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(54) **SURFACE TREATMENT METHOD FOR METAL MEMBER AND METAL MEMBER OBTAINED BY SAME**

(57) A surface treatment method improves the surface properties of a metal member while maintaining the metal surface texture, and a metal member is obtained by the surface treatment method. The surface-treated metal member is obtained by bringing a solution of a fluorine-based polymer into contact with a surface of an anodic oxidation coating that is formed on a surface of a metal and has not been subjected to a sealing treatment,

and subjecting the anodic oxidation coating to a steam sealing treatment, the surface-treated metal member comprising a fluorine-based polymer layer having a thickness of 100 nm or less, and a composite sealed layer that is formed continuously under the fluorine-based polymer layer, the composite sealed layer having a configuration in which the fluorine-based polymer is present inside pores formed in the anodic oxidation coating.

FIG. 1

	PRETREATMENT			COATING			STEAM SEALING
	TREATMENT LIQUID	TEM- PERA- TURE	TIME	PRIMER	TOPCOAT	COATING METHOD	
		°C	MIN				
EXAMPLE 1	—	—	—	NO	FLUORORESIN	DIP	YES
EXAMPLE 2	PURIFIED WATER	80	10	NO	FLUORORESIN	DIP	YES
EXAMPLE 3	PURIFIED WATER	80	10	NO	FLUORORESIN	SPRAYING	YES
COMPARATIVE EXAMPLE 1	PURIFIED WATER	100	20	NO	NO	—	NO
COMPARATIVE EXAMPLE 2	PURIFIED WATER	100	20	YES	FLUORORESIN	DIP	NO
COMPARATIVE EXAMPLE 3	PURIFIED WATER	80	10	NO	FLUORORESIN	DIP	NO
COMPARATIVE EXAMPLE 4	PURIFIED WATER	80	10	NO	FLUORORESIN	DIP	BOILING WATER SEALING

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Description

TECHNICAL FIELD

[0001] The present invention relates to a surface treatment method for an anodizable metal member, and a metal member that is obtained by the surface treatment method and exhibits improved surface properties.

BACKGROUND ART

[0002] The surface of a metal member produced using aluminum, an aluminum alloy, magnesium, a magnesium alloy, titanium, a titanium alloy, or the like is generally provided with an anodic oxidation coating in order to improve corrosion resistance, design, and the like.

[0003] However, a metal member provided with only an anodic oxidation coating may exhibit insufficient corrosion resistance during long-term use.

[0004] A metal member provided with only an anodic oxidation coating may also be easily contaminated.

[0005] When a coloring step (e.g., secondary electrolytic coloring) is performed after anodizing, significant discoloration may occur due to insufficient corrosion resistance of the anodic oxidation coating.

[0006] In the fields of aluminum building materials and the like, a clear coating is provided after anodizing via anionic electrodeposition coating or the like in order to deal with the above problems.

[0007] However, since a clear coating has a thickness as large as 10 to 20 μm , the metal surface texture may be impaired.

[0008] Therefore, it is difficult to deal with the above problems by providing a clear coating when producing an automotive decorative member (e.g., decorative trim) for which the metal surface texture is important.

[0009] A transparent fluororesin coating that can provide corrosion resistance with a reduced thickness as compared with an acrylic clear coating or a urethane clear coating has been proposed.

[0010] Patent Document 1 that aims at dealing with a wax remover discloses a technique that forms a polytetrafluoroethylene (PTFE) coating layer on the surface of an alumite coating.

[0011] However, since Patent Document 1 states that it is appropriate that the thickness of the PTFE coating layer is 3 μm , a film-like surface texture is necessarily observed. Moreover, since Patent Document 1 states that it is necessary to apply a primer or enlarge the pores formed in the anodic oxidation coating, the process is complex, and the treatment cost increases.

