheets. The shape of the target material 14 is not limited and may be formed in a sheet shape, a wire shape, a rod shape, or a pipe shape, or may be a machined component. The target material 14 is required to be immersed into the electrolytic solution 12 and is required to be at least deeper from the liquid surface by 1 mm or more.

[0054] A discharge condition can be in the range of from a partial plasma state in which asperities are formed on the surface of the target material 14 to the perfect plasma state. However, the discharge condition is required to be performed at a voltage range lower than a voltage at which the target material 14 melts. Specifically, the range is from a state where emission of light observable by the naked eye in a dark place while the discharge voltage is increased, to a state just before where the whole material glows, via a state where a spots of orange light are emitted. When the dimensions of the target material 14 are 1 mm×1 mmx20 mm, the application voltage is preferably within the range of from 70 V to 200 V and more preferably within the range of from 80 V to 150 V. This voltage range can be used for almost all steel materials including alloy steel such as stainless steel. However, this voltage range changes in accordance with the type and arrangement of the target material 14, and the voltage range may be determined by observing the surface of the target material 14 with a voltage condition changed with a SEM.

[0055] The discharge voltage is required to be a voltage that forms microscopic protrusions on the surface of a steel material. A voltage less than a lower limit voltage does not form the microscopic protrusions on the surface, and the lower limit can be determined by observing the presence or absence of the microscopic protrusions with a SEM. When the voltage exceeds an upper limit, the target surface melts. A voltage at which the surface melts can be therefore determined as the upper limit. However, it is more desirable not to oxidize the surface. In that case, the upper limit can be determined easily by examining a voltage at which the surface is oxidized using a SEM and an energy-dispersive X-ray spectrometer (EDS) attached to the SEM. When oxygen is detected with X-ray intensity similar to that of an oxide of the target material 14, it can be determined that the surface has been oxidized. It is required that the X-ray intensity of oxygen normalized with Fe-L line intensity in the target material 14 is 1/3 or less of the X-ray intensity of oxygen normalized with the intensity of the L line of Fe of an oxide (meaning an oxide of Fe for cold-rolled steel sheets and low-alloy steel, for example) of the target material 14. The above surface examination is performed by changing the voltage, performing discharge for 30 minutes, taking out the target material 14, washing it, drying it, setting it into the SEM, and observing it.

[0056] A discharge treatment time is required to be 3 seconds or more. Although the discharge treatment time may be such a long time as 60 minutes, a discharge treatment time of 30 minutes or more is not preferable, because a too long discharge treatment time may wear the target material 14. It is known that within the desirable voltage range a higher application voltage provides higher water-repellent properties of a surface after the final process. The most preferable condition is therefore to select an application voltage close to the upper limit of the preferable condition range.

[0057] FIG. 13 is an example of a treated SUS316L stainless steel sheet with a thickness of 0.8 mm. This SUS316L stainless steel sheet was cut to 2 mm wide and 30 mm long and was given conduction through a copper wire to form a cathode electrode. For an anode electrode, a Pt wire with a length of 50 cm was bent to form a planar shape so as to avoid mutual contact. A heat-resistant resin was heat-crimped to a connecting part between the SUS316L stainless steel sheet and the copper wire, and a part with a length of 20 mm of the electrode was immersed into an electrolytic solution so that the copper wire will not be in contact with the electrolytic solution. An aqueous K_2CO_3 solution with a concentration of 0.1 mol/L was used as the electrolytic solution and discharge was performed for 10 minutes with the voltage set to be 130 V. Immediately after that, the electrode was washed with water.

[0058] As illustrated in FIG. 13, it has been found out that microscopic protrusion structures having an average diameter of 1 μm or less are formed on the surface of the SUS316L stainless steel sheet. It has been found out from elementary analysis by EDS that the surface of the SUS316L stainless steel sheet is not oxidized. With an application voltage exceeding 160 V, the tip of the SUS316L stainless steel sheet melted. This demonstrated that the upper limit of the application voltage was 160 V. It has been found out from the elementary analysis by EDS that the surface of the SUS316L stainless steel sheet is not oxidized with an application voltage of 140 V or less. It has been therefore found out that the preferable upper limit of the application voltage for these experimental conditions and this test material is 140 V. The lower limit of the application voltage was determined to be 80 V from the presence or absence of the protrusion structures. The most preferable application voltage was determined to be 140 V.

[0059] Returning back to FIG. 11, after the microstructures have been formed on the surface of the target material 14, the target material 14 is taken out of the electrolytic solution 12, and then the target material 14 is washed (Step S2). Finally, a water-repellent treatment is performed on the target surface of the washed target material 14 (Step S3). Examples of the method of washing, which is performed in order to remove the electrolytic solution on the surface, may include immersion into or spraying pure water. Without limited to pure water, weak acids or alkaline solutions may be used so long as the microstructures on the surface are not damaged. During the process, electrolysis may be applied. After the washing, the target surface may be dried or may not be dried and advanced to the next process depending on the subsequent water-repellent treatment. Examples of the method of water-repellent treatment may include a method of applying a water-repellent spray and a method of absorbing an organic substance having a water-repellent function such as fluororesins on the surface in a liquid phase or a gaseous phase. In the present embodiment, Nanopro manufactured by Collonil (component: a carbon fluoride resin and a silicone resin) was sprayed onto the surface of the target material 14 and dried for 12 hours or more to perform the water-repellent treatment on the surface of the target material 14. This ends a series of surface treatment.

[0060] FIG. 14 is a side-view observation of a state after the water-repellent treatment was performed on the specimen surface illustrated in FIG. 13 and distilled water was dropped thereon. From this observation, it has been measured that the contact angle of water is 152° and it has been found out that super water repellency is achieved. The contact angle of water for a specimen without the water-repellent treatment performed was 51°. A similar water-repellent treatment was performed on a material without performing in-liquid plasma discharge, and the contact angle of water for the material was 125°. It has been thus found out that both the in-liquid plasma discharge and the water-repellent treatment are required to obtain a super water-repellent surface.

Example 1

[0061] A commercial SUS316L stainless steel sheet with a thickness of 0.8 mm was cut to 2 mm wide and 30 mm long, immersed into dilute hydrochloric acid to be degreased, and given conduction through a copper wire to form a cathode electrode. For an anode electrode, a Pt wire with a length of 50 cm and a diameter of 0.5 mm was bent to form a planar shape so as to avoid mutual contact. A heat-resistant resin was heat-crimped to a connecting part between the cathode electrode and the copper wire, and a part with a length of 20 mm of the electrode was immersed into an electrolytic solution so that the copper wire will not be in contact with the electrolytic solution. An aqueous K_2CO_3 solution with a concentration of 0.1 mol/L was used as the electrolytic solution and discharge was performed for 10 minutes with the application voltage set to be within the range of from 60 V to 180 V. Immediately after that, the electrode was washed with pure water and dried. Nanopro manufactured by Collonil was then sprayed onto the target material and dried for 12 hours or more to perform the water-repellent treatment on the surface of the target material, and water wettability was examined. The water wettability was evaluated by dropping distilled water onto the electrode surface at equally spaced six places by 1 μm using a micropipette, photographing the distilled water with a digital camera EOS Kiss X2 manufactured by Canon Inc. from just beside, measuring a contact angle from an obtained photograph, and taking the average of the six places. The distilled water 049-16787 manufactured by Wako Pure Chemical Industries, Ltd. was used as the distilled water. Table 4 lists the test results. As listed in Table 4, it has been found out that all the inventive examples result in higher contact angles than the untreated materials. In particular, it has been found out that Inventive Examples 3, 4, and 5 with an application voltage within the range of from 120 V to 140 V achieve super water repellency with a contact angle of 150° or more and that Inventive Example 5 with an application voltage of 140 V results in the highest contact angle of 153.6°.

Table 4

Test No.	Plasma voltage(V)	Water-repellent treatment	Contact angle of water (°)	Remarks
1	0 (No treatment)	Absent	77.2	Comparative Example 1
2	0 (No treatment)	Present	125.1	Comparative Example 2
3	60	Present	126.9	Comparative Example 3
4	80	Present	140.2	Inventive Example 1
5	100	Present	145.8	Inventive Example 2
6	120	Present	150.0	Inventive Example 3
7	130	Present	152.0	Inventive Example 4
8	140	Absent	51.6	Comparative Example 4
9	140	Present	153.6	Inventive Example 5
10	160	Present	143.0	Inventive Example 6
11	180 (Melted)	-	-	Comparative Example 5

Surface Treatment apparatus for Electroconductive Material

[0062] Aiming at manufacturing an electroconductive material of which the surface is provided with microstructures at low cost and efficiently, the inventors of the present invention have earnestly conducted study including consideration for the availability of in-liquid plasma discharge, which had been conventionally considered impossible to form nano-level microstructures. Consequently, the inventors of the present invention, has found out that nano-level microstructures can be formed on the surface of an electroconductive material by causing in-liquid plasma discharge partially using the electroconductive material as a cathode electrode. The inventors of the present invention has considered a method for manufacturing nano-level microstructures on a specific part in the surface of the electroconductive material and has found out that the nano-level microstructures can be formed on the specific part in the surface of the electroconductive material by immersing a part to be treated of the electroconductive material into an electrolytic solution together with an anode electrode and placing a shield having an opening between the electroconductive material and the anode electrode. The inventors of the present invention has further found out that the nano-level microstructures can be formed on the surface of the electroconductive material continuously or discretely by changing the relative positions of the opening of the shield and/or the anode electrode and the electroconductive material.

