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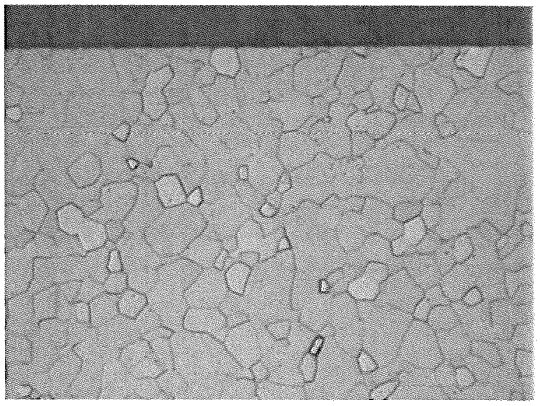
(54) TITANIUM ALLOY MATERIAL

(57) [Object] To provide a titanium alloy material containing a platinum group metal, the titanium alloy material being able to sufficiently suppress corrosion accompanying surface roughening.

[Solution] Provided is a titanium alloy material including a platinum group metal. When an average value of intensity of background signals in surface mapping analysis using an EPMA surface analysis apparatus is N and $N+3N^{1/2}$ is maximum intensity of the background signal of an Fe or S characteristic X-ray, an area ratio at which a signal of an Fe or S characteristic X-ray exceeding the maximum intensity is obtained is 0.1 % or less.

FIG. 3



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Description

[Technical Field]

[0001] The present invention relates to a titanium alloy material, particularly to a titanium alloy material containing a platinum group metal.

[Background Art]

[0002] Titanium is being actively used in the aircraft field and the like, utilizing its feature of lightness and strength. Further, having high corrosion resistance, titanium is beginning to be used in wide range of fields as a material for chemical industry equipment, a material for thermal and nuclear power generation equipment, and a material for seawater desalination equipment, and the like.

[0003] However, the environment in which titanium can exhibit its high corrosion resistance is limited to oxidizing acid (nitric acid) environment and neutral chloride environment such as seawater. Titanium does not have sufficient crevice corrosion resistance in a high-temperature chloride environment, nor sufficient corrosion resistance in a non-oxidizing acid solution such as hydrochloric acid (hereinafter, in this section, the crevice corrosion resistance and the corrosion resistance are referred to as "corrosion resistance").

[0004] An example of a titanium alloy having improved corrosion resistance is a Ti-0.15 Pd alloy (Gr. 7 and Gr. 11 according to the ASTM standard) (hereinafter, "Gr." (Grade) complies with the ASTM standard). This titanium alloy is produced by using the phenomenon that Pd in the alloy reduces hydrogen overvoltage to maintain the natural potential within a passivation range. That is, in this alloy, Pd eluted from the alloy by corrosion is precipitated again on the surface of the alloy to be deposited, and thereby hydrogen overvoltage is reduced and the natural potential is maintained within the passivation range. Accordingly, this alloy has high corrosion resistance.

[0005] Gr. 7 having high corrosion resistance, however, contains Pd, which is a very expensive platinum group metal; accordingly, the fields using Gr. 7 have been limiting.

[0006] To solve this problem, as disclosed in Patent Document 1 below, a titanium alloy (Gr. 17) and the like having high crevice corrosion resistance while having a lower content rate of Pd, which is 0.01 to 0.12 % by mass, than Gr. 7, is proposed and put into practical use. In this manner, a titanium alloy containing a platinum group metal is gaining widespread use, so that the titanium alloy is beginning to be used even in a harsh environment such as a high-temperature chloride environment.

[0007] However, the titanium alloy containing a platinum group metal and having high corrosion resistance may cause corrosion that is different from pitting corrosion or so-called crevice corrosion (accompanying whitening and wastage due to the generation of TiO_2). The present inventors have closely examined this kind of corrosion.

[0008] FIG. 1 is a photograph showing the outside appearance of a Gr. 17 titanium alloy material in which corrosion has occurred. As shown in FIG. 1, a corroded part often has high surface roughness (hereinafter, getting high surface roughness is referred to as "surface roughening"). Further, it is found that black matter has adhered or the titanium alloy has changed its color into black in the vicinity of the corroded part. Then, the present inventors have confirmed the existence of hydride (TiH or TiH_2) in the corroded part. Therefore, this corrosion is closely related to hydrogen.

[0009] FIG. 2 is a photograph showing a cross-sectional structure of the corroded Gr. 17 titanium alloy material. On the surface of the corroded part of the titanium alloy material, a plurality of concave portions are formed (in FIG. 2, arrows denote the parts where concave portions are formed.). From FIG. 2, it is found that spotted or pointed substances are formed in the range from the vicinity of the surface to the inside. The present inventors have confirmed that the substances are hydride. Hydride is considered to have been generated from hydrogen that entered from the surface of the material.

[0010] FIG. 3 is a photograph showing a cross-sectional structure of a non-corroded Gr. 17 titanium alloy material. Surface roughening of the titanium alloy material has not progressed, and in such a titanium alloy material, there is not as much hydride as in the titanium alloy material shown in FIG. 2, at least.

[0011] Patent Document 2 below discloses a material having improved grain-boundary corrosion resistance by orienting precipitates (Ti_2Ni) contained in a titanium alloy containing a platinum group along a rolling direction.

[0012] Patent Document 3 discloses a material in which, in order to prevent embrittlement caused by hydrogen absorption, a hydride layer is formed in advance only in the vicinity of the surface and further hydrogen absorption and hydrogen embrittlement are prevented in the usage environment of the material.

[Prior Art Document(s)]

[Patent Document(s)]

[0013]

[Patent Document 1] JP 3916088B
[Patent Document 2] JP 2012-12636A
[Patent Document 3] JP 2005-36314A

[Non-Patent Document(s)]

[0014] [Non-Patent Document 1] Soejima, Hiroyoshi, Electron Probe Microanalysis: Scanning Electron Microscope and X-ray Micro-analyzing Method, Nikkan Kogyo Shimbun, LTD., 1987, Chapter 4: Spatial Resolution by EPMA, 4.2.4.3 Statistical Fluctuation, p. 112.

[Summary of the Invention]

[Problem(s) to Be Solved by the Invention]

[0015] Although various measured have been proposed for the problems of corrosion accompanying surface roughening of a titanium alloy material, conventional measures cannot suppress this kind of corrosion sufficiently.

[0016] The present invention has been made in view of the above circumstance, and aims to provide a titanium alloy material containing a platinum group metal, the titanium alloy material being able to sufficiently suppress corrosion accompanying surface roughening.

[Means for Solving the Problem(s)]

[0017] The present inventors have closely studied to solve the above problems of corrosion, and have made the present invention. The present invention relates to a titanium alloy material as described in the following (1) to (7).

(1) A titanium alloy material including:

a platinum group metal,
wherein, when an average value of intensity of background signals in surface mapping analysis using an EPMA surface analysis apparatus is N and $N+3N^{1/2}$ is maximum intensity of the background signal of an Fe characteristic X-ray, an area ratio at which a signal of an Fe characteristic X-ray exceeding the maximum intensity is obtained is 0.1 % or less.

(2) A titanium alloy material including:

a platinum group metal,
wherein, when an average value of intensity of background signals in surface mapping analysis using an EPMA surface analysis apparatus is N and $N+3N^{1/2}$ is maximum intensity of the background signal of a S characteristic X-ray, an area ratio at which a signal of a S characteristic X-ray exceeding the maximum intensity is obtained is 0.1 % or less.

(3) The titanium alloy material according to (1) or (2),
wherein the area ratio at which the signal of the Fe characteristic X-ray exceeding the maximum intensity is 0.05 % or less and the area ratio at which the signal of the S characteristic X-ray exceeding the maximum intensity is 0.05 % or less.
(4) The titanium alloy material according to (1) or (3),
wherein a content of Fe obtained by point analysis of part in which Fe is present on the surface of the titanium alloy material is 0.5 or less in atomic ratio of Fe with respect to Ti.
(5) The titanium alloy material according to any one of (1) to (4),
wherein the platinum group metal is contained in 0.01 to 0.25 % by mass.
(6) The titanium alloy material according to any one of (1) to (5),
wherein at least one selected from the group consisting of Ni in 0.05 to 1.0 % by mass, Cr in 0.05 to 0.3 % by mass, and Mo in 0.05 to 0.5 % by mass is further contained.
(7) The titanium alloy material according to any one of (1) to (6),
wherein Pd is contained in 0.01 to 0.25 % by mass as the platinum group metal. [Effect(s) of the Invention]

[0018] The titanium alloy material according to the present invention can be used for applications that need high corrosion resistance (e.g., crevice corrosion resistance and acid resistance), resistance against corrosion progress,

processability, and economic efficiency Specifically, the titanium alloy material according to the present invention can be used in a harsh environment such as an anode of a brine electrolytic cell and salt processing equipment.