[0012] Patent Document 2 discloses immersing a metal material provided with an anodic oxidation coating in a solution that contains a hydrophilic amorphous fluororesin so that the amorphous fluororesin enters the pores formed in the anodic oxidation coating. However, it is necessary to perform a preliminary heat treatment in order to improve the quality, and polymerize the fluororesin

layer on the anodic oxidation coating by heating at 200°C for 30 minutes.

[0013] Therefore, the coating layer disclosed in Patent Document 2 has a large thickness, and a film-like surface texture is necessarily observed. Moreover, cracks may occur in the anodic oxidation coating when the anodic oxidation coating is heated at a high temperature of 200°C.

10 Patent Document 1: JP-A-2006-257552
Patent Document 2: JP-A-2006-126680

DISCLOSURE OF THE INVENTION

15 TECHNICAL PROBLEM

[0014] An object of the invention is to provide a surface treatment method that improves the surface properties of a metal member while maintaining the metal surface texture, and a metal member that is obtained by the surface treatment method.

SOLUTION TO PROBLEM

25 **[0015]** According to one aspect of the invention, a surface-treated metal member that is obtained by bringing a solution of a fluorine-based polymer (hereinafter may be referred to as "fluorine-based polymer solution") into contact with a surface of an anodic oxidation coating that is formed on a surface of a metal and has not been subjected to a sealing treatment, and subjecting the anodic oxidation coating to a steam sealing treatment, the surface-treated metal member comprising:

35 a fluorine-based polymer layer having a thickness of 100 nm or less, and
a composite sealed layer that is formed continuously under the fluorine-based polymer layer, wherein the composite sealed layer has a configuration in which the fluorine-based polymer is present inside pores formed in the anodic oxidation coating.

45 **[0016]** An electrolytic coloring step may be performed after forming the anodic oxidation coating as long as the fluorine-based polymer solution is brought into contact with the anodic oxidation coating that has not been subjected to a sealing treatment, and the anodic oxidation coating is then subjected to the steam sealing treatment.

50 **[0017]** According to another aspect of the invention, a surface treatment method for a metal member comprising:

55 forming a porous anodic oxidation coating on a surface of a metal, bringing a fluorine-based polymer solution into contact with the anodic oxidation coating in a state in which the anodic oxidation coating is unsealed or semi-sealed, and subjecting the anodic oxidation coating to a steam

sealing treatment.

[0018] The surface treatment method may further include subjecting the anodic oxidation coating to electrolytic coloring after forming the anodic oxidation coating, but before bringing the fluorine-based polymer solution into contact with the anodic oxidation coating.

[0019] The surface-treated metal member according to one aspect of the invention is characterized by including the composite sealed layer that is formed by subjecting the anodic oxidation coating to the steam sealing treatment in a state in which the fluorine-based polymer is present inside the pores formed in the anodic oxidation coating from the viewpoint of maintaining the metal surface texture. It suffices that the fluorine-based polymer layer that is formed continuously over the composite sealed layer have a small thickness.

[0020] The thickness of the fluorine-based polymer layer is adjusted to 100 nm or less, and preferably 10 nm or less, in order to prevent a situation in which the surface of the anodic oxidation coating has a film-like texture.

[0021] The aspects of the invention are applied to a metal member on which a porous anodic oxidation coating can be formed. The aspects of the invention are mainly applied to a metal member formed of aluminum, magnesium, titanium, or an alloy thereof.

[0022] The type of the anodic oxidation coating is not particularly limited as long as the anodic oxidation coating is porous. The metal member is anodized using a known electrolytic solution such as sulfuric acid or an organic acid.

[0023] The expression "has not been subjected to a sealing treatment" used herein in connection with the anodic oxidation coating means that the anodic oxidation coating has not been subjected to the steam sealing treatment, and means that the anodic oxidation coating may have been washed with water, washed with hot water, or semi-sealed using hot water at 60 to 90°C.

[0024] The anodic oxidation coating may have been washed with water, subjected to electrolytic coloring, and washed with water or hot water.