[0063] FIG. 15 is a schematic diagram illustrating the configuration of a surface treatment apparatus for an electroconductive material as an embodiment according to the present invention. As illustrated in FIG. 15, this apparatus 21 for treating the surface of an electroconductive material as an embodiment according to the present invention includes a modifying treatment cell 22, an electrolytic solution 23 stored in the modifying treatment cell 22, an anode electrode 24 and a cathode electrode 25 formed of an electroconductive target material that are immersed into the electrolytic solution 23 spaced apart from each other, and a direct current power supply 26 that is connected to the anode electrode 24 and the cathode electrode 25. The cathode electrode 25 is covered with a box 27 formed of an insulating material, and the box 27 is provided with an opening 28 that limits a part to be treated of the cathode electrode 25. The box 27 is arranged so that its upper part will be positioned higher than the liquid surface of the electrolytic solution 23. The upper part of the box 27 may be open or may have a lid having a hole through which a conducting wire connecting the cathode electrode 25 and the direct current power supply 26 is passed.

[0064] The modifying treatment cell 22 may be any known cell formed of a stable material. The cell may be formed of, for example, glass, Teflon (registered trademark), or polyethyl ether ketone (PEEK). The modifying treatment cell 22 may be a ceramic cell. The surface treatment apparatus 21 illustrated in FIG. 16 described later can use even a metallic cell.

[0065] The electrolytic solution 23 is a solution that has electroconductivity and, when a voltage is applied between the anode electrode 24 and the cathode electrode 25 to form nano-level microstructures on the surface of the target material (the surface of the cathode electrode 25), hardly etches the surface of the target material excessively, adheres to or precipitates on the surface of the anode electrode 24 and the cathode electrode 25, and forms a sediment. The electrolytic solution 23 may be an aqueous solution containing at least one type selected from the group consisting of potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), sodium hydrogencarbonate ($NaHCO_3$), ammonium carbonate ($(NH_4)_2CO_3$), lithium hydroxide ($LiOH$), sodium hydroxide ($NaOH$), magnesium hydroxide ($Mg(OH)_2$), potassium hydroxide (KOH), ammonium hydroxide (NH_4OH), sodium chloride ($NaCl$), potassium chloride (KCl), magnesium chloride ($MgCl_2$), ammonium chloride (NH_4Cl), sulfates of lithium, sulfates of sodium, sulfates of magnesium, sulfates of potassium, sulfates of ammonium, nitrates of lithium, nitrates of sodium, nitrates of magnesium, nitrates of potassium, nitrates of ammonium, citrates of lithium, citrates of sodium such as sodium citrate ($NaH_2(C_3H_5O(COO)_3)$), citrates of magnesium, citrates of potassium, citrates of ammonium, sulfuric acid, nitric acid, hydrochloric acid, and citric acid.

[0066] The electrolytic solution 23 may have any pH and concentration so long as it can perform a surface treatment on the cathode electrode 25. When an aqueous potassium carbonate solution is used as the electrolytic solution 23, for example, its concentration may be, but not limited to, 0.001 mol/L or more and more preferably 0.005 mol/L or more. This is because when the concentration is too low, it may be difficult to maintain a favorable discharge state when a voltage is applied between the anode electrode 24 and the cathode electrode 25. The upper limit of the concentration may be, but not limited to, 0.50 mol/L or less, for example. The pH of the electrolytic solution 23 may be any value so long as excessive corrosion or etching of the electrodes does not occur and may be from 5 to 12, for example.

[0067] The anode electrode 24 is an insoluble anode electrode formed of an electrode material that is not ionized and solved in the electrolytic solution 23 when a voltage is applied between the anode electrode 24 and the cathode electrode 25 to form nano-level microstructures on the target surface, thereby not precipitating on the cathode electrode 25 or hindering the formation of the nano-level microstructures. Examples of the anode electrode 24 may include platinum (Pt) electrodes, palladium (Pd) electrodes, iridium (Ir) electrodes, and electrodes whose surface is coated with Pt, Pd, or Ir, and graphite electrodes.

[0068] The cathode electrode 25 is a target material whose surface is subjected to a modifying treatment by the application of a voltage and is formed of a material (electroconductive material) having electroconductivity such as metallic materials and alloy materials. Examples of the target material that functions as the cathode electrode 25 may include carbon steel materials, alloy steel materials, stainless steel materials, and nickel materials. The shape of the cathode electrode 25 (target material) may be, but not limited to, a sheet shape, a band shape, or a component having an electroconductive material part. The target material may be used as the cathode electrode 25 after the surface is mirror-polished with sand paper or other tools as needed.

[0069] The direct current power supply 26 applies a voltage of, for example, 60 V or more and 300 V or less between the anode electrode 24 and the cathode electrode 25. The voltage is required for the modifying treatment on the surface of the cathode electrode 25 as the target material. The direct current power supply 26 may be a known power supply.

[0070] Although in the present embodiment the cathode electrode 25 is covered with the box 27, the anode electrode

24 is covered with the box 27 provided with the opening 28 as illustrated in FIG. 16. Without limiting the part to be treated by the box 27 provided with the opening 28, as illustrated in FIG. 17, at least the surface of the cathode electrode 25 immersed into the electrolytic solution 23 may be covered with a insulating heat-resistant material such as a heat-resistant resin and glass, leaving the opening 28 for limiting the part to be treated of the cathode electrode 25.

[0071] The shape and size of the opening 28 are not limited, and the box 27 may be provided with a plurality of openings. In the case where a plurality of openings 28 are provided, the positions of the openings 28 are not limited in the same surface of the cathode electrode 25. The openings 28 may be arranged on the front side and back side of the cathode electrode 25. As illustrated in FIG. 18, an inclined part 28a may be provided on the upper (liquid surface side) end of the opening 28. Providing the inclined part 28a allows gas generated from the part to be treated to efficiently escape to the electrolytic solution 23.

[0072] The surface treatment apparatus 21 may include a heating unit such as a heater for heating the electrolytic solution 23 or a thermometer for measuring the temperature of the electrolytic solution 23. The angle at which the cathode electrode 25 is placed may be perpendicular to the liquid surface of the electrolytic solution 23, which is not limiting. In order to facilitate plasma generation on the surface of the cathode electrode 25, a mechanism may be provided that supplies gas such as hydrogen, argon, and water vapor to the surface of the cathode electrode 25.

[0073] The surface treatment apparatus 21 having such a configuration manufactures a surface-modified electroconductive material as follows. Described below is a method for surface treatment of an electroconductive material using this surface treatment apparatus 21.

Method for Surface Treatment of Electroconductive Material

[0074] To manufacture a surface-modified electroconductive material using the surface treatment apparatus 21, first, the box 27 is immersed into the electrolytic solution 23 stored in the modifying treatment cell 22, and then the anode electrode 24 and the cathode electrode 25 are immersed thereinto spaced apart from each other, whereby a system (a surface modifying treatment system) that performs a surface modifying treatment on the cathode electrode 25 is constructed. During the process, the cathode electrode 25 is immersed into the box 27, and a part desired to be treated is made visible through the opening 28 of the box 27. The surface modifying treatment on the cathode electrode 25 is performed on a part exposed to the electrolytic solution 23 through the opening 28. In the configuration of the surface treatment apparatus 21 illustrated in FIG. 16, the anode electrode 24 is put into the box 27, and the box 27 is placed so that the opening 28 of the box 27 will face a part to be treated of the cathode electrode 25. As the part desired to be treated is spaced apart from the opening 28, the part desired to be treated becomes larger than the opening; because of this, the spacing (distance) between the opening 28 and the part desired to be treated of the cathode electrode 25 is generally preferably 5 mm or less and more preferably 1 mm or less.

[0075] Next, a certain voltage is applied between the anode electrode 24 and the cathode electrode 25 to perform a modifying treatment on the surface of the cathode electrode 25 (a surface modifying treatment process). The certain voltage is a voltage that can be determined by a preliminary experiment and can be determined as follows. Specifically, first, a voltage applied to the surface modifying treatment system and a treatment time are changed within desired ranges. When the treatment time is not designated, it may be performed for 15 minutes. A range within which the voltage is changed may be about from 50 V to 300 V. Next, in order to determine a condition, the treated surface is observed with a SEM to check the following: protrusion structures having an average diameter of 1 μm or less are formed on the surface; the surface is not oxidized (except a natural oxide film with a thickness about a few nanometers); and the surface is not melted. Whether the surface is oxidized can be checked using the EDS in the SEM.

[0076] The voltage range, which may change depending on the type of the cathode electrode 25, is within the range of from 60 V to 300 V and is preferably within the range of from 60 V to 180 V. The lower limit voltage corresponds to a voltage at which plasma is generated. The upper limit voltage is determined by the fact that the surface is oxidized or the surface melts owing to high temperatures, whereby the microscopic protrusion structures disappear. Although a preferable voltage range is determined as above, a higher application voltage may be set when the treatment is desired to be performed in a short time or when the protrusion structures are desired to be increased in size.