[Brief Description of the Drawing(s)]

[0019]

[FIG. 1] FIG. 1 is a photograph showing the outside appearance of a corroded Gr. 17 titanium alloy material.
[FIG. 2] FIG. 2 is a photograph showing a cross-sectional structure of a corroded Gr. 17 titanium alloy material.
[FIG. 3] FIG. 3 is a photograph showing a cross-sectional structure of a non-corroded Gr. 17 titanium alloy material.
[FIG. 4] FIG. 4 shows results of surface mapping analysis with an EPMA surface analysis apparatus for samples according to the present invention.
[FIG. 5] FIG. 5 shows results of surface mapping analysis with an EPMA surface analysis apparatus for samples not according to the present invention.
[FIG. 6] FIG. 6 is a schematic diagram of a sample used for corrosion testing and a schematic diagram of a sample for crevice corrosion testing.

[Mode(s) for Carrying out the Invention]

[0020] The present invention is based on the present inventors' knowledge as follows.
[0021] In a case in which a titanium alloy is used in a crevice structure, corrosion may occur accompanying surface roughening, which is different from so-called crevice corrosion. This kind of corrosion may rarely accompany expansion. The present inventors have studied parts where such corrosion has occurred, and have confirmed that one or both of Fe and S is detected in the corroded parts in many cases. Further, the present inventors have studied the relation between the surface state of a titanium alloy material and the presence and absence of the occurrence of corrosion. Accordingly, as will be described later, they have found out that the occurrence of corrosion accompanying surface roughening can be suppressed by adjusting the ratio of Fe and/or S existing on the surface to be a certain level or lower.
[0022] As shown above, when a cross section of the part where corrosion accompanying surface roughening has occurred is observed, spotted or pointed hydride can be seen only in the vicinity of the corroded surface, and accordingly, the corrosion is considered to be related to hydride. It is after a long period of time lapses after the titanium alloy is placed in a crevice structure in a normal environment, for example, when such corrosion can be visually observed as a change in appearance; such a change in appearance cannot be seen after a short period time lapses. Accordingly, the present inventors have conducted acceleration testing in which such corrosion has been caused to analyze the relation between the surface state before corrosion of the titanium alloy and corrosion.

1) Identify surface contaminating element

[0023] Gr. 11, Gr. 13, and Gr. 17 materials having different surface contaminating degrees were commercially obtained and were subjected to surface analysis with an electron probe micro analyzer (EPMA) surface analysis apparatus to find out elements that are present on the surface. For each of the Gr. 11, Gr. 13, and Gr. 17 materials, elements that are present on the surface are as follows.
[0024] On the surface of the Gr. 11 and Gr. 17 materials, Ti and Pd were detected as matrix components, and C, O, Fe, Zn, S, Cl, Na, and F were detected as components other than matrix components.
[0025] On the surface of the Gr. 13 material, Ti, Ni, and Ru were detected as matrix components, and C, O, Fe, Zn, S, Cl, Na, Ca, and F were detected as components other than matrix components.
[0026] The factor of detection of the elements other than the matric components among the above elements was studied.
[0027] C is considered to be from rolling oil used in a manufacturing process. O is from a passivation film of titanium, so that O is generally observed on the surface of a titanium material.
[0028] On the other hand, Fe, Zn, and S are elements that are not observed in a general titanium alloy material, and are each defined as "surface contaminating element" in this specification. Note that Fe is in some cases added to a titanium material in order to improve strength, and such a titanium alloy material contains Fe in a base material regardless of contamination by Fe. Such Fe is normally molten in the titanium material and distributed uniformly, so that, when the titanium alloy material is analyzed with the EPMA surface analysis apparatus, signals of Fe are counted as backgrounds. Fe that the present application focuses on is Fe that is brought by Fe contamination and is present in a condensed state on the surface of the titanium material, without being molten therein.
[0029] The surface analysis detects Ca, Na, and Cl. However, the detected amounts of such elements are minute, and accordingly such elements are excluded from the contaminating elements defined in this specification. Such elements

are assumed to have been adhered on the titanium alloy material mainly from humans who handled the titanium alloy material commercially.

[0030] The surface contamination by Fe is assumed to be from a stainless steel product or steel product produced in the same manufacturing line as the target titanium alloy material, or from a shot piece remaining on the surface of the titanium alloy material, the shot piece being used for shot peening at a time of descaling of a hot rolled sheet (Fe contamination caused by a shot piece will be described later in detail in the section "6) Method of manufacturing titanium alloy material according to the present invention"). In a case in which a titanium alloy material is used in a crevice structure, a black oxide that is assumed to be Fe_3O_4 may be generated on the surface thereof in the crevice structure. A part where such an oxide is generated undergoes surface roughening by corrosion, as shown in FIG. 1, and hydride is generated right below the part. Accordingly, Fe that generates oxide is considered to be related to corrosion of a titanium alloy material accompanying surface roughening.

[0031] Surface contamination by Zn is assumed to be caused by zinc phosphate that is used as a seizure prevention agent in a manufacturing process of the target titanium alloy material, and Zn remaining on the surface after rolling processing. When metal-like Zn is present on the surface of the titanium alloy material, heterologous metals are in contact with each other. In such a state, hydrogen absorption is promoted, and a part contaminated by Zn may generate hydride.

[0032] S is a component that is contained in a part of an extreme pressure additive used for rolling lubricating oil, and accordingly, surface contamination by S is assumed to be from such an additive. In a part of a crevice structure, the surface of the titanium alloy material is contaminated by S and a solution containing chlorine ions is present on the surface thereof, sulfur chloride (S_2Cl_2) is produced in a crevice. Sulfur chloride accelerates corrosion of pure titanium, and accordingly may also have a function of progressing corrosion of a titanium alloy.

[0033] Next, various samples using the Gr. 11 material were fabricated, and on the surface of each sample, ratios of areas (area ratios) where the presence of Fe and S, among the elements defined as contaminating elements above, is recognized is studied. Then, crevice corrosion treatment that will described later in Examples was performed, and the relation among the distribution of Fe and S, the amount thereof, and corrosion resistance was studied (by visual observation and measurement of corrosion weight loss).

2) Area ratio of Fe contamination

[0034] On the surface of each sample, for a 200-μm square region, surface mapping analysis for Fe was performed with an EPMA surface analysis apparatus. When the average value of intensity of background signals is N and $N+3N^{1/2}$ is maximum intensity of the background signal of an Fe characteristic X-ray, the area ratio at which a signal of the Fe characteristic X-ray exceeding the maximum intensity (hereinafter referred to as "Fe area ratio") is obtained was calculated (a detailed method of calculating the area ratio will be described later).

[0035] Five regions that were arbitrarily selected on the surface of the sample had Fe area ratios of 0.002 % to 2.4 % according to the surface mapping analysis. After crevice corrosion treatment was performed on the samples, corroded regions having high surface roughness were formed locally. Among these corroded regions, a sample for which corrosion weight loss was confirmed had an Fe area ratio exceeding 0.1 %.

[0036] Surface roughening was recognized in some samples of which the Fe area ratio was 0.1 % or less and for which corrosion weight loss was not confirmed. In a sample of which the Fe area ratio was 0.01 % or less, such rough parts were not recognized. From the above results, in order to secure corrosion resistance, in particular, in a case of contamination only by Fe (not accompanying contamination by S), the Fe area ratio on the surface of the titanium alloy material needs to be 0.1 % or less. The Fe area ratio on the surface of the titanium alloy material in a case of F-only contamination is preferably 0.01 % or less.

3) Area ratio of S contamination

[0037] On the surface of each sample, for a 200-μm square region, surface mapping analysis for S was performed with an EPMA surface analysis apparatus. When the average value of intensity of background signals is N and $N+3N^{1/2}$ is maximum intensity of the background signal of a S characteristic X-ray, the area ratio at which a signal of the S characteristic X-ray exceeding the maximum intensity (hereinafter referred to as "S area ratio") was calculated.

