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(72) Inventors:
• **KAMINAKA, Hideya**
Tokyo 100-8071 (JP)
• **KAMIO, Hiroshi**
Tokyo 100-8071 (JP)
• **ABE, Masaru**
Tokyo 100-8071 (JP)
• **TAKEUCHI, Kouichi**
Tokyo 100-8071 (JP)

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(71) Applicant: **Nippon Steel & Sumitomo Metal Corporation**
Tokyo 100-8071 (JP)

(74) Representative: **Vossius & Partner**
Patentanwälte Rechtsanwälte mbB
Siebertstrasse 3
81675 München (DE)

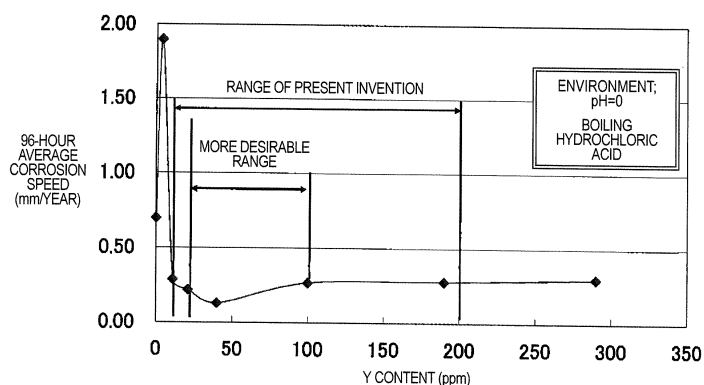
(54) **TITANIUM ALLOY HAVING EXCELLENT CORROSION RESISTANCE IN ENVIRONMENT CONTAINING BROMINE IONS**

(57) [Object] To provide a titanium alloy having corrosion resistance that is as high as or higher than before, and high corrosion resistance in a bromine-ion-containing environment, the alloy being able to be manufactured at low cost.

[Solution] Provided is a titanium alloy to be used in a bromine-ion-containing environment, the titanium alloy consisting of, in mass%, a platinum group element: greater than or equal to 0.01% and less than or equal to 0.10%, a rare earth element: greater than or equal to 0.001 %

and less than 0.02%, O: greater than or equal to 0% and less than 0.1 %, and the balance: Ti and impurities. The titanium alloy may contain, instead of part of Ti, one or more selected from the group consisting of Ni, Co, Mo, V, Cr, and W. The platinum group element is desirably contained in, in mass%, greater than or equal to 0.01% and less than or equal to 0.05%. The rare earth element is desirably contained in, in mass%, greater than or equal to 0.001% and less than 0.02%.

FIG. 4



Description

[Technical Field]

5 **[0001]** The present invention relates to a titanium alloy, particularly to a titanium alloy having high corrosion resistance (crevice corrosion resistance, acid resistance, and the like in a bromine-ion-containing environment) and high economic efficiency.

[Background Art]

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[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.

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[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, the crevice corrosion resistance and the corrosion resistance are simply referred to as "corrosion resistance" unless otherwise specified). In order to solve this problem, a titanium alloy

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in which titanium contains a platinum group element (hereinafter referred to as "platinum-group-element-containing titanium alloy") is proposed and normalized to be used in various usages.

[0004] Specifically, in the alkali industry field, an anode electrode used for electrolysis is used in a high-concentration, 20% to 30% brine containing hydrochloric acid at a high temperature of 100°C or more. In this anode electrode, a platinum-group-element-containing titanium alloy is used for a part where crevice corrosion may occur.

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[0005] In the Ni refining industry field, a reaction vessel is subjected to a high-concentration sulfuric acid including slurry at a high temperature, which is higher than 100°C. The reaction vessel is made of a platinum-group-element-containing titanium alloy.

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[0006] In the heat exchanger field, a heat exchanger tube used in the salt manufacture field is subjected to high-temperature and high-concentration salt water, and a heat exchanger tube used for heat exchange of an exhaust gas of a furnace is subjected to an exhaust gas containing chlorine, NO_x, and SO_x. These heat exchanger tubes are made of a platinum-group-element-containing titanium alloy.