[0077] Specific examples are described next. In the specific examples, the surface modifying treatment system illustrated in FIG. 15 was constructed with a stainless steel sheet (SUS316) as the cathode electrode 25. The dimensions of the opening 28 were set to be 25 mm×4 mm. A voltage was applied for 15 minutes with a 0.1 mol/L aqueous potassium carbonate (K_2CO_3) solution as the electrolytic solution 23. The surface of the stainless steel sheet after the treatment was observed with a SEM. The observation revealed that the lower limit voltage was 80 V. The upper voltage was found to be 250 V. FIG. 19A, FIG. 19B, and FIG. 19C illustrate secondary electron images of the longitudinal (a) left part, (b) central part, and (c) right part of the opening 28, respectively, when 150 V was applied between the anode electrode 24 and the cathode electrode 25.

[0078] As illustrated in FIG. 19A, FIG. 19B, and FIG. 19C, it has been found out that the microscopic protrusion structures with a diameter of 1 μm or less are formed on the surface of the stainless steel sheet. From the fact that similar protrusion structures are observed in the longitudinal left part, right part, and central part of the opening 28, it has been found out that an appropriate treatment is performed across the entire opening. It has also been found out that a lower voltage within the desirable voltage range gives a larger protrusion structure and an increased number of protrusion structures. Given this situation, the application voltage may be adjusted in accordance with required surface properties. When luminescence properties are desired to be obtained, for example, the application voltage may be set to be lower, because the protrusion structure is preferably smaller.

[0079] Although the principle on which the microscopic protrusions are formed has not been revealed, it is supposed that they are formed based on the occurrence of partial in-liquid plasma discharge in the vicinity of the cathode electrode 25. In other words, in this method, when the voltage applied between the anode electrode 24 and the cathode electrode 25 is less than the lower limit voltage, the partial in-liquid plasma discharge does not occur sufficiently and hence the microscopic protrusions are not formed. When the voltage applied between the anode electrode 24 and the cathode electrode 25 is the upper limit voltage or more, the occurrence of perfect plasma melts the surface of the cathode electrode 25, which is disadvantageous for the formation of the microscopic protrusions.

[0080] It is considered that the in-liquid plasma discharge occurs as follows: When the temperature of the electrolytic solution 23 in the vicinity of the cathode electrode 25 locally reaches or exceeds its boiling temperature by application of a voltage and a gaseous phase is generated in the vicinity of the cathode electrode 25, the plasma discharge occurs in the gaseous phase. Given this situation, although the voltage application can be started at room temperature, it is more effective to perform the voltage application after setting the temperature of the entire electrolytic solution 23 or in the vicinity of the cathode electrode 25 is set to be within the range of from 80°C to 100°C. This is because the temperature in the vicinity of the cathode electrode 25 is effectively increased, whereby the in-liquid plasma discharge occurs efficiently. A voltage application time can be any time, which is 1 second or more and 30 minutes or less, for example. Because a shorter voltage application time gives a smaller size of the formed microscopic protrusions, the voltage application time may be appropriately selected in accordance with desired surface shape and properties.

[0081] As is evident from the foregoing description, this method of surface treatment can manufacture an electroconductive material whose surface is formed with nano-level microstructures only by controlling the voltage applied between the anode electrode 24 and the cathode electrode 25 immersed into the electrolytic solution 23 at low cost and effectively without using expensive apparatuses and high-level techniques. The electroconductive material whose surface is formed with nano-level microstructures can exhibit various functions caused by the microstructures. By moving the cathode electrode 25 with the box 27 fixed or by moving the box 27 with the cathode electrode 25 fixed, surface modification can be performed for a wider area of the cathode electrode 25. By moving the cathode electrode 25 or the box 27 continuously while performing the treatment, a continuous treated surface can be obtained. By moving the cathode electrode 25 or the box 27 stepwise, or by moving them and discharging repeatedly, a discrete pattern can also be formed. In the surface treatment apparatus 21 illustrated in FIG. 16 in particular, the cathode electrode 25 is not required to be covered with the box 27, and the surface treatment apparatus 21 can be expanded to continuous treatment equipment and a method of continuous treatment by forming the cathode electrode 25 to be a large-sized specimen or a band-shaped specimen.

Example 1

[0082] Boxes 27 were manufactured from alumina plates having a thickness of 1.7 mm provided with various-sized openings (five types consisting of 5 mm×5 mm, 5 mm in diameter, 10 mm in diameter, 10 mm×2 mm, and 20 mm×1 mm). The upper end face of each opening 28 was formed inclined with an angle of 30 degrees as illustrated in FIG. 18. SUS316 stainless steel with a thickness of 1 mm as the cathode electrode 25 and Pt as the anode electrode 24 were immersed into an aqueous K_2CO_3 solution with a concentration of 0.3 mol/L to construct the surface modifying treatment system as illustrated in FIG. 15. A voltage was applied between the cathode electrode 25 and the anode electrode 24. The surface of the SUS316 stainless steel after the voltage application was observed with a SEM. FIG. 20 illustrates an example of the appearance of the cathode electrode 25 after being treated when the dimensions of the openings 28 were 5 mm×5 mm and 5 mm in diameter. The application voltage was 160 V, whereas the application time was 15 minutes. As illustrated in FIG. 20, it has been found out that the surface of the cathode electrode 25 is treated in the shape of the opening 28.

[0083] FIG. 21 illustrates an example of a SEM image of the surface of the cathode electrode 25 after being treated when the dimension of the opening 28 was 5 mm in diameter. As illustrated in FIG. 21, it has been found out that microscopic protrusion structures with a diameter of 1 μm or less, which are not present on a surface without any surface treatment performed (refer to FIG. 22), are formed on the surface of the cathode electrode 25. It has been found out that the microscopic protrusion structures were formed with an application voltage of from 90 V to 200 V even when the opening 28 having another shape is used, but the number of the microscopic protrusion structures decreases with a voltage of 220 V or more. It is estimated that this is caused by the melting of the surface. When a uniform water-repellent treatment was performed on the entire surface of the cathode electrode 25 illustrated in FIG. 20, higher water-repellency properties were obtained than that of the surface without any surface treatment performed. In an experiment in which

170 V (with an application time of 15 minutes) was applied using the box 27 having the openings 28 of 5 mm in diameter and 5 mm×5 mm on both sides, it has been found out from a SEM observation that microscopic protrusion structures are formed on both sides thereof and that the surface modifying treatment can be performed on the front and back sides simultaneously.

Example 2

[0084] A stainless steel sheet (SUS316) was used as a cathode electrode, the anode electrode 24 was covered with the box 27 formed of alumina (thickness: 1.7 mm) provided with the opening 28 with dimensions of 1 mm (longitudinally)×20 mm (laterally) to construct the surface modifying treatment system as illustrated in FIG. 16. The side having the opening 28 was placed spaced apart from the cathode electrode 25 by 1 mm. The application voltages between the electrodes were 140 V and 220 V. The voltage was applied between the electrodes for 5 minutes, the stainless steel sheet was moved upward (vertically) by 5 mm, and then the voltage was applied thereto again for 5 minutes. The upward movement and the voltage application were repeated 10 times. Two experiments were performed for the application voltages between the electrodes of 140 V and 220 V. Both experiments obtained a stainless steel sheet having areas in which microscopic protrusion structures exist at intervals of 5 mm.

Example 3

[0085] A galvanized steel sheet was used as a cathode electrode, the anode electrode 24 was covered with the box 27 formed of alumina (thickness: 1.7 mm) provided with the opening 28 with dimensions of 1 mm (longitudinally)×20 mm (laterally) to construct the surface modifying treatment system as illustrated in FIG. 16. The side provided with the opening 28 was placed spaced apart from the cathode electrode 25 by 1 mm. With an application voltage between the electrodes of 120 V, the galvanized steel sheet was moved downward (vertically) by 20 mm with a velocity of 1 mm/minutes while applying the voltage between the electrodes, whereby a galvanized steel sheet having a treated area of 20 mm×20 mm was prepared. When a methylene blue decolorization reaction test was performed on this surface, a remarkably higher photocatalytic effect was obtained than the surface without any surface treatment performed.

Example 4

[0086] A commercial cold-rolled steel sheet with a thickness of 0.8 mm was cut to form cathode electrodes each having dimensions of 80 mm long and 6 mm wide. The cathode electrodes each were bent in the width direction with the longitudinal direction as an axis so that the section in the width direction will have an arc shape with a radius of curvature of 10 mm. A heat-resistant resin was applied onto the surfaces of the cathode electrodes 25 except connecting parts to the electrodes. The openings 28 with a width of 2 mm and 4 mm and a length of 25 mm were formed on one side of each curved electrode. A voltage of 150 V was applied between Pt and the cathode electrode 25. For both specimens, microscopic protrusion structures having an average diameter of 1 μm or less were formed on the surfaces of the openings 28.

Industrial Applicability

[0087] The present invention can provide a metallic material having new functions such as hydrophilic properties and luminescence properties.