[0038] Five regions that were arbitrarily selected on the surface of the sample had S area ratios of 0.002 % to 3.9 % according to the surface mapping analysis. After crevice corrosion treatment was performed on the samples, corroded regions having high surface roughness were formed locally. Among the samples in which these corroded regions were recognized, a sample for which corrosion weight loss was confirmed had a S area ratio exceeding 0.1 %. From these results, in order to secure corrosion resistance, in particular, in a case of S-only contamination (not accompanying Fe contamination), the S area ratio on the surface of a titanium alloy material needs to be set to 0.1 % or less.

4) Fe and S complex contamination area ratio

[0039] In some cases, the above described commercially available material is contaminated by both Fe and S.

[0040] Five regions that were arbitrarily selected from the sample had Fe area ratios of 0.001 % to 2.4 % and S area ratios of 0.001 % to 3.9 % according to surface mapping analysis performed for both Fe and S with an EPMA surface analysis apparatus.

[0041] After crevice corrosion treatment was performed on the samples, corroded regions having high surface roughness were formed locally. A sample for which corrosion weight loss was confirmed had an Fe area ratio exceeding 0.05 % and a S area ratio exceeding 0.05 %. From these results, in order to secure corrosion resistance of a titanium alloy material that is contaminated by both Fe and S, it is preferable to set the Fe area ratio to be 0.05 % or less and the S area ratio to be 0.05 % or less on the surface of the titanium alloy material.

5) Fe content

[0042] For the samples contaminated by Fe, not only the Fe area ratio, but also the relation between the content of Fe that is present in the vicinity of the surface of the sample (according to point analysis) and temporal change of contained hydrogen amount was studied.

[0043] When samples having an Fe area ratio of 0.1 % or less and a S area ratio of 0.1 % or less and containing a platinum group metal in 0.01 to 0.25 % by mass are compared with each other, the sample that has an Fe content of over 0.5 in an atomic ratio of Fe to Ti, the contained hydrogen amount has been changed over time more largely than the sample that has an Fe content of below 0.5 in an atomic ratio of Fe to Ti, even when the samples have the same Fe area ratio.

[0044] Further, as described in the above "2) Area ratio of Fe contamination", although the corrosion weight loss was not confirmed, some samples generated surface roughening. Since such samples had high Fe contents, Fe is considered to increase hydrogen absorption speed and accelerate corrosion related to hydrogen embrittlement.

[0045] From the above description, it is preferable that the Fe content obtained by point analysis on the part where Fe is present on the surface of the titanium alloy material is 0.5 or less in an atomic ratio of Fe to Ti. On the surface of the titanium alloy material, the content of C (atomic%) varies by remaining fat or the like. Accordingly, the content of Fe (atomic%) also varies by being influenced by the variation of the content of C in the part there Fe is present. In order to avoid such variations, in the present invention, the Fe content is regulated by the ratio of the Fe content (atomic%) to the Ti content (atomic%) which is a component of a base material.

6) M method of manufacturing titanium alloy material according to the present invention

[0046] An example of a method of manufacturing the titanium alloy material according to the present invention will be described.

[0047] Usually, a process of manufacturing a titanium alloy material is divided into a hot rolling step and a cold rolling step. In hot rolling, scale (oxide) is generated on the surface of the titanium alloy material. For descaling, shot peening is performed on the surface of the hot rolled sheet obtained by hot rolling to remove scale, and in addition, a crack is given to the scale generated in the superficial layer part of the hot rolled sheet, and then acid cleaning is performed. In acid cleaning, since acid for cleaning penetrates the crack, the remaining scale is removed easily. However, a part of a shot piece remains on the surface of the titanium alloy material and cannot be removed completely by acid cleaning performed later. In particular, in a case of using a large shot piece, the descaling property is high but the remaining shot piece is hardly removed only by Kolene treatment and acid cleaning treatment, as will be described later. Accordingly, in some cases, cleaning with an aqueous solution of ferric chloride ($FeCl_3$) is necessary.

[0048] The titanium alloy material that has been subjected to the hot rolling step is then subjected to cold rolling and annealing plural times until a desired sheet thickness is obtained. Usually, as the annealing treatment, bright annealing (BA) is performed in an argon atmosphere. Since descaling is not performed on the annealed titanium alloy material that has been subjected to bright annealing, contamination by Fe and S is not likely to be removed by descaling.

[0049] Through the hot rolling and cold rolling steps, on the titanium alloy material, Fe contamination due to the above described remaining shot piece and S contamination due to rolling lubricating oil for cold rolling are generated. In the annealing step, S and Fe as the source of contamination diffuse in the entire surface of the titanium alloy material by thermal diffusion and penetrate inside thereof.

[0050] To remove S and Fe, the source of contamination, after annealing, the superficial layer part of the titanium alloy material is removed by being dissolved by acid cleaning or being grinded mechanically. Further, it is more preferable to perform, before the acid cleaning, treatment with an alkali molten salt bath (salt bath which contains NaOH as a main component and to which oxidizing agents such as $NaNO_3$ and KNO_3 are added) (commonly known as "Kolene treatment"). The removal of the superficial layer part is preferably performed every time after annealing is performed; however, the

removal after the first and last annealing can efficiently remove S and Fe contamination. The removal amount (thickness) at each time is 1 μm or more, preferably 5 μm or more, for a target plane of the titanium alloy material.

[0051] As described above, treatment for removal of the contamination source is not limited to once, but plural times of treatment may be needed to achieve the surface as defined in the present invention.

[0052] Further, after descaling of the hot rolled sheet, it is also effective to perform both cleaning with the aqueous solution of ferric chloride and brushing of the surface of the hot rolled steel sheet. This is because the aqueous solution of ferric chloride does not hardly dissolve titanium but dissolves Fe faster than a mixed solution of fluonitric acid, so that a shot piece and a titanium base material on the shot piece side are dissolved, and brushing treatment performed concurrently can remove the shot piece efficiently. This step becomes necessary in a case of using a large shot piece.

[0053] Further, it is effective to perform cleaning before annealing and to add a step of removing lubricating oil and the like in order to reduce the contamination amount of S.

7) Alloy element

[0054] The content of a platinum group metal is preferably 0.01 to 0.25 % by mass. Thus, the raw material cost can be suppressed and the corrosion resistance of the titanium alloy material can be obtained. The platinum group metal may be Pd, for example.

[0055] The titanium alloy material according to the present invention may further contain one or more selected from the group consisting of Ni in 0.05 to 1.0 % by mass, Cr in 0.05 to 0.3 % by mass, and Mo in 0.05 to 0.5 % by mass.

[0056] Containing Ni, the titanium alloy material has higher crevice corrosion resistance. Note that, this effect saturates when Ni in more than 1.0 % by mass is contained. Further, processability is reduced by the addition of Ni. Accordingly, in a case of adding Ni, it is preferable to set the content thereof to 1.0 % by mass or less. In order to surely obtain the above effect, it is preferable to set the content of Ni to 0.05 % by mass or more, more preferably 0.1 % by mass or more.

[0057] Containing Cr, the titanium alloy material has higher crevice corrosion resistance. Note that, this effect saturates when Cr in more than 0.3 % by mass is contained. Accordingly, in a case of adding Cr, it is preferable to set the content thereof to 0.3 % by mass or less. In order to surely obtain the above effect, it is preferable to set the content of Cr to 0.05 % by mass or more.

[0058] Containing Mo, the titanium alloy material has higher crevice corrosion resistance and higher resistance against sulfuric acid. Note that, this effect saturates when Mo in more than 0.5 % by mass is contained. Further, processability is reduced by the addition of Mo. Accordingly, in a case of adding Mo, it is preferable to set the content thereof to 0.5 % by mass or less. In order to surely obtain the above effect, it is preferable to set the content of Mo to 0.05 % by mass or more.

[Example 1]

[0059] To confirm effects of the present invention, samples having different contamination amounts of Fe and S were fabricated and corrosion resistance testing was conducted.

1. Method of fabricating sample used for corrosion resistance testing

[0060] Base materials used for the samples each have a sheet thickness of 3 mm, are Gr. 11, Gr. 13, Gr. 17, Gr. 33 materials according to the ASTM standard and a laboratory sample material (fabricated by performing vacuum arc remelting (VAR), hot forging, and hot rolling in order), and have compositions shown in Table 1. After defatting and ultrasonic cleaning were performed on these base materials, the following treatment was performed in order to reproduce contamination at the time of manufacture using actual equipment.