[0025] The term "electrolytic coloring" used herein refers to subjecting the anodic oxidation coating that has not been subjected to a sealing treatment to a DC electrolysis, AC electrolysis, or the like in an aqueous solution that includes metal ions (e.g., nickel ions or tin ions) to deposit the metal ions inside the pores formed in the anodic oxidation coating.

[0026] The term "steam sealing treatment" used herein refers to a sealing treatment that utilizes normal-pressure steam or pressurized steam.

[0027] The fluorine-based polymer used in connection with the aspects of the invention is a fluorine-based polymer that has such a molecular weight that the fluorine-based polymer can be dissolved in a solvent to prepare a solution.

[0028] Examples of the fluorine-based polymer include polytetrafluoroethylene, a polytetrafluoroethylene copol-

mer such as an ethylene-tetrafluoroethylene copolymer, polyvinyl fluoride, a copolymer thereof, polyvinylidene fluoride, a copolymer thereof, polychlorotrifluoroethylene, a copolymer thereof, and the like.

[0029] It is also effective to use a perfluoroalkyl group-containing fluorine-based polymer that is provided with water repellency and oil repellency and exhibits improved stain-proof properties.

[0030] Examples of the perfluoroalkyl group-containing fluorine-based polymer include a polyperfluoroalkyl (meth)acrylate, a poly(2-(perfluoroalkyl)ethyl (meth)acrylate), a tetrafluoroethylene-perfluoroalkyl vinyl ether, a poly(perfluoroalkyl vinyl ether), a poly(2-(perfluoro(alkyl)ethyl vinyl ether), and the like.

[0031] The perfluoroalkyl group is preferably represented by C_nF_{2n+1} (wherein n is an integer from 1 to 6).

[0032] The solvent used in connection with the aspects of the invention may be an organic solvent such as a ketone (e.g., acetone, MEK, or MIBK), ethyl acetate, butyl acetate, diethyl ether, dioxane, ethanol, or isopropyl alcohol. It is preferable to use a fluorine-based solvent that exhibits high affinity to the fluorine-based polymer.

[0033] The fluorine-based solvent also has an advantage in that it is unnecessary to use special ventilation/explosion-proof equipment.

[0034] Examples of the fluorine-based solvent include a perfluorocarbon, a hydrofluorocarbon, a hydrochlorofluorocarbon, a hydrofluoroether, a perfluoropolyether, a hydrofluoropolyether, and the like.

[0035] The fluorine-based polymer solution may be brought into contact with the anodic oxidation coating using an arbitrary means such as dipping, spraying, or brush coating.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0036] Since the surface-treated metal member according to one aspect of the invention includes the composite sealed layer in which the fluorine-based polymer is present inside the pores formed in the anodic oxidation coating, the surface-treated metal member exhibits excellent adhesion. Since the fluorine-based polymer layer that is formed continuously over the composite sealed layer has a thickness as small as 100 nm or less, the surface-treated metal member does not show a film-like texture.

[0037] Therefore, the surface-treated metal member exhibits excellent long-term corrosion resistance, is not easily contaminated, and can be easily cleaned by wiping the surface-treated metal member due to the water repellency and the oil repellency of the fluorine-based polymer.

[0038] When the surface-treated metal member has been subjected to electrolytic coloring, discoloration can be suppressed due to the improved corrosion resistance of the anodic oxidation coating.

BRIEF DESCRIPTION OF DRAWINGS

[0039]

FIG. 1 shows sample production conditions.

FIG. 2 shows evaluation results for samples.

FIG. 3 shows an SEM image.

FIG. 4 shows cross-sectional elemental analysis results.

FIG. 5 shows evaluation results for samples subjected to secondary electrolytic coloring.

FIG. 6 shows photographs of samples subjected to secondary electrolytic coloring after a salt spray test.

DESCRIPTION OF EMBODIMENTS

[0040] Metal member production examples according to several embodiments of the invention are described in detail below. Note that the invention is not limited to the following examples.

[0041] The surface of an extruded shape (T5 material) produced by extrusion using a JIS A 6063 alloy was subjected to a pretreatment (buffing and chemical polishing).