[0088] The present invention can provide a method for surface treatment of a metallic material and a method for manufacturing a water-repellent material using a metallic material as a base that can impart high water-repellent properties to a metallic material surface without requiring much labor and cost.

[0089] The present invention can provide a surface treatment apparatus for and a method for surface treatment of an electroconductive material that can manufacture an electroconductive material formed with nano-level microstructures at low cost and efficiently by performing a treatment on a specific part in a surface or across a wide area in the surface.

Reference Signs List

[0090]

1	metallic material
2	substrate
3	protrusion

11	container
12	electrolytic solution
13	anode electrode
14	target material (cathode electrode)
15	conducting wire
16	power supply
17	thermometer
21	surface treatment apparatus
22	modifying treatment cell
23	electrolytic solution
24	anode electrode
25	cathode electrode (target material)
26	direct current power supply
27	box
28	opening
28a	inclined part

Claims

1. A metallic material, comprising:

   a metal substrate; and
   a modified layer formed on a surface of the metal substrate,
   wherein the modified layer comprises three or more protrusions in an area of 10 μm^2 on average protruding from the surface of the metal substrate, the protrusions having an average diameter of 1 μm or less when viewed in a direction perpendicular to the surface of the metal substrate.

2. The metallic material according to claim 1, wherein the modified layer comprises, in an area of 10 μm^2 on average, one or more protrusions comprising a base part protruding from the surface of the metal substrate and a tip part formed on the end of the base part, the protrusions having an average diameter of 1 μm or less when viewed in a direction perpendicular to the surface of the metal substrate and a constricted structure with the outer diameter of the base part being smaller than the outer diameter of the tip part.

3. The metallic material according to claim 1 or 2, wherein the average diameter of the protrusions is 500 nm or less when viewed in a direction perpendicular to the surface of the metal substrate.

4. The metallic material according to any one of claims 1 to 3, wherein positions on which the protrusions are formed have no periodicity in the in-plane direction of the metal substrate.

5. The metallic material according to any one of claims 1 to 4, wherein the modified layer comprises recesses having an average diameter of 500 nm or less when viewed in a direction perpendicular to the surface of the metal substrate.

6. The metallic material according to any one of claims 1 to 5, wherein the metal substrate is formed of alloy steel.

7. The metallic material according to claim 6, wherein the metal substrate is formed of a steel material.

8. The metallic material according to any one of claims 1 to 7, wherein the metal substrate has a composition different from that of the protrusions.

9. The metallic material according to any one of claims 1 to 7, wherein the metal substrate and the protrusions are connected continuously.

10. A method for surface treatment of a metallic material, the method comprising:

    immersing a target material as a cathode electrode formed of a metallic material having a target surface and an anode electrode into an electrolytic solution;
    applying a voltage that is 70 V or more and is in such a range that does not oxidize or melt the target material

between the cathode electrode and the anode electrode to form microstructures on the target surface;
taking the target material out of the electrolytic solution and washing the target material; and
performing a water-repellent treatment on the target surface of the washed target material.

11. A method for surface treatment of a metallic material, the method comprising:

immersing a target material as a cathode electrode formed of a metallic material having a target surface and an anode electrode into an electrolytic solution;
applying a voltage of 70 V or more and 200 V or less between the cathode electrode and the anode electrode to form microstructures on the target surface;
taking the target material out of the electrolytic solution and washing the target material; and
performing a water-repellent treatment on the target surface of the washed target material.

12. A method for manufacturing a water-repellent material using a metallic material as a base, the method comprising:

immersing a metallic material as a target material as a cathode electrode having a target surface and an anode electrode into an electrolytic solution;
applying a voltage of 70 V or more and 200 V or less between the cathode electrode and the anode electrode to form microstructures on the surface of the metallic material as the target material;
taking the metallic material out of the electrolytic solution and washing the metallic material; and
performing a water-repellent treatment on the target surface of the washed metallic material.

13. A surface treatment apparatus for an electroconductive material, the apparatus comprising:

an anode electrode and a cathode electrode formed of an electroconductive material that are immersed into an electrolytic solution spaced apart from each other;
a shield that is interposed between the anode electrode and the cathode electrode and has an opening that limits a part to be treated of the cathode electrode; and
a power supply that applies a voltage between the anode electrode and the cathode electrode.

14. The surface treatment apparatus for an electroconductive material according to claim 13, further comprising a mechanism that changes the position of the opening and/or the relative positions of the anode electrode and the cathode electrode.

15. The surface treatment apparatus for an electroconductive material according to claim 13 or 14, wherein the power supply applies a voltage of 60 V or more and 300 V or less between the anode electrode and the cathode electrode.

16. The surface treatment apparatus for an electroconductive material according to any one of claims 13 to 15, wherein the shield is an insulating heat-resistant material provided with the opening that is covered with the surface of the cathode electrode.

17. The surface treatment apparatus for an electroconductive material according to any one of claims 13 to 16, wherein the electroconductive material is a metallic material.

18. A method for surface treatment of an electroconductive material, the method comprising modifying a surface of an electroconductive material using the surface treatment apparatus for an electroconductive material according to any one of claims 13 to 17.