[Table 1]

Base Material	C	H	O	N	Fe	Pd	Ru	Ni	Cr	Mo	Ti
Gr.11	0.011	0.0014	0.098	0.0046	0.005	0.17	-	-	-	-	Remain
Gr.13	0.004	0.0008	0.09	0.0058	0.02	-	0.044	0.52	-	-	Remain
Gr.17	0.004	0.0002	0.0033	0.003	0.025	0.054	-	-	-	-	Remain
Gr.33	0.006	0.001	0.045	0.002	0.016	0.015	0.025	0.42	0.15	-	Remain
Sample	0.005	0.0011	0.068	0.003	0.02	0.051	-	-	-	0.17	Remain
% by mass											

[0061] Table 2 shows conditions for fabrication of samples provided for the corrosion testing and contamination amounts of Fe and S in the samples. In order to easily fabricate samples having different degrees of Fe and S contamination, the mixing rates of iron powder in a rolling lubricating agent and an extreme-pressure additive to be applied onto the base materials were adjusted in a manner that the contamination amounts of Fe and S became different among the samples (Example 4 to Example 16 and Comparative Example 1 to Comparative Example 12 in Table 2).

[0062] [Table 2]

Table 2

Classification	Base Material	Rate of palm oil-derived component in rolling lubricating oil (% by mass)	Mixing rate of iron powder in rolling lubricating oil (% by mass)	Mixing rate of extreme-pressure additive in rolling lubricating oil	Treatment with aqueous solution of ferric chloride on hot rolled	Kolen treatment with alkali molten salt bath (470 °C)	Fluonitric acid cleaning time (second)	Fe area ratio (%)	S area ratio (%)	Remarks
Example 1 (clean material)	Gr.11	100	-	-	Yes	-	10	0.004	0.004	-
Example 2 (clean material)	Gr.13	100	-	-	Yes	-	10	0.006	0.007	-
Example 3 (clean material)	Gr.17	100	-	-	Yes	-	10	0.002	0.002	-
Example 4	Gr.11	99.90	0.10	-	-	-	10	0.09	0.002	Fe contamination
Example 5	Gr.11	99.95	0.05	-	-	-	10	0.03	0.004	Fe contamination
Example 6	Gr.11	95	-	5	-	-	10	0.008	0.03	S contamintaion
Example 7	Gr.11	90	-	10	-	-	10	0.009	0.09	S contamintaion
Example 8	Gr.11	97.74	0.08	2.18	-	-	10	0.05	0.02	Complex contamination
Example 9	Gr.13	99.90	0.10	-	-	-	10 (performed twice, before and after annealing)	0.0094	0.002	Fe contamination
Example 10	Gr.17	99.90	0.10	-	-	-	10	0.08	0.003	Fe contamination

(continued)

Classification	Base Material	Rate of palm oil-derived component in rolling lubricating oil (% by mass)	Mixing rate of iron powder in rolling lubricating oil (% by mass)	Mixing rate of extreme-pressure additive in rolling lubricating oil	Treatment with aqueous solution of ferric chloride on hot rolled	Kolen treatment with alkali molten salt bath (470 °C)	Fluonitric acid cleaning time (second)	Fe area ratio (%)	S area ratio (%)	Remarks
Example 11	Gr.17	95	-	5	-	-	10	0.003	0.04	S contamintaion
Example 12	Gr.17	97.74	0.08	2.18	-	-	10	0.06	0.03	Complex contamination
Example 13	Gr.11	92.92	0.08	7.00	-	-	10	0.06	0.070	Complex contamination
Example 14	Gr.33	99.90	0.10	-	-	-	10	0.09	0.003	Fe contamination
Example 15	Sample	92.92	0.08	7.00	-	-	10	0.05	0.07	Complex contamination
Example 16 (Kolene treatment)	Gr.17	99.50	0.50	-	-	Yes	10	0.007	0.006	-
Comparative Example 1	Gr.11	99.90	0.10	-	-	-	5	* 0.13	0.008	Fe contamination
Comparative Example 2	Gr.11	99.50	0.50	-	-	-	10	* 2.4	0.007	Fe contamination
Comparative Example 3	Gr.11	80.00	-	20.00	-	-	10	0.008	* 2.110	S contamintaion
Comparative Example 4	Gr.11	70.00	-	30.00	-	-	10	0.009	* 3.900	S contamintaion
Comparative Example 5	Gr.11	84.85	0.15	15	-	-	10	* 0.22	* 1.840	Complex contamination
Comparative Example 6	Gr.11	84.5C	0.50	15	-	-	10	* 2.20	* 1.640	Complex contamination

(continued)

Classification	Base Material	Rate of palm oil-derived component in rolling lubricating oil (% by mass)	Mixing rate of iron powder in rolling lubricating oil (% by mass)	Mixing rate of extreme-pressure additive in rolling lubricating oil	Treatment with aqueous solution of ferric chloride on hot rolled	Kolen treatment with alkali molten salt bath (470 °C)	Fluonitric acid cleaning time (second)	Fe area ratio (%)	S area ratio (%)	Remarks
Comparative Example 7	Gr.11	87.85	0.15	12	-	-	10	* 0.30	* 0.300	Complex contamination
Comparative Example 8	Gr.17	99.5	0.50	-	-	-	10	*1.72	0.008	Fe contamination
Comparative Example 9	Gr.17	75.00	-	25.00	-	-	10	0.007	*2.470	S contamintaion
Comparative Example 10	Gr.17	87.67	0.15	12.18	-	-	10	* 0.940	* 1.020	Complex contamination
Comparative Example 11	Gr.13	99.5	0.50	-	-	-	10	* 2.110	0.006	Fe contamination
Comparative Example 12	Gr.13	86	-	14	-	-	10	0.008	* 1.140	S contamintaion
"*" indicates an item beyond the scope of the present invention.										

(i) Fe contamination

[0063] FEE13PB iron powder (purity: 2 Nup, grain size: 3 to 5 μm) produced by Kojundo Chemical Laboratory Co., Ltd. was mixed to rolling lubricating oil containing palm oil as a main component in various amounts (% by mass) as shown in Table 2, this rolling lubricating oil was applied onto the base materials with a sheet thickness of 4 mm, and the base materials were rolled so that the sheet thickness became 3 mm. In this manner, remaining shot pieces at the time of shot peening were imitated, and samples having different amounts of Fe contamination (Fe contamination degrees) were obtained.

(ii) S contamination

[0064] DAILUBE GS-440L olefin metal working oil (preliminary sulfurizing agent containing sulfur in 40%) which is an extreme-pressure additive produced by DIC Corporation was mixed to rolling lubricating oil in % by mass as shown in Table 2, this rolling lubricating oil was applied onto the base materials with a sheet thickness of 4 mm, and the base materials were rolled so that the sheet thickness became 3 mm. In this manner, samples having different amounts of S contamination (S contamination degrees) were obtained.

(iii) Fe and S complex contamination

[0065] By combining treatment in (i) and (ii), samples that are complex-contaminated by Fe and S were obtained.

(iv) Samples without contamination treatment

[0066] Samples denoted by "(clean material)" (Example 1 to Example 3) in Table 2 were not subjected to contamination treatment of Fe and S. That is, these samples were obtained by applying a rolling lubricating agent, to which neither Fe (iron powder) nor S (extreme-pressure additive containing sulfur) were added, onto base materials with a sheet thickness of 4 mm, and by rolling the base materials so that the sheet thickness became 3 mm.

(v) Treatment after rolling

[0067] After defatting, the rolled materials obtained through treatment (i) to (iv) were subjected to annealing treatment in an Ar atmosphere furnace at 750 °C for 30 minutes, and then to fluonitric acid cleaning to be provided for corrosion testing. A sample denoted by "(Kolene treatment) (Example 16) in Table 2 was obtained by performing Kolene treatment after the above described treatment of Fe contamination and before fluonitric acid cleaning. For some samples, in order to obtain the surface as defined in the present invention, the Kolene treatment or treatment using an aqueous solution of ferric chloride (including brushing treatment) was performed. Further, for a sample (Example 9), fluonitric cleaning was performed twice, which is before and after annealing.