[0042] The extruded shape was anodized using a 15% sulfuric acid electrolytic solution at a current density of 1 A/dm² and a bath temperature of 20°C to form an anodic oxidation coating having a thickness of 10 μm on the surface of the extruded shape (metal).

[0043] In Example 1, the anodic oxidation coating was washed with water. In Example 2, the anodic oxidation coating was subjected to a semi-sealing treatment (washing) at 80°C for 10 minutes using purified water. In Examples 1 and 2, the anodic oxidation coating was then dipped in a fluorine-based polymer solution prepared by dissolving a fluorine-based polymer in a fluorine-based solvent ("OPC-800" manufactured by Noda Screen Co., Ltd.), and removed from the solution.

[0044] In Example 3, the fluorine-based polymer solution was sprayed onto the surface of the anodic oxidation coating.

[0045] The thickness of the fluorine-based polymer that adhered to the surface of the anodic oxidation coating removed from the fluorine-based polymer solution after dipping was estimated to be about 10 nm.

[0046] In Examples 1 to 3, the anodic oxidation coating was then subjected to a sealing treatment for 20 minutes using steam at 150°C.

[0047] Note that the steam sealing treatment may be performed under normal pressure. In this case, however, the sealing time may relatively increase. Therefore, it is preferable to perform the steam sealing treatment using pressurized steam at 130 to 180°C (for 10 to 30 minutes).

[0048] In Comparative Example 1, the anodic oxidation coating was subjected to a boiling water sealing treatment at 100°C for 20 minutes using purified water.

[0049] In Comparative Example 2, a fluororesin primer was applied to the anodic oxidation coating subjected to a boiling water sealing treatment in the same manner as

in Comparative Example 1, and the anodic oxidation coating was then dipped in the fluorine-based polymer solution, and dried.

[0050] In Comparative Example 3, the anodic oxidation coating was treated, and dipped in the fluorine-based polymer solution in the same manner as in Example 2, but was then dried without subjecting the anodic oxidation coating to the steam sealing treatment.

[0051] In Comparative Example 4, the anodic oxidation coating was treated, and dipped in the fluorine-based polymer solution in the same manner as in Example 2, but was then subjected to a boiling water sealing treatment at 100°C for 20 minutes using purified water.

[0052] The external appearance of the samples obtained in Examples 1 to 3 and Comparative Examples 1 to 4 was evaluated with the naked eye. The samples were then subjected to a 200 hr salt spray test, and the color difference due to the test was measured (chroma meter: "CR-400" manufactured by KONICA MINOLTA INC.).

[0053] FIG. 1 shows the sample production conditions, and FIG. 2 shows the evaluation results.

[0054] Note that "DIP" in FIG. 1 refers to "dipping".

[0055] As shown in FIG. 2, the samples obtained in Examples 1 to 3 maintained their metal surface texture, and did not show a change in surface quality due to the salt spray test.

[0056] In contrast, the sample obtained in Comparative Example 1 showed slight surface whitening, and the sample obtained in Comparative Example 2 showed a trace of the primer, and had an inferior texture.

[0057] The sample obtained in Comparative Example 3 was not subjected to the steam sealing treatment after dipping the anodic oxidation coating in the fluorine-based polymer solution. As a result, the sample obtained in Comparative Example 3 showed whitening (discoloration) when subjected to the salt spray test.

[0058] The sample obtained in Comparative Example 4 was subjected to the boiling water sealing treatment after dipping the anodic oxidation coating in the fluorine-based polymer solution. As a result, the sample obtained in Comparative Example 4 showed slight surface whitening.

[0059] It was thus confirmed that it is insufficient to merely dip the anodic oxidation coating in the fluorine-based polymer solution, or spray the fluorine-based polymer solution onto the anodic oxidation coating, and it is effective to perform the steam sealing treatment after dipping the anodic oxidation coating in the fluorine-based polymer solution, or spraying the fluorine-based polymer solution onto the anodic oxidation coating.