FIG.1A

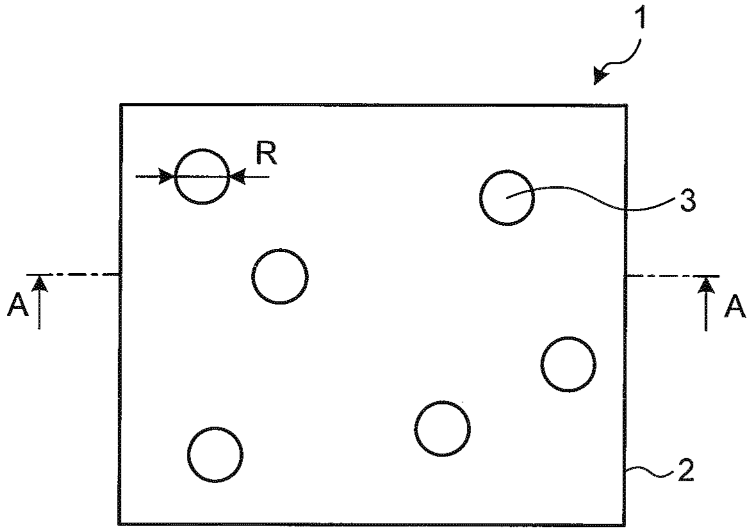


FIG.1B

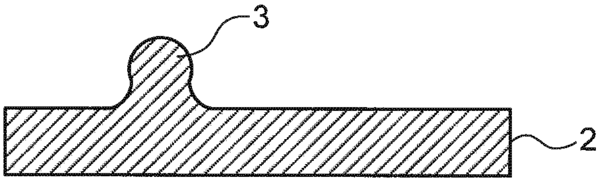


FIG.2

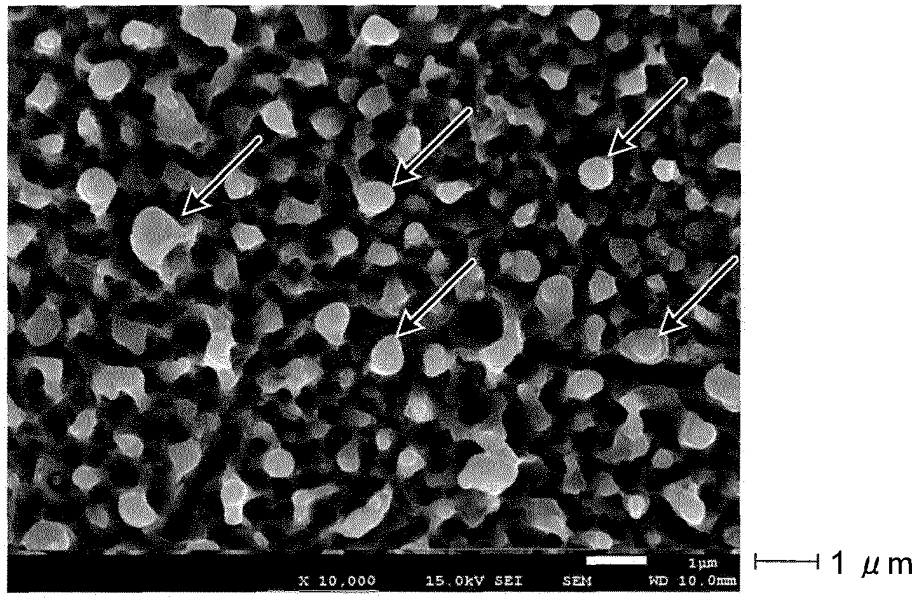


FIG.3

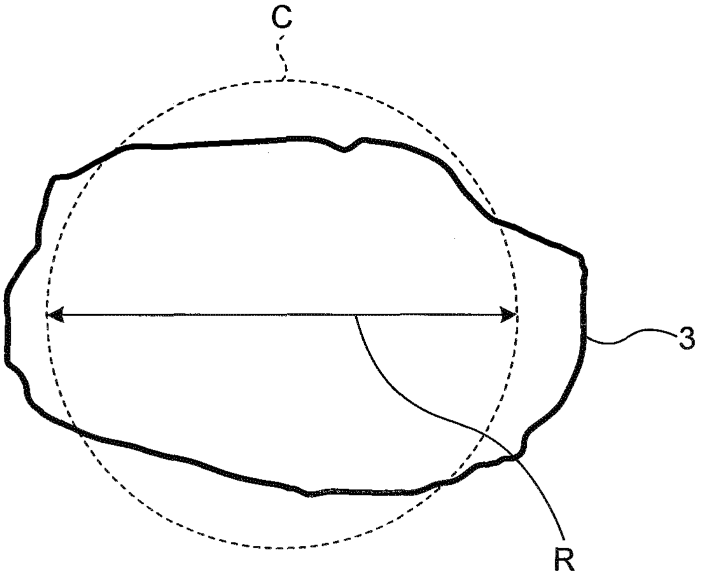


FIG.4

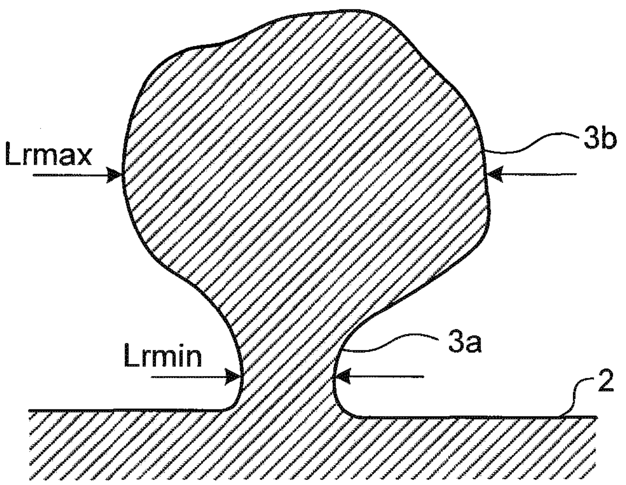


FIG.5

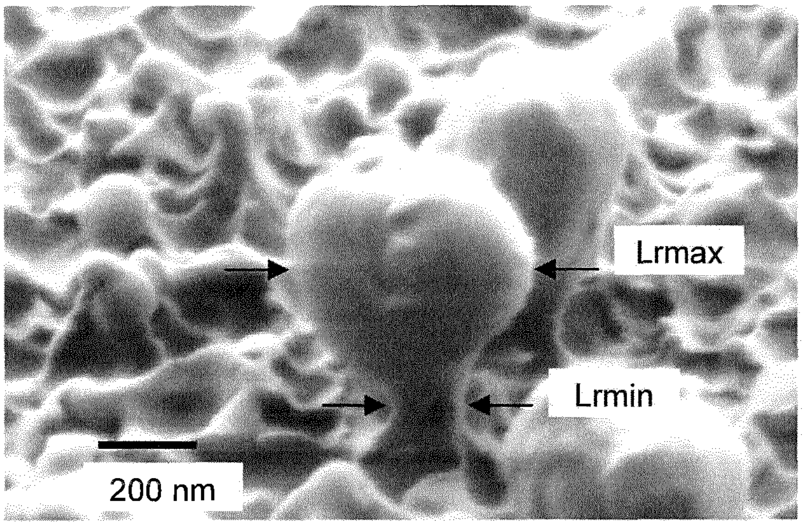


FIG.6

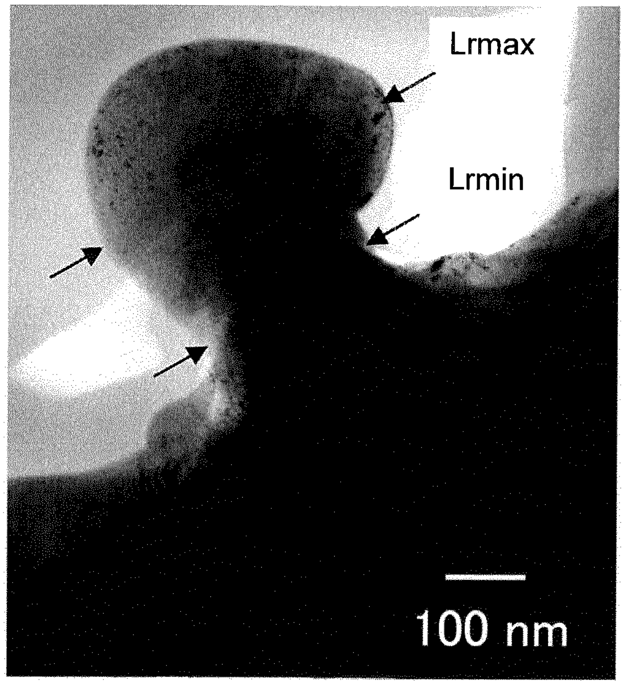

Lrmax
Lrmin
100 nm

FIG.7

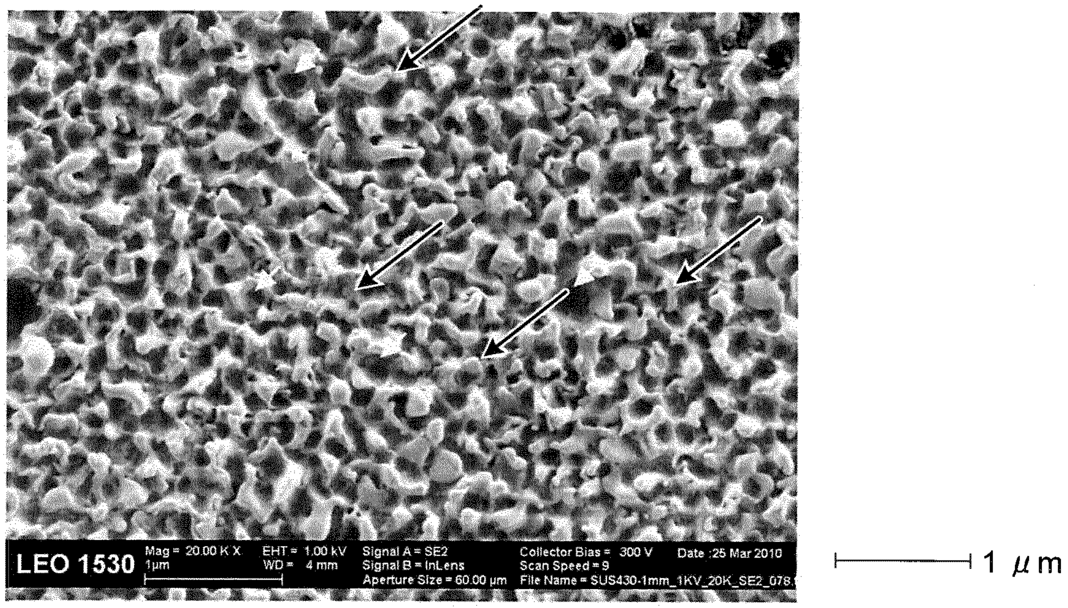

LEO 1530
Mag = 20.00 K X
1μm
EHT = 1.00 kV
WD = 4 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 60.00 μm
Collector Bias = 300 V
Scan Speed = 9
File Name = SUS430-1mm_1KV_20K_SE2_078.
Date :25 Mar 2010
1 μm

FIG.8

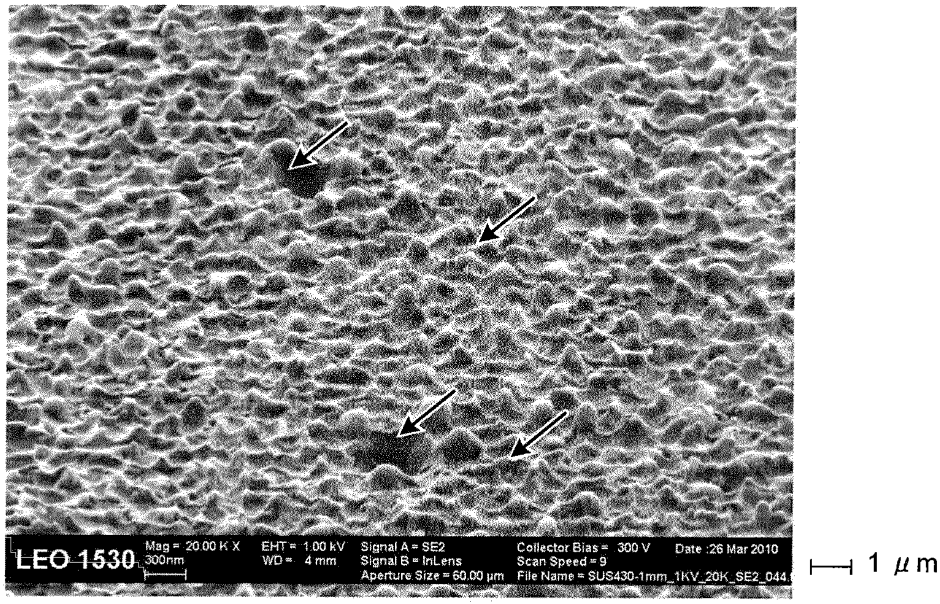

LEO 1530
Mag = 20.00 K X
300nm
EHT = 1.00 kV
WD = 4 mm
Signal A = SE2
Signal B = InLens
Aperture Size = 60.00 μm
Collector Bias = 300 V
Scan Speed = 9
Date :26 Mar 2010
File Name = SUS430-1mm_1KV_20K_SE2_044.
1 μm