2. Method of measuring surface contamination degree

[0068] The samples before corrosion treatment were subjected to surface analysis with the EPMA surface analysis apparatus.

(2-1) Conditions for EPMA analysis

[0069]

Apparatus: JXA-8530F produced by JEOL Ltd.
Accelerating voltage: 15 kv
Irradiation current: 100 nA
Number of measured points (pixels): 500 × 500
Shape of beam: spot
Measured pitch: 0.4 μm
Measured time: 30 msec (for each point)
Spectroscopic crystals used: LIFH (for Fe Kα-ray), PETH (for S Kα-ray), LIF (for Ti Kα-ray), LIFH (for Zn Kα-ray)

(2-2) Measurement of background intensity of Fe, S, and Zn analysis

[0070] High-purity Ti of standards (UHV STANDARDS) for electron spectroscopy for chemical analysis (ESCA), auger electron spectroscopy (AES), and EPMA was analyzed under the above described conditions, background count intensity of Fe, S, and Zn was measured at 500 × 500 points arranged in a lattice, and average values N(Fe), N(S), and N(Zn) of background counts (intensity) of the respective elements were calculated.

[0071] According to Non-Patent Document 1 above, when the average value of a plurality of measured values N is set to No, the ratio of the measured value N being beyond the range of $N_0 \pm 3N_0^{1/2}$ is 0.3 %. Accordingly, by substituting the average value of background intensity to No in this equation, the obtained value can be set as the threshold to distinct a signal whose intensity is raised by an existing element from the background signal. The threshold intensity for Fe, S, and Zn is as follows.

Fe threshold intensity: $N(Fe) + 3N(Fe)^{1/2}$
S threshold intensity: $N(S) + 3N(S)^{1/2}$
Zn threshold intensity: $N(Zn) + 3N(Zn)^{1/2}$

[0072] In the present Example, specific values of the threshold intensity for Fe, threshold intensity for S, and threshold intensity for Zn are 25 counts (cnt), 15 cnt, and 50 cnt, respectively.

[0073] When a count having intensity higher than the above threshold intensity, 99.85 % of the time, there is an element corresponding to the threshold intensity at the measured point, and a signal from the element is measured.

[0074] Among the 500 × 500 measured points, the rate of points at which the intensity higher than the threshold intensity is counted is defined as contamination area ratio. For example, in a case in which the intensity higher than the threshold intensity is counted at 300 points, the contamination area ratio is as follows.

$$\text{Contamination area ratio} = 300 / (500 \times 500) = 0.12\ \%$$

In Table 2, Table 4, and Table 5, the contamination amounts of Fe and S in the samples are shown as the contamination area ratios of Fe and S (Fe area ratio and S area ratio).

[0075] FIG. 4 and FIG. 5 shows results of the surface mapping analysis with an EPMA surface analysis apparatus for the samples according to the present invention and the samples not according to the present invention. As for Fe, S, and Zn, points are binarized depending on whether or not the value is higher than the threshold intensity; a point having intensity less than or equal to the threshold intensity is shown in black, and a point having intensity over the threshold intensity is shown in white.

[0076] FIG. 4 shows results of analysis of the sample of "Example 3 (clean material)" in Table 2. In this sample, it is found that, for each of Fe, S, and Zn, there are almost no points having intensity over the threshold intensity.

[0077] FIG. 5 shows results of analysis of the sample of "Comparative Example 6" in Table 2. This sample was obtained by performing contamination treatment of both Fe and S. From the analysis results in FIG. 5, it is found that, for both Fe and S, there are points having intensity over the threshold intensity throughout the analyzed region.

(2-3) Measurement of quantitative concentration of contaminants

[0078] Quantitative concentration of contaminants can be measured by using general analyzing means such as EPMA or AES. In Examples, in order to measure surface contamination, a field emission-auger electron spectroscopy (FE-AES) by which information on the vicinity of the surface is obtained was employed as the analyzing means. The analyzing conditions are as follows.

Apparatus: Model 680 produced by ULVAC-PHI Incorporated.
Primary beam: Accelerated voltage 10 kV, Sample current 10 nA
Detection depth: Several nanometers (for Ti and Fe, 3 to 5 nm)

[0079] On the basis of the obtained measurement results, the ratio of Fe content (atomic%) / Ti content (atomic%) was calculated. The results are shown in Table 5.

3. Evaluation of corrosion resistance

[0080] In order to study the influence of surface contamination on the corrosion resistance, an environment in which

a titanium alloy containing a platinum group metal is used was imitated, and testing based on general crevice corrosion resistance testing was conducted.

[0081] FIG. 6 is a schematic diagram of a sample used for corrosion testing and a schematic diagram of a sample for crevice corrosion testing. As shown in FIG. 6(a) and FIG. 6(b), a sample 1 provided for corrosion testing has a thickness of 3 mm and a plane shape of a 30-mm square, in which, in a central portion, a hole with a diameter of 7 mm is formed. Two samples 1 formed under the same conditions were disposed on opposite sides of a crevice formation film (crevice formation material) 2 as shown in FIG. 6(c). A bolt of a CP Ti bolt-nut 4 was made to penetrate the hole of the sample 1, and the CP Ti bolt-nut 4 was tightened between the samples 1 via a PTFE bush 3. In this manner, a sample for crevice corrosion testing 5 was obtained.

[0082] The surface skin of the samples 1 was made to maintain the state at the time when the treatment described in the section "1. Method of fabricating sample used for corrosion resistance testing" above was completed. As the crevice formation film 2, a NEOFLON (trademark) PCTFE film (thickness: 50 μm) produced by DAIKIN INDUSTRIES, LTD. was used. As the CP Ti bolt-nut 4, a bolt-nut that was heated by a gas burner, the surface of which was oxidized sufficiently, was used. The tightening torque of the CP Ti bolt-nut 4 was 40 kgf·cm (1 kgf is approximately 9.8 N).

[0083] In order to conduct acceleration testing that reveals the influence of contamination on the corrosion resistance, the sample was subjected to treatment using an autoclave (autoclave treatment). Prior to the autoclave treatment, as a pre-measurement of testing, the weight of the samples 1 was measured by a precision balance. The weight of the samples 1 was in a range from 11 to 11.5 g. After that, the sample for crevice corrosion testing 5 was subjected to treatment using the autoclave. Conditions for the autoclave treatment are shown in Table 3.

[Table 3]

Apparatus used	hastelloy C276-lined autoclave
Condition for solution	pH = 2, 250 g/L-NaCl
Condition for corrosion treatment	150 °C × 1000 hours

[0084] After the treatment was completed, the CP Ti bolt-nut 4 was untightened and the sample for crevice corrosion testing 5 was decomposed. The samples 1 were subjected to ultrasonic cleaning in which cleaning water was exchanged three times, and dried sufficiently, and then the weight thereof was measured by the precision balance. Further, a corrosion weight loss D was calculated from the following equation.

$$\text{Corrosion weight loss D (mg)} = \text{Weight after corrosion treatment (mg)} - \text{Weight before corrosion treatment (mg)}$$

[0085] The weight of each of the two samples 1 (on the bolt side and on the nut side) of the sample for crevice corrosion testing 5 was measured, and the average value of the corrosion weight losses of these two samples was set as the corrosion weight loss D of the sample for crevice corrosion testing 5.

[0086] According to results of the corrosion weight loss measurement, some samples 1 showed a minute amount of increase in weight, not a loss or 0; however, this increase in weight is considered to be caused by oxidation, so that the corrosion weight loss D of such samples 1 is assumed to be 0.

[0087] Further, the increased amount (the absorbed amount) of hydrogen H was calculated from the following equation.

[0088] Increased amount of hydrogen H (ppm) = Hydrogen content rate (ppm) in the sample 1 (bulk) after corrosion treatment - Hydrogen content rate (ppm) in the sample 1 (bulk) before corrosion treatment

[0089] Table 4 shows base materials of the samples 1 provided for the corrosion testing, the Fe area ratios, the S area ratios, and results of the corrosion testing.