[0060] The cross section of the sample obtained in Example 2 was observed using a scanning electron microscope (SEM), and the elements were semi-quantitatively analyzed.

[0061] The results are shown in FIGS. 3 and 4.

[0062] A scanning electron microscope "JSM-7000FZ" (manufactured by JEOL Ltd.) was used for cross-sec-

tional observation, and an EDS analyzer "EX-2300×BU" (manufactured by JEOL Ltd.) was used for semi-quantitative elemental analysis.

[0063] FIG. 3 shows the resulting SEM photograph.

[0064] FIG. 4 shows the elemental analysis results for the surface, the upper part of the cross section, and the lower part of the cross section (see FIG. 3).

[0065] The thickness of the fluorine-based polymer layer formed on the surface could not be measured since the thickness of the fluorine-based polymer layer was very small. Since fluorine was detected (deposited) in the upper part of the cross section of the anodic oxidation coating, it was confirmed that a composite sealed layer was formed in which fluorine was present inside the pores formed in the anodic oxidation coating.

[0066] In order to check the effects of electrolytic coloring, a sample of Example 4 was obtained in the same manner as in Example 1, and subjected to the salt spray test, except that the anodic oxidation coating was washed with water, and subjected to secondary electrolytic coloring (black) using a nickel-tin mixed bath.

[0067] In Comparative Example 5, the anodic oxidation coating was subjected to secondary electrolytic coloring in the same manner as in Example 4, and then subjected to the boiling water sealing treatment in the same manner as in Comparative Example 1 without bringing the fluorine-based polymer solution into contact with the anodic oxidation coating.

[0068] FIG. 5 shows the measurement results for the color difference due to the salt spray test.

[0069] FIG. 6 shows photographs of the samples obtained in Example 4 and Comparative Example 5 after the salt spray test.

[0070] It was thus confirmed that the anodic oxidation coating subjected to secondary electrolytic coloring maintained its metal surface texture, and exhibited improved corrosion resistance as a result of forming the fluorine-based polymer layer on the anodic oxidation coating, and subjecting the anodic oxidation coating to the steam sealing treatment.

INDUSTRIAL APPLICABILITY

[0071] The surface treatment method according to the embodiments of the invention is suitable for a metal member on which a porous anodic oxidation coating can be formed, and may be applied to various fields (e.g., automotive parts) that utilize such a metal member.

Claims

1. A surface-treated metal member that is obtained by bringing a solution of a fluorine-based polymer into contact with a surface of an anodic oxidation coating that is formed on a surface of a metal and has not been subjected to a sealing treatment, and subjecting the anodic oxidation coating to a steam sealing

treatment,

the surface-treated metal member comprising:

a fluorine-based polymer layer having a thickness of 100 nm or less; and
a composite sealed layer that is formed continuously under the fluorine-based polymer layer, wherein the composite sealed layer has a configuration in which the fluorine-based polymer is present inside pores formed in the anodic oxidation coating.

2. The surface-treated metal member as defined in claim 1, wherein the anodic oxidation coating that has not been subjected to a sealing treatment has been subjected to electrolytic coloring.

3. A surface treatment method for a metal member comprising:

forming a porous anodic oxidation coating on a surface of a metal;
bringing a fluorine-based polymer solution into contact with the anodic oxidation coating in a state in which the anodic oxidation coating is unsealed or semi-sealed; and
subjecting the anodic oxidation coating to a steam sealing treatment.

4. The surface treatment method as defined in claim 3, further comprising:

subjecting the anodic oxidation coating to electrolytic coloring after forming the porous anodic oxidation coating, but before bringing the fluorine-based polymer solution into contact with the anodic oxidation coating.