FIG.9

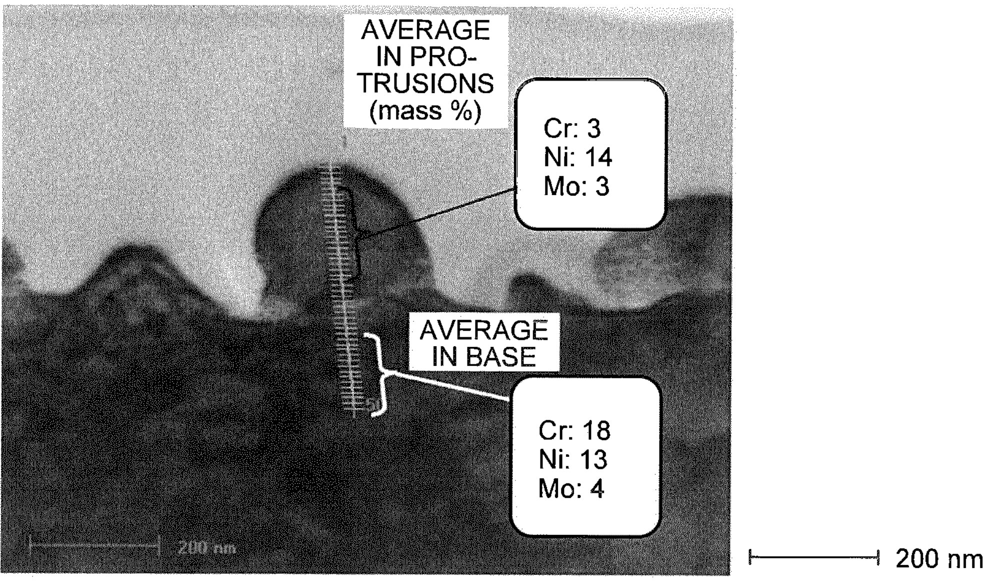

AVERAGE IN PRO-TRUSIONS (mass %)
Cr: 3
Ni: 14
Mo: 3
AVERAGE IN BASE
Cr: 18
Ni: 13
Mo: 4
200 nm
200 nm