[Table 4]

Classification	Base Material	Fe area ratio (%)	S area ratio (%)	Corrosion weight loss D (mg)	Surface roughening	Increased amount of hydrogen H in bulk (ppm)	Remarks
Example 1 (clean material)	Gr.11	0.004	0.004	0.0	No	2	-

(continued)

Classification	Base Material	Fe area ratio (%)	S area ratio (%)	Corrosion weight loss D (mg)	Surface roughening	Increased amount of hydrogen H in bulk (ppm)	Remarks
Example 2 (clean material)	Gr.13	0.006	0.007	0.0	No	3	-
Example 3 (clean material)	Gr.17	0.002	0.002	0.0	No	1	-
Example 4	Gr.11	0.09	0.002	0.0	Yes (slightly)	12	Fe contamination
Example 5	Gr.11	0.03	0.004	0.0	Yes (slightly)	11	Fe contamination
Example 6	Gr.11	0.008	0.03	0.0	No	5	S contamintaion
Example 7	Gr.11	0.009	0.09	0.0	No	4	S contamintaion
Example 8	Gr.11	0.05	0.02	0.0	Yes (slightly)	13	Complex contamination
Example 9	Gr.13	0.0094	0.002	0.0	No	14	Fe contamination
Example 10	Gr.17	0.08	0.003	0.0	Yes (slightly)	15	Fe contamination
Example 11	Gr.17	0.003	0.04	0.0	No	7	S contamintaion
Example 12	Gr.17	0.06	0.03	0.0	Yes (slightly)	10	Complex contamination
Example 13	Gr.11	0.06	0.070	0.1	Yes (slightly)	19	Complex contamination
Example 14	Gr.33	0.09	0.003	0.0	Yes (slightly)	11	Fe contamination
Example 15	Sample	0.05	0.07	0.1	Yes (slightly)	18	Complex contamination
Example 16 (Kolene treatment)	Gr.17	0.007	0.006	0.0	No	3	-
Comparative Example 1	Gr.11	* 0.13	0.008	3.1	Yes	2	Fe contamination
Comparative Example 2	Gr.11	* 2.4	0.007	16.2	Yes	24	Fe contamination
Comparative Example 3	Gr.11	0.008	* 2.130	2.1	Yes	42	S contamintaion
Comparative Example 4	Gr.11	0.009	* 3.900	3.5	Yes	45	S contamintaion
Comparative Example 5	Gr.11	*0.22	* 1.840	4.1	Yes	63	Complex contamination

(continued)

Classification	Base Material	Fe area ratio (%)	S area ratio (%)	Corrosion weight loss D (mg)	Surface roughening	Increased amount of hydrogen H in bulk (ppm)	Remarks
Comparative Example 6	Gr.11	* 2.20	* 1.640	18.7	Yes	73	Complex contamination
Comparative Example 7	Gr.11	* 0.30	* 0.300	1.5	Yes	39	Complex contamination
Comparative Example 8	Gr.17	* 1.72	0.008	18.4	Yes	03	Fe contamination
Comparative Example 9	Gr.17	0.007	* 2.470	2.8	Yes	44	S contamintaion
Comparative Example 10	Gr.17	* 0.940	* 1.020	14.7	Yes	87	Complex contamination
Comparative Example 11	Gr.13	* 2.110	0.006	17.3	Yes	26	Fe contamination
Comparative Example 12	Gr.13	0.008	* 1.140	5.4	Yes	72	S contamintaion
"*" indicates an item beyond the scope of the present invention.							

[0090] From the testing results shown in FIG. 4, the following 1) to 3) are found.

1) The Fe area ratios of the samples of "Example 1 (clean material)" to "Example 3 (clean material)", "Example 4" to "Example 7", "Example 9" to "Example 11", and "Example 14" (hereinafter these samples are each referred to as "non-complex contamination sample") were each 0.1 % or less, and accordingly, the Fe contamination degree on the surface was low. In the same manner, the S area ratios of the non-complex contamination samples were each 0.1 % or less, and accordingly, the S contamination degree on the surface was low.
Further, as for the non-complex contamination samples, corrosion weight loss due to corrosion treatment was not recognized, and it is obvious that the non-complex contamination samples have high corrosion resistance. Furthermore, the increased amount of hydrogen H due to corrosion treatment on the non-complex contamination samples was 20 ppm or less. Among the non-complex contamination samples, on samples whose Fe area ratio is 0.01 % or less (Examples 1 to 3, 6,7,11, and 16), surface roughening was not recognized on the plane that became a crevice. Accordingly, the samples have extremely high corrosion resistance, and the absorbed amount of hydrogen is less than 10 ppm, which is extremely small.
2) Even when the Fe area ratio was 0.1 % or less, corrosion weight loss was recognized for the sample in which complex contamination with S was recognized and the Fe area ratio and the S area ratio each exceeded 0.05 % (the sample of "Example 13" in Table 4). Further, the increased amount of hydrogen H of this sample is larger than 15 ppm. In a case of Fe and S complex contamination, in order to achieve a material having higher corrosion resistance, it is preferable that each of the Fe area ratio and the S area ratio is 0.05 % or less.
3) As described in the section "(v) Treatment after rolling", the sample of Example 16 was obtained by performing Kolene treatment after Fe contamination treatment (in which rolling lubricating oil mixed with iron powder was applied and rolling was performed) and before fluonitric acid cleaning. Although the sample of Example 16 was subjected to Fe contamination treatment, it showed almost as low Fe contamination area ratio as a clean material, so that it is found that Kolene treatment is effective to obtain a titanium alloy material having a clean surface.

[0091] From the above testing results, it is revealed that corrosion resistance (crevice corrosion resistance: resistance against corrosion accompanying surface roughening) that is much higher than before can be secured by suppressing the contamination amounts of Fe and S that are present on the surface of the titanium alloy material.

[Example 2]

[0092] Next, the influence of the concentration of Fe as a contamination element was studied. Table 5 shows conditions

for fabricating samples provided for testing and evaluation results.

[0093] Samples of Examples 17, 19, and 21 were each obtained by rolling a base material with a thickness of approximately 4 mm through two-time passes in a manner that the thickness of each sample was reduced to 3.5 mm through the first pass and was again reduced to 3.0 mm through the second pass. Meanwhile, samples of Examples 18 and 20 were each obtained by rolling a base material with a thickness of approximately 4 mm through one-time pass in a manner that the thickness thereof became 3.0 mm. Further, samples of Comparative Examples 13, 14, and 15 were each obtained by rolling a base material with a thickness of approximately 4 mm through one-time pass in a manner that the thickness thereof became 3.0 mm.

[0094] For each of the obtained samples, in arbitrarily selected five regions, the Fe area ratio and the S area ratio were measured, quantitative analysis was performed in a part of each region in which maximum Fe intensity was obtained, and the ratio of the Fe content (atomic%) to the Ti content (atomic%) was calculated. The average values of the five regions are shown in Table 5 as Fe/Ti (atomic ratio) representing each sample.

[0095] The samples of Example 17 to 21 and the samples of Comparative Examples 13 to 15 were subjected to the autoclave treatment (corrosion treatment) under the conditions shown in Table 3, and hydrogen content rates before and after the treatment were analyzed.

[0096] [Table 5]

Table 5

Classification	Base Material	Rate of palm oil-derived component in rolling lubricating oil (% by mass)	Mixing rate of iron powder in rolling lubricating oil (% by mass)	Mixing rate of extreme-pressure additive in rolling lubricating oil (% by mass)	Fluonitric acid cleaning time (second)	Fe area ratio (%)	S area ratio (%)	Fe/Ti (atomic ratio)	Corrosion weight loss D (mg)	Hydrogen content rate before treatment (ppm)	Hydrogen content rate after treatment (ppm)
Example 17	Gr.11	99.90	0.10	4 → 3.5 → 3.0	10	0.08	0.003	0.37	0	42	53
Example 18	Gr.11	99.90	0.10	4 → 3.0	10	0.09	0.002	0.67	0	42	113
Example 19	Gr.17	99.90	0.10	4 → 3.5 → 3.0	10	0.07	0.003	0.41	0	38	44
Example 20	Gr.17	99.90	0.10	4 → 3.0	10	0.08	0.003	0.65	0	38	106
Example 21	Gr.17	99.88	0.12	4 → 3.5 → 3.0	10	0.09	0.004	0.78	0	38	122
Comparative Example 13	Gr.11	99.50	0.50	4 → 3.0	10	* 2.4	0.005	1.4	9.8	42	249
Comparative Example 14	Gr.13	99.40	0.60	4 → 3.0	10	* 3.2	0.007	2.1	10.2	35	274
Comparative Example 15	Gr.17	99.50	0.50	4 → 3.0	10	* 2.2	0.004	1.7	9.6	38	241
"*" indicates an item beyond the scope of the present invention.											