FIG. 1

	PRETREATMENT			COATING			STEAM SEALING
	TREATMENT LIQUID	TEM- PERA- TURE	TIME	PRIMER	TOPCOAT	COATING METHOD	
		°C	MIN				
EXAMPLE 1	—	—	—	NO	FLUORORESIN	DIP	YES
EXAMPLE 2	PURIFIED WATER	80	10	NO	FLUORORESIN	DIP	YES
EXAMPLE 3	PURIFIED WATER	80	10	NO	FLUORORESIN	SPRAYING	YES
COMPARATIVE EXAMPLE 1	PURIFIED WATER	100	20	NO	NO	—	NO
COMPARATIVE EXAMPLE 2	PURIFIED WATER	100	20	YES	FLUORORESIN	DIP	NO
COMPARATIVE EXAMPLE 3	PURIFIED WATER	80	10	NO	FLUORORESIN	DIP	NO
COMPARATIVE EXAMPLE 4	PURIFIED WATER	80	10	NO	FLUORORESIN	DIP	BOILING WATER SEALING

FIG. 2

	EXTERNAL APPEARANCE AFTER SURFACE TREATMENT	EXTERNAL APPEARANCE AFTER SALT SPRAY TEST	COLOR DIFFERENCE MEASUREMENT RESULTS								ΔE
			BEFORE SALT SPRAY TEST				AFTER SALT SPRAY TEST				
			L*	a*	b*	L*	a*	b*			
EXAMPLE 1	ACCEPT-ABLE	ACCEPT-ABLE	79.82	-0.64	0.58	79.88	-0.69	0.56	0.08		
EXAMPLE 2	ACCEPT-ABLE	ACCEPT-ABLE	79.34	-0.48	0.07	79.28	-0.45	0.05	0.07		
EXAMPLE 3	ACCEPT-ABLE	ACCEPT-ABLE	80.22	-0.65	0.34	80.27	-0.70	0.35	0.07		
COMPAR-ATIVE EXAMPLE 1	ACCEPT-ABLE	SLIGHT WHITENING WAS OBSERVED	80.12	-0.47	-0.10	80.49	-0.46	0.13	0.44		
COMPAR-ATIVE EXAMPLE 2	TRACE OF PRIMER WAS OBSERVED	ACCEPT-ABLE	80.10	-0.49	0.28	80.19	-0.51	0.29	0.09		
COMPAR-ATIVE EXAMPLE 3	ACCEPT-ABLE	WHITENING WAS OBSERVED	80.68	-0.59	0.02	83.90	-0.66	0.45	3.25		
COMPAR-ATIVE EXAMPLE 4	ACCEPT-ABLE	SLIGHT WHITENING WAS OBSERVED	79.83	-0.68	0.78	80.12	-0.73	0.76	0.29		