FIG.10

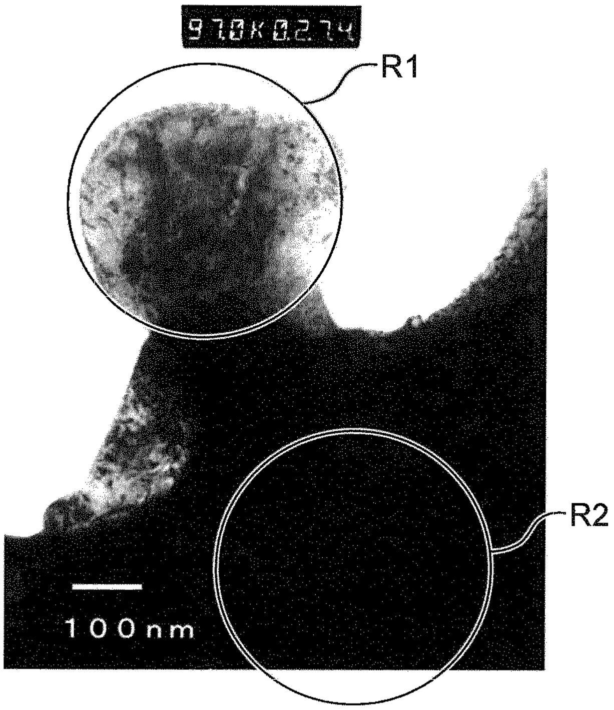


FIG.11

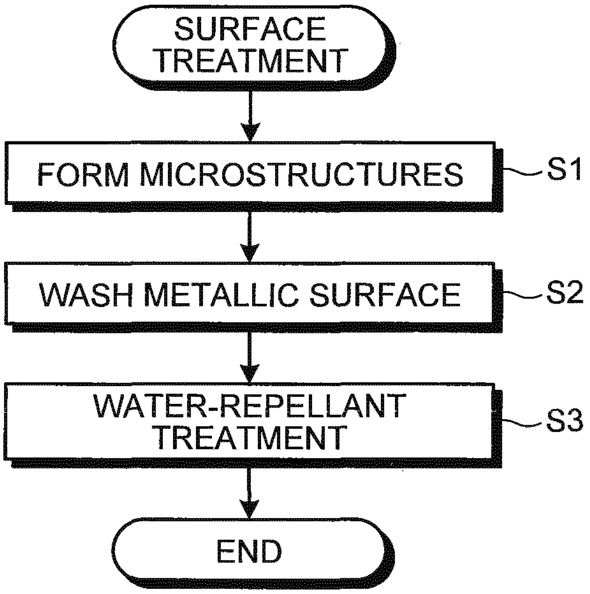

SURFACE TREATMENT
FORM MICROSTRUCTURES
S1
WASH METALLIC SURFACE
S2
WATER-REPELLANT TREATMENT
S3
END

FIG.12

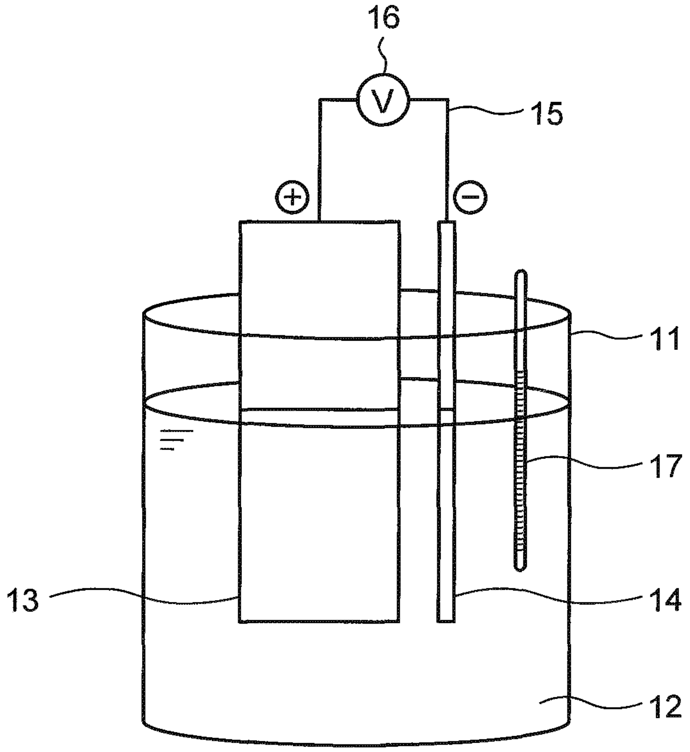


FIG.13

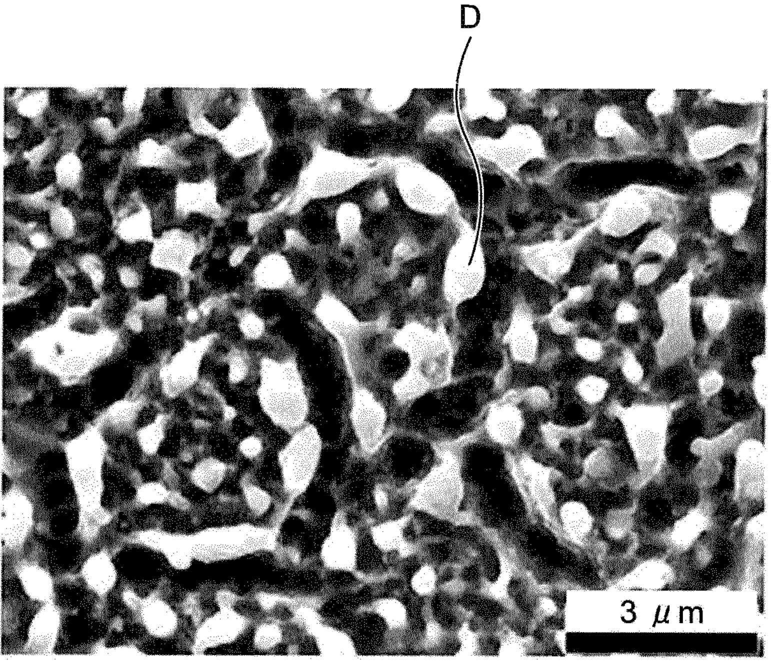


FIG.14

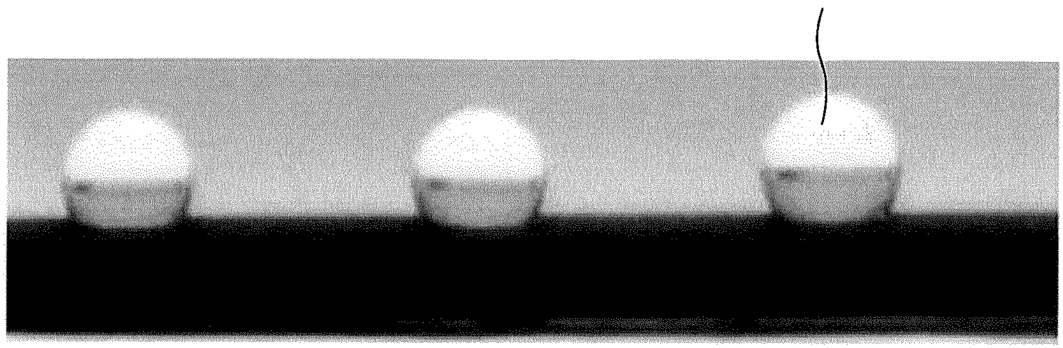


FIG.15

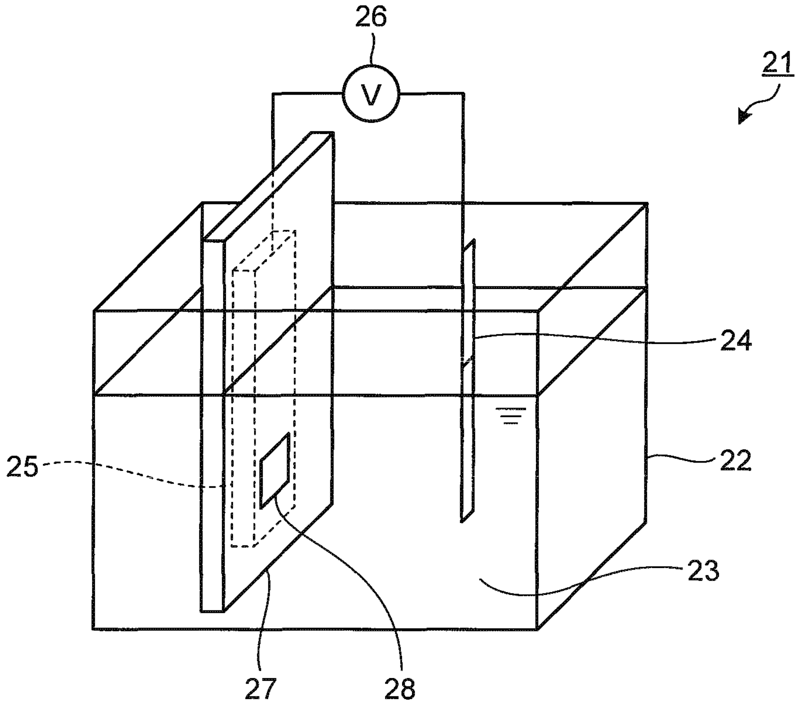


FIG.16

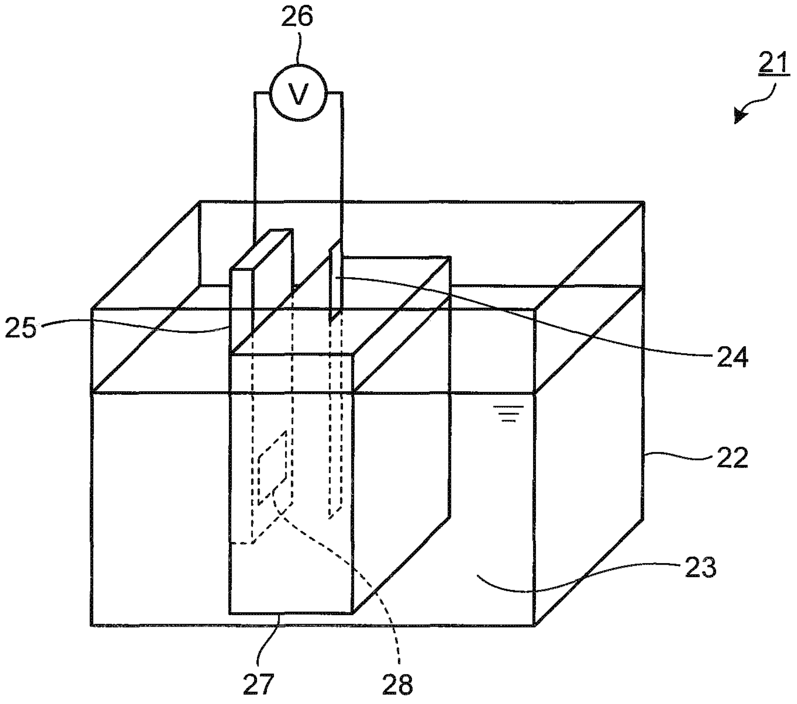


FIG.17

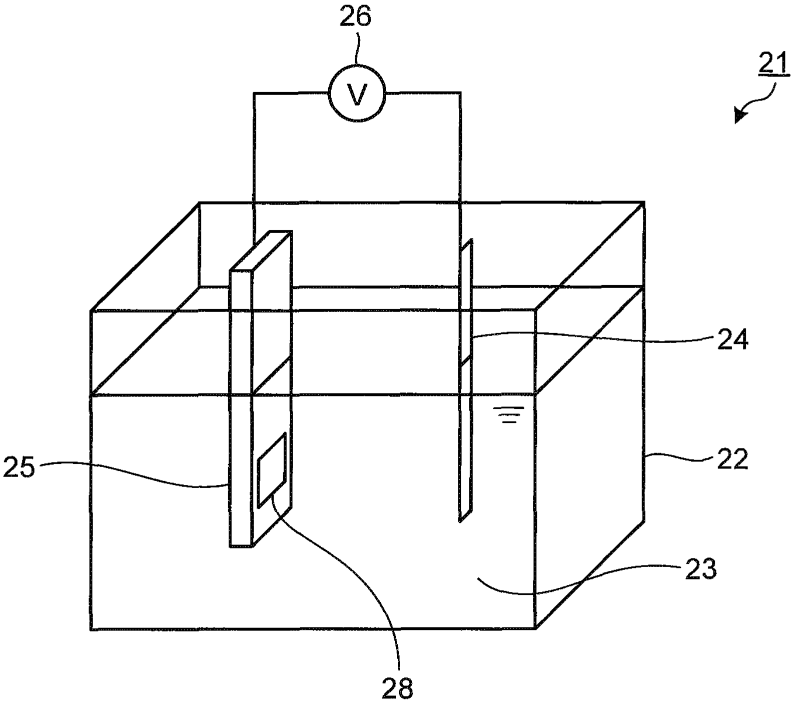


FIG.18

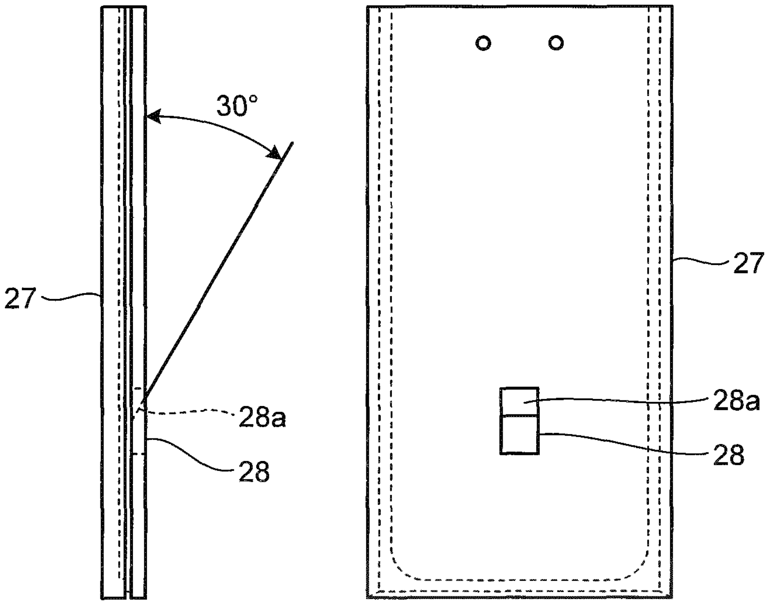


FIG.19A

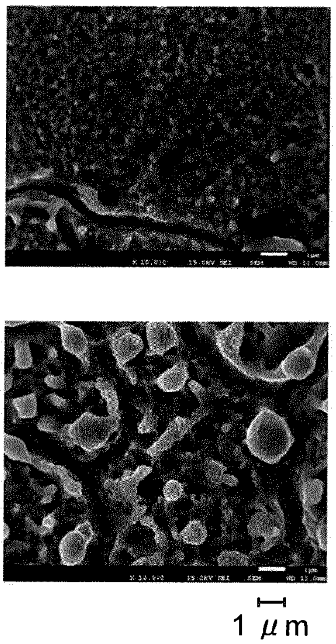


FIG.19B

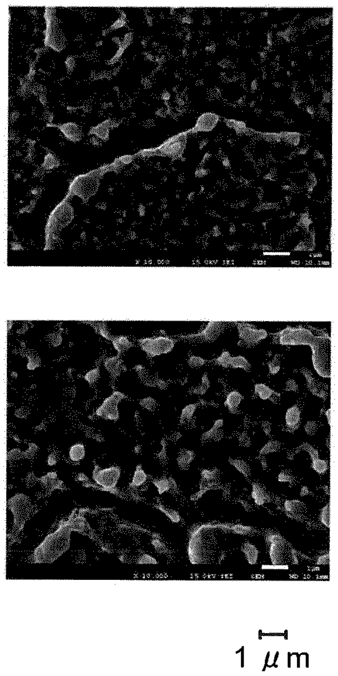


FIG.19C

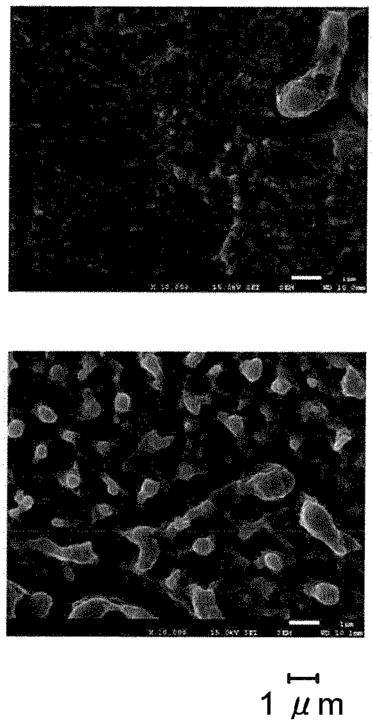


FIG.20

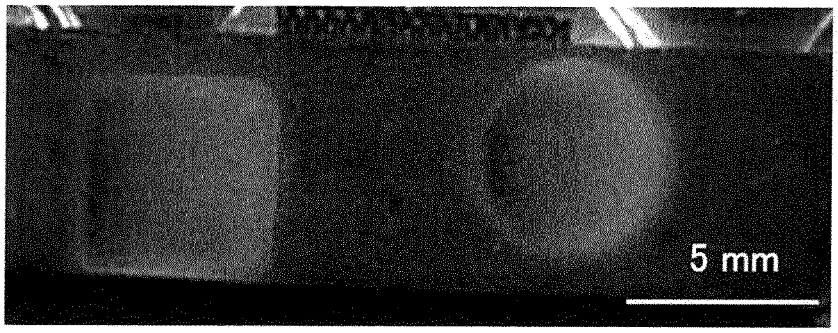
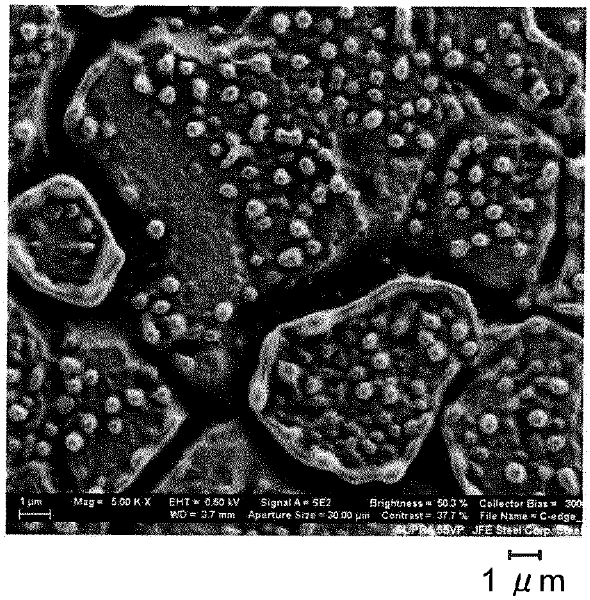


FIG.21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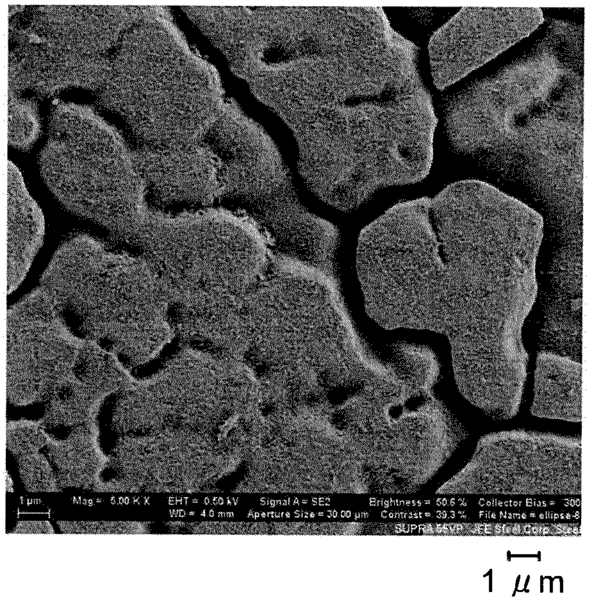
Mag = 5.00 K X
EHT = 0.50 kV
WD = 3.7 mm
Signal A = SE2
Aperture Size = 30.00 µm
Brightness = 50.3 %
Contrast = 37.7 %
Collector Bias = 300
File Name = C-edge_
SUPRA 55VP JFE Steel Corp. Steel
1 μm

FIG.22


1 µm
Mag = 5.00 K X
EHT = 0.50 kV
WD = 4.0 mm
Signal A = SE2
Aperture Size = 30.00 µm
Brightness = 50.6 %
Contrast = 39.3 %
Collector Bias = 300
File Name = ellipse-8
SUPRA 55VP JFE Steel Corp. Steel
1 μm

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/054413

A. CLASSIFICATION OF SUBJECT MATTER
C23C26/00(2006.01)i, *B23H1/00*(2006.01)i, *C25D3/02*(2006.01)i, *C25D5/02*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C26/00, B23H1/00, C25D3/02, C25D5/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 9-241865 A (Kawasaki Steel Corp.), 16 September 1997 (16.09.1997), claims; paragraphs [0011] to [0017]; table 1	1,3,4,6-9 5
Y	JP 6-297252 A (Sony Corp.), 25 October 1994 (25.10.1994), paragraphs [0050] to [0094]; fig. 4 to 14	5
X Y	JP 42-18043 B1 (Kubota Tekko Kabushiki Kaisha), 19 September 1967 (19.09.1967), entire text	10-12 15
X Y	JP 2004-521186 A (Nutool, Inc.), 15 July 2004 (15.07.2004), claims; paragraphs [0043] to [0080]; fig. 1 to 16	13,14,16-18 15

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 09 May, 2013 (09.05.13)	Date of mailing of the international search report 21 May, 2013 (21.05.13)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/054413

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2010-287648 A (Seiko Epson Corp.), 24 December 2010 (24.12.2010), entire text	13,16-18 15
A	JP 2008-285754 A (Nippon Mining & Metals Co., Ltd.), 27 November 2008 (27.11.2008), entire text	2