[0097] From Table 5, the following 1) to 5) are found.

1) By the autoclave treatment (150 °C × 1000 hours), none of the samples (Examples 17 to 21) according to the present invention showed corrosion weight loss.
2) As for samples whose Fe/Ti (atomic ratio) exceeded 0.5, an increase in the hydrogen content rate was recognized by the corrosion treatment. In these samples, it is assumed that the amount of hydrogen after the corrosion treatment exceeded 100 ppm, and hydrogen was increased by absorption over time.
3) Among Examples 17 to 21, samples whose Fe/Ti (atomic ratio) exceeded 0.5 (Examples 18, 20, and 21) are also within the scope of the present invention. However, considering a case of being used in an environment in which hydrogen embrittlement might occur (high-temperature environment), it is preferable that Fe/Ti (atomic ratio) is 0.5 or less.
4) Samples that are beyond the scope of the present invention (samples of "Comparative Example 13" to "Comparative Example 15" in Table 5) had concave portions on the surface, and large corrosion weight losses were recognized. Even if a Ti alloy containing a platinum group metal is used, these samples cannot be said to be corrosion-resistant against treatment under harsh conditions (the above autoclave treatment). In these samples, it is considered that the increased amount of hydrogen H due to treatment is over 35 ppm and corrosion of these samples are related to hydrogen absorption. The increased amount of hydrogen H of these samples exceeded 200 ppm, which might cause hydrogen embrittlement.
5) Among the samples of Comparative Examples 13 to 15, samples having high Fe area ratio and high Fe/Ti (atomic ratio) had large corrosion weight losses and the hydrogen content rate after corrosion treatment exceeded 200 ppm, which might cause hydrogen embrittlement.

[0098] Heretofore, preferred embodiments of the present invention have been described in detail with reference to the appended drawings, but the present invention is not limited thereto. It should be understood by those skilled in the art that various changes and alterations may be made without departing from the spirit and scope of the appended claims.

Claims

1. A titanium alloy material comprising:

a platinum group metal,
wherein, when an average value of intensity of background signals in surface mapping analysis using an EPMA surface analysis apparatus is N and $N+3N^{1/2}$ is maximum intensity of the background signal of an Fe characteristic X-ray, an area ratio at which a signal of an Fe characteristic X-ray exceeding the maximum intensity is obtained is 0.1 % or less.

2. A titanium alloy material comprising:

a platinum group metal,
wherein, when an average value of intensity of background signals in surface mapping analysis using an EPMA surface analysis apparatus is N and $N+3N^{1/2}$ is maximum intensity of the background signal of a S characteristic X-ray, an area ratio at which a signal of a S characteristic X-ray exceeding the maximum intensity is obtained is 0.1 % or less.

3. The titanium alloy material according to claim 1 or 2,
wherein the area ratio at which the signal of the Fe characteristic X-ray exceeding the maximum intensity is 0.05 % or less and the area ratio at which the signal of the S characteristic X-ray exceeding the maximum intensity is 0.05 % or less.

4. The titanium alloy material according to claim 1 or 3,
wherein a content of Fe obtained by point analysis of part in which Fe is present on the surface of the titanium alloy material is 0.5 or less in atomic ratio of Fe with respect to Ti.

5. The titanium alloy material according to any one of claims 1 to 4,
wherein the platinum group metal is contained in 0.01 to 0.25 % by mass.

6. The titanium alloy material according to any one of claims 1 to 5,

wherein at least one selected from the group consisting of Ni in 0.05 to 1.0 % by mass, Cr in 0.05 to 0.3 % by mass, and Mo in 0.05 to 0.5 % by mass is further contained.

7. The titanium alloy material according to any one of claims 1 to 6, wherein Pd is contained in 0.01 to 0.25 % by mass as the platinum group metal.