FIG. 3

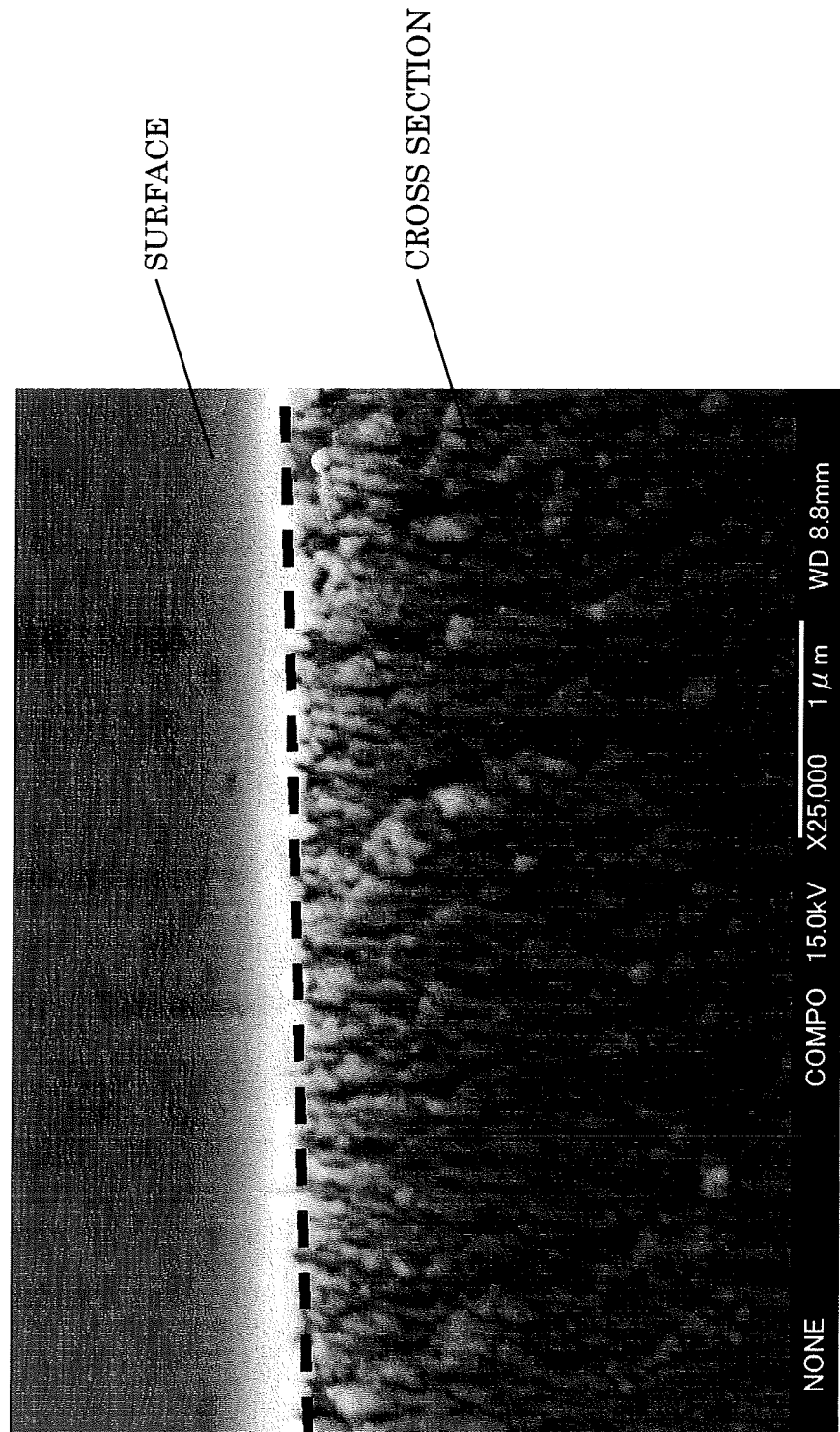


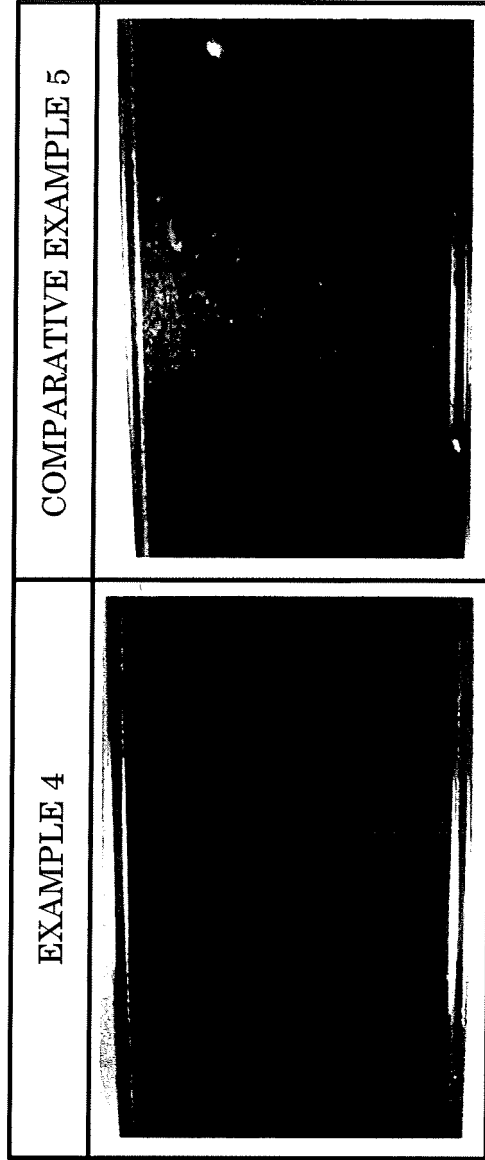
FIG. 4

	ELEMENT	(keV)	MASS (%)	ERROR (%)	NUMBER OF ATOMS (%)
SURFACE	O K	0.525	49.12	0.36	61.40
	F K	0.677	3.66	0.68	3.85
	Al K	1.486	45.00	0.40	33.36
	S K	2.307	2.23	0.56	1.39
	TOTAL		100.00		100.00
UPPER PART OF CROSS SECTION (0.5 ~ 1 μm)	O K	0.525	38.31	0.25	51.10
	F K	0.677	1.87	0.44	2.11
	Al K	1.486	55.68	0.17	44.04
	S K	2.307	4.13	0.24	2.75
	TOTAL		100.00		100.00
LOWER PART OF CROSS SECTION (NEAR ALUMINUM)	O K	0.525	18.13	0.89	27.23
	F K	0.677	0.97	0.90	1.23
	Al K	1.486	77.53	0.29	69.02
	S K	2.307	3.37	0.49	2.52
	TOTAL		100.00		100.00

FIG. 5

	EXTERNAL APPEARANCE AFTER SURFACE TREATMENT	EXTERNAL APPEARANCE AFTER SALT SPRAY TEST	COLOR DIFFERENCE MEASUREMENT RESULTS						ΔE
			BEFORE SALT SPRAY TEST			AFTER SALT SPRAY TEST			
			L*	a*	b*	L*	a*	b*	
EXAMPLE 4	ACCEPTABLE	ACCEPTABLE	16.44	0.72	0.18	16.67	0.47	0	0.38
COMPARATIVE EXAMPLE 5	ACCEPTABLE	SPOT-LIKE WHITENING WAS OBSERVED	16.44	0.72	0.18	15.34	0.6	-4.19	4.5

FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/053635

A. CLASSIFICATION OF SUBJECT MATTER C25D11/18(2006.01) i, C25D11/22(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) C25D11/18, C25D11/22		
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 1996-2012 Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012		
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.