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[0007] In the petrochemical industry field, a reaction vessel or the like of desulfurization equipment used at a time of oil refining is subjected to high-temperature hydrogen sulfide. Such a reaction vessel is made of a platinum-group-element-containing titanium alloy.

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[0008] Further, a platinum-group-element-containing titanium alloy is considered to be applied to a separator material for a fuel cell, utilizing its high corrosion resistance.

[0009] Gr. 7 ("Gr." (Grade) complies with the ASTM standard. The same holds true in the following description.), which is a Ti-0.15 Pd alloy, is a titanium alloy that has been developed to have corrosion resistance in the above described usages. Pd contained in this titanium alloy reduces hydrogen overvoltage to maintain a natural potential within a passivation area. That is, Pd eluted from the alloy by corrosion is precipitated again on the surface of the alloy to be deposited, and thereby the hydrogen overvoltage of the alloy is reduced and the natural potential is maintained within the passivation area. Accordingly, this alloy has high corrosion resistance.

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[0010] Pd contained in Gr. 7 is, however, very expensive (¥1905/g according to the morning edition of Nihon Keizai Shimbun on December 13, 2012, for example); accordingly, the fields using Pd have been limiting.

[0011] In order to solve this problem, as disclosed in Patent Document 1 below, a titanium alloy (Gr. 17) having a lower content of Pd, which is 0.03 to 0.1 mass%, than Gr. 7, and also having high crevice corrosion resistance is proposed and put into practical use.

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[0012] Patent Document 2 below discloses, as a titanium alloy that can be manufactured at low cost while preventing a reduction in corrosion resistance, a titanium alloy containing one or more platinum group elements in 0.01 to 0.12 mass% in total, and one or more of Al, Cr, Zr, Nb, Si, Sn, and Mn in 5 mass% or less in total. In a usage at a time of development of the titanium alloy, sufficient corrosion resistance is obtained when Pd is in a range of 0.01 to 0.12 mass%. In a usage of recent years, however, a further increase in characteristics is required, so that the corrosion resistance has become insufficient particularly when the content of Pd is less than 0.05 mass%. Also in the usage at the time of development, a further reduction in cost is required.

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[0013] According to Non-Patent Document 1 below, however, by adding Co, Ni, or V, as a third element, to a Ti-Pd alloy, the crevice corrosion resistance is increased, but the content of Pd needs to be 0.05 mass% or more in order to obtain sufficient crevice corrosion resistance.

[0014] As for a reduction in cost, Ru, which is the most inexpensive element in the platinum group element, has been

actively used to develop a material. Patent Document 3 below discloses a titanium alloy to which 0.005 to 0.2 mass% Ru is added. As shown in an example in this document, in order to obtain sufficient crevice corrosion resistance, the addition of Ru to this titanium alloy needs to be 0.05 mass% or more.

[0015] Patent Document 4 below discloses a material of a system in which Ru and Ni are added in order to further increase corrosion resistance. This material has not only crevice corrosion resistance, but also high corrosion resistance in an environment containing non-oxidizing acid such as sulfuric acid or hydrochloric acid. Ti-0.06Ru-0.5Ni is an alloy having a structure within the range shown in Patent Document 4 below and is normalized as Gr. 13 to be used practically as a corrosion-resistant titanium alloy. However, the addition of Ni results in a problem that a Ti_2Ni compound is precipitated in the titanium alloy. Further, due to this compound precipitation, the processability of the titanium alloy, such as stretch, becomes inferior to that of Gr. 17.

[0016] In addition to these problems, in some cases in which a Ti-Pd alloy is applied to a usage as an anode for electrolysis and an inexpensive raw material (brine) is used, crevice corrosion has occurred by bromine (bromine ions) contained in the raw material, although crevice corrosion has been considered not to occur in a case of using normal brine. In addition, corrosion due to bromine (bromine ions) has sometimes occurred also in a chemical plant, for example. Accordingly, a titanium alloy having high corrosion resistance even in a bromine-ion-containing environment has been demanded.