FIG. 1

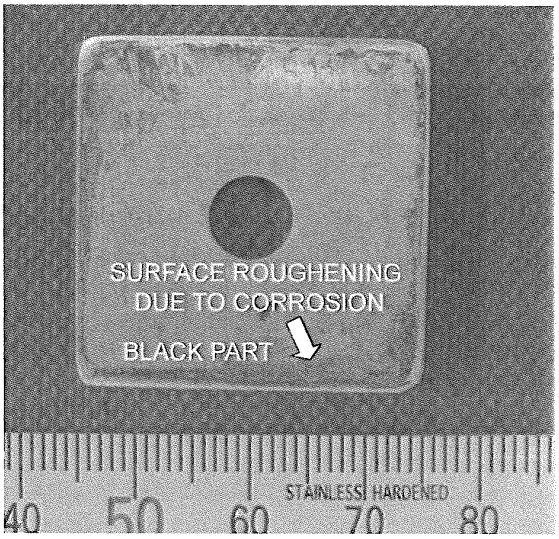


FIG. 2

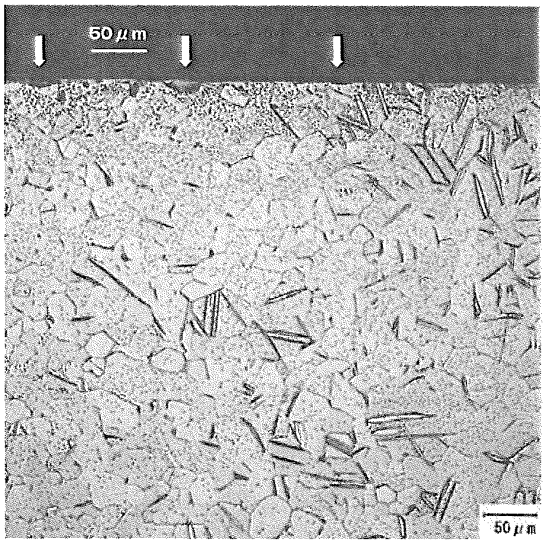


FIG. 3

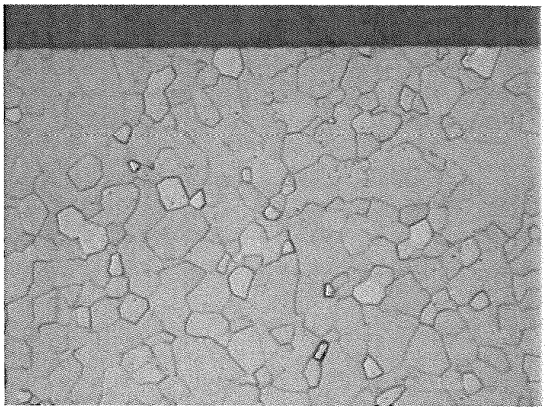


FIG. 4

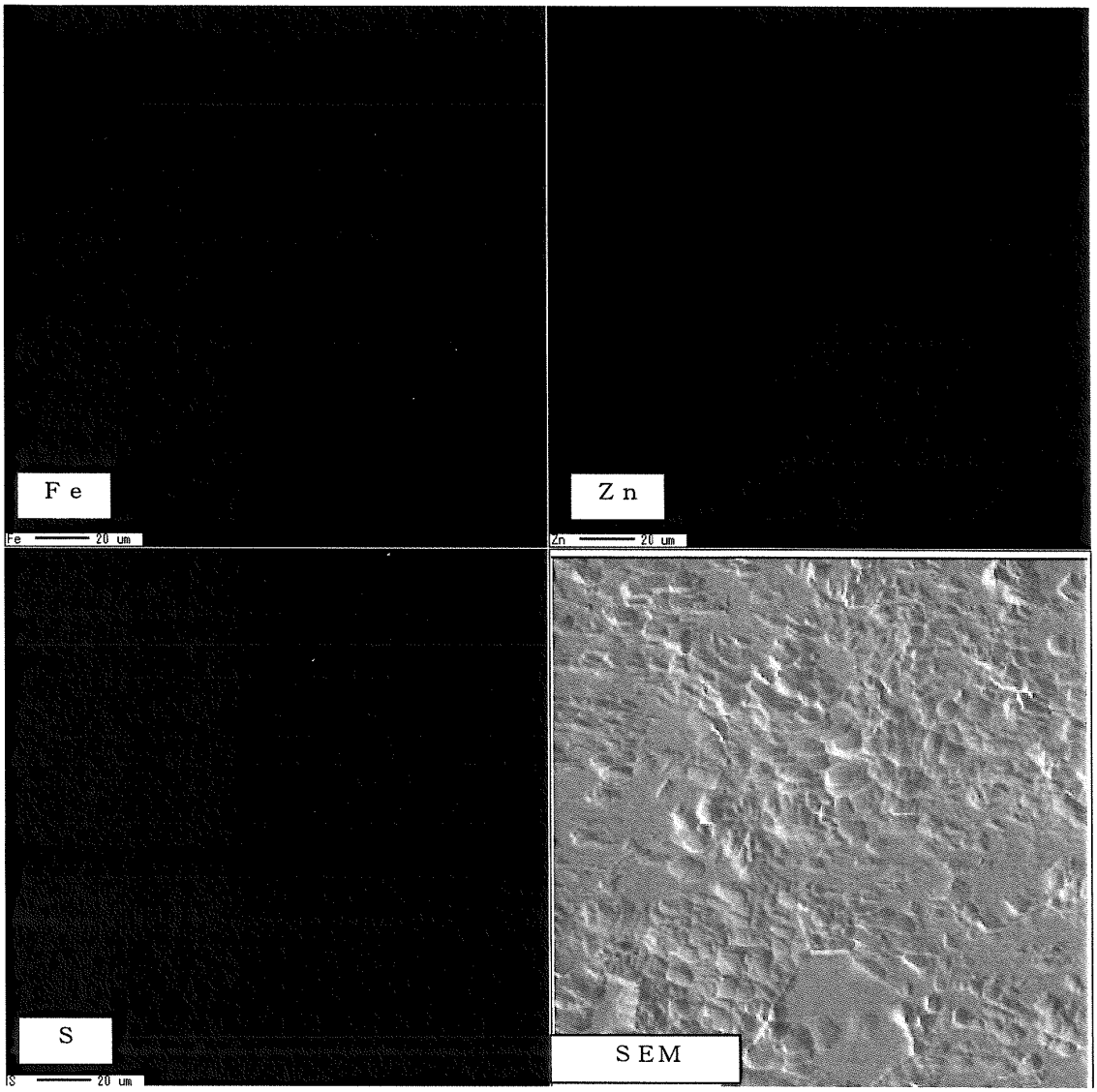


FIG. 5

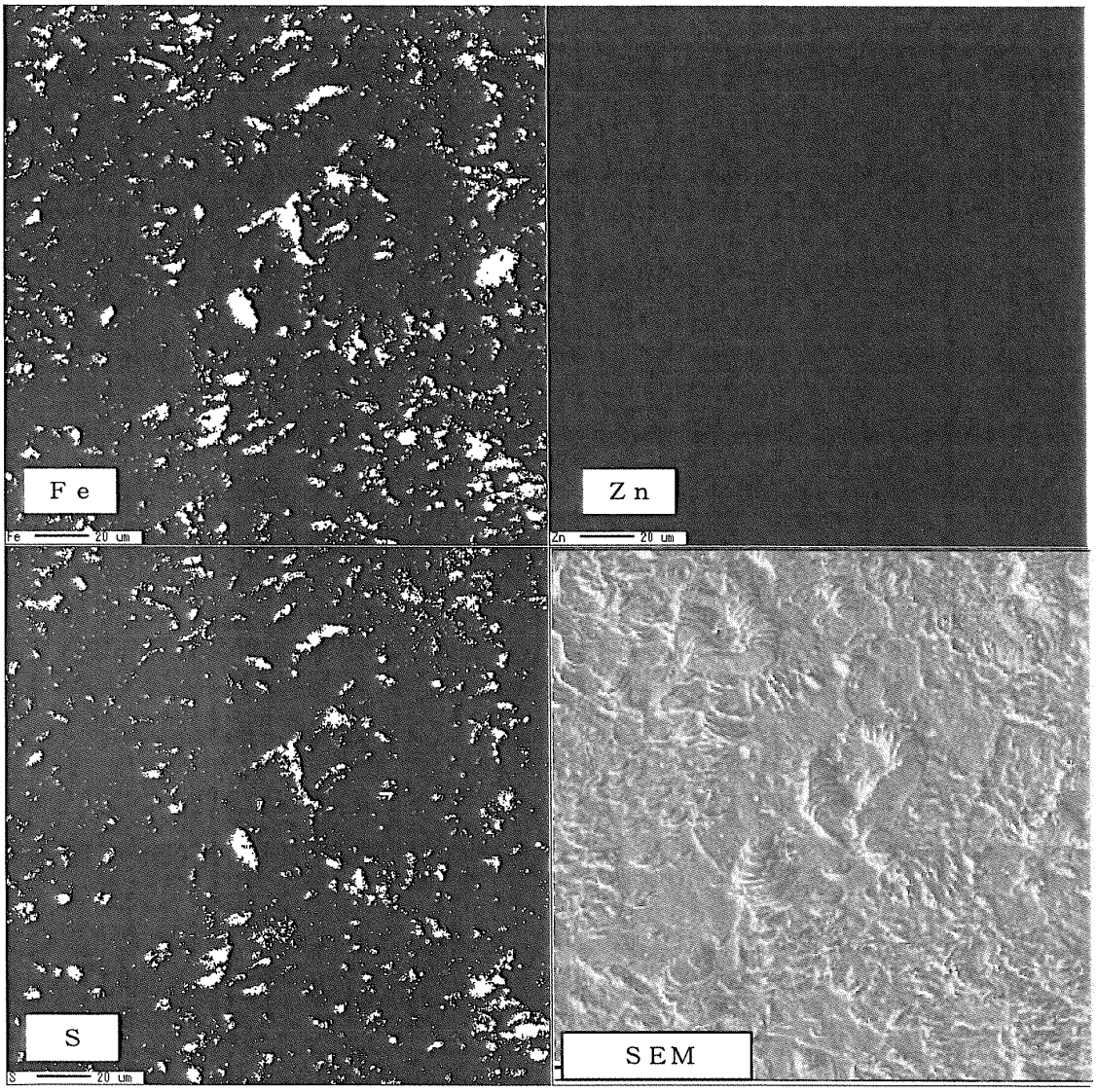
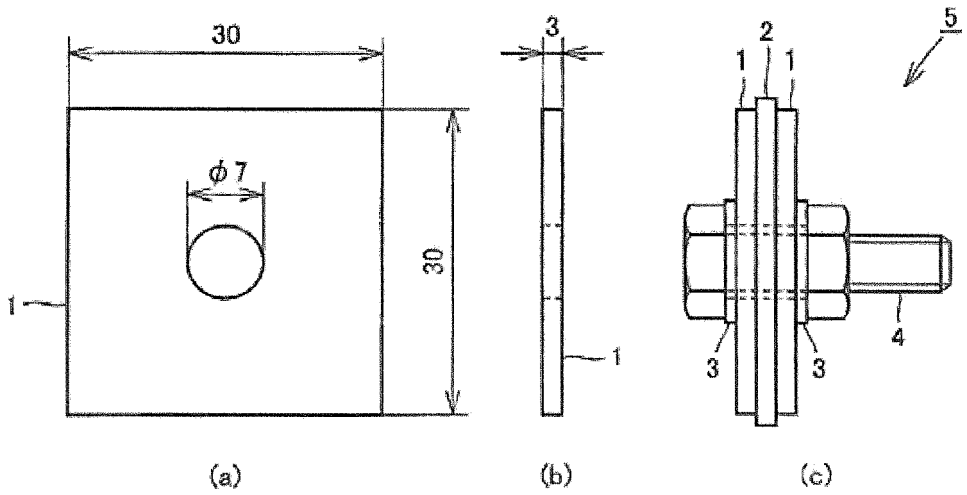


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/071788

A. CLASSIFICATION OF SUBJECT MATTER
C22C14/00(2006.01)i, *C23G1/10*(2006.01)i, *C23G1/32*(2006.01)i, *C22F1/00*(2006.01)n, *C22F1/18*(2006.01)n

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)
C22C1/00-49/14, C23G1/10, C23G1/32, C22F1/00-3/02

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.
A	JP 2002-194591 A (Nippon Steel Corp.), 10 July 2002 (10.07.2002), (Family: none)	1-7
A	JP 5-51777 A (Nippon Steel Corp.), 02 March 1993 (02.03.1993), (Family: none)	1-7

☐ 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
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Date of the actual completion of the international search	Date of mailing of the international search report
23 October, 2013 (23.10.13)	05 November, 2013 (05.11.13)
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