A	JP 46-26231 B1 (Sumitomo Electric Industries, Ltd.), 29 July 1971 (29.07.1971), entire text (Family: none)	1-4
A	JP 5-261852 A (Electro Chemical Engineering GmbH), 12 October 1993 (12.10.1993), paragraph [0012] & DE 4239391 A1 & US 5487825 A & CH 690174 A	1-4
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> 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 14 May, 2012 (14.05.12)		Date of mailing of the international search report 22 May, 2012 (22.05.12)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/053635

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 6-184793 A (Mitsubishi Heavy Industries, Ltd.), 05 July 1994 (05.07.1994), claims (Family: none)	1-4
A	JP 11-104560 A (Sky Aluminium Co., Ltd.), 20 April 1999 (20.04.1999), claims (Family: none)	1-4
A	JP 2000-203970 A (Placeram Co., Ltd.), 25 July 2000 (25.07.2000), claims (Family: none)	1-4
A	JP 2005-513277 A (Leybold Vakuum GmbH), 12 May 2005 (12.05.2005), claims & WO 2003/056187 A1 & DE 10163864 A & AU 2002360993 A & EP 1485622 A & CN 1608174 A & US 2005/0098441 A1 & DE 50203798 D & HK 1069423 A	1-4
A	JP 2009-506202 A (Oerlikon Leybold Vakuum GmbH), 12 February 2009 (12.02.2009), paragraph [0006] & DE 102005040648 A1 & WO 2007/025868 A1 & EP 1919632 A & KR 10-2008-0043316 A & CN 101253004 A & US 2009/0068451 A1 & RU 2008111634 A	1-4

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2006257552 A [0013]
- JP 2006126680 A [0013]