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2013/054413

JP 9-241865 A	1997.09.16	(Family: none)
JP 6-297252 A	1994.10.25	(Family: none)
JP 42-18043 B1	1967.09.19	(Family: none)
JP 2004-521186 A	2004.07.15	JP 2005-508445 A US 2002/0074230 A1 US 2002/0020628 A1 US 2003/0106807 A1 US 2003/0146089 A1 US 2004/0124089 A1 US 2005/0258046 A1 US 2005/0279641 A1 US 2006/0207885 A1 US 2007/0051635 A1 US 2008/0102251 A1 US 2010/0224501 A1 US 2004/0170753 A1 US 2006/0081477 A1 US 2005/0016868 A1 EP 1307905 A EP 1499759 A WO 2002/015245 A2 WO 2003/025255 A2 WO 2005/105356 A2 AU 8119601 A TW 520407 B CN 1559081 A TW 241639 B CN 1625611 A AU 2002327682 A KR 10-2010-0029249 A
JP 2010-287648 A	2010.12.24	(Family: none)
JP 2008-285754 A	2008.11.27	US 2004/0065545 A1 EP 1371748 A1 WO 2002/072911 A1 TW 570993 B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/054413

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The invention in claims 1-9 relates to a metallic material which comprises a metallic material base and a specific modification layer formed on the surface thereof.

Meanwhile, the invention in claims 10 and 11 relates to a method for treating the surface of a metallic material. However, this invention is not a method especially for use in producing the metallic material which is the invention in claims 1-9.

(Continued to extra sheet)

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/054413

Continuation of Box No.III of continuation of first sheet(2)

The invention in claim 12 relates to a process for producing a water-repellent material that includes a metallic material as the base. However, this invention is not a method especially for use in producing the metallic material which is the invention in claims 1-9.

The inventions in claims 13-18 relate to a surface treatment device for a conductive material and to a method utilizing the surface treatment device. However, these inventions are not a device especially designed for producing the metallic material which is the invention in claims 1-9.

Consequently, the present application involves three inventions which comprise claims 1-9, claims 10-12 and claims 13-18.

REFERENCES CITED IN THE DESCRIPTION

Non-patent literature cited in the description

- **HIDEAKI TAKAHASHI ; MASATOSHI SAKAIRI ; TATSUYA KIKUCHI ; HIMENDRA JHA.** *Hyomen Gijutsu,* 2009, vol. 60 (3), 14 **[0003]**
- **WATARU NATSU.** Application and Theory of Micro Electrochemical Machining. *Hyomen Gijutsu,* 2010, vol. 61 (4), 294 **[0004]**