[0017] Patent Document 5 and Patent Document 6 disclose materials to which a platinum group element, a rare earth element, and a transition element are added. Each of these materials is, however, a titanium alloy for an ultra-high vacuum vessel. In Patent Document 5 and Patent Document 6, the platinum group element and the rare earth element are added in order to obtain an effect of preventing a phenomenon in which a gas component dissolved in a material is dispersed and released to a vacuum in the ultra-high vacuum. It is known that the platinum group element has a function of trapping hydrogen and that the rare earth element has a function of trapping oxygen in the titanium alloy. Further, in Patent Document 5 and Patent Document 6, in addition to the platinum group element and the rare earth element, a transition element such as Co, Fe, Cr, Ni, Mn, or Cu is given as a necessary element. It is known that the transition element has a role of fixing atomic hydrogen that is adsorbed on the surface of the vacuum vessel by the platinum group element. However, none of Patent Document 5 and Patent Document 6 is made considering corrosion resistance, and refers to corrosion resistance in a bromine-ion-containing environment.

[Prior Art Document(s)]

[Patent Document(s)]

[0018]

[Patent Document 1] JP H4-57735B
 [Patent Document 2] WO 2007/077645
 [Patent Document 3] JP S62-56219B
 [Patent Document 4] JP S62-20269B
 [Patent Document 5] JP H6-65661A
 [Patent Document 6] JP H6-64600A

[Non-Patent Document(s)]

[0019]

[Non-Patent Document 1] Hideaki MIYUKI, and one other, "Low alloy titanium SMI-ACE with high crevice corrosion resistance", The Society of Materials Science, Japan, Committee on Corrosion and Protection, September 12, 2001.
 [Non-Patent Document 2] Chihiro TAKI, "Characteristics of corrosion-resistant titanium alloy TICOREX and usage examples thereof", Nippon Steel Cooperation Technical Report, 2011, Vol. 375, pp. 73-77.
 [Non-Patent Document 3] Tatsuhiko OKADA, "Pitting potential of titanium in bromide solution", DENKI KAGAKU, 1981, Vol. 49, No. 9, pp. 584-588.

[Summary of the Invention]

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

[0020] The present invention has been made in view of the above problems, and aims to provide a titanium alloy having high corrosion resistance, particularly in a bromine-ion-containing environment.

[Means for Solving the Problem(s)]

[0021] Further, by obtaining a titanium alloy by adding Ru, which is less expensive than Pd, instead of adding Pd, which is an expensive platinum group element, the price of the titanium alloy can be lower than before.

[0022] In order to achieve the above object, the present inventors have studied the following.

(i) Revealing a mechanism by which corrosion resistance is expressed in a Ti-Pd alloy, and adding an element that promotes a preferable surface state to increase corrosion resistance. Increasing corrosion resistance also in a case of a Ti-Ru alloy.

(ii) Obtaining corrosion resistance that is as high as or higher than before and high corrosion resistance in a bromine-existing environment by using a platinum group element at a low content.

[0023] FIG. 1 is a schematic diagram showing a mechanism by which corrosion resistances of a Ti-Pd alloy and a Ti-Pd-Co alloy are expressed. The surface of the Ti-Pd alloy and the Ti-Pd-Co alloy is active in an initial state before being immersed in a solution. When being immersed in an acid solution such as boiling hydrochloric acid, Ti and Pd on the surface, or Ti, Pd, and Co on the surface are melted, and the melted Pd, or Pd and Co is/are precipitated on the surface to be condensed. Accordingly, the hydrogen overvoltage of the entire titanium alloy is decreased. Thus, the potential of the titanium alloy is maintained in a passivation area, and the titanium alloy has high corrosion resistance.

[0024] The present inventors have studied the Ti-Ru alloy and confirmed that the corrosion resistance of the Ti-Ru alloy is secured by the same mechanism as in Ti-Pd. However, when Pd and Ru in the same addition amount are compared with each other under the same conditions, Pd has a higher effect of increasing corrosion resistance. Therefore, it is revealed that a greater amount of Ru needs to be added in order to obtain the same level of corrosion resistance.

[0025] Patent Document 4 and Non-Patent Document 2 above disclose that high corrosion resistance can be obtained by precipitating a large amount of $Ti_2Ni_{1-x}Ru_x$ (a compound including Ru instead of part of Ni in Ti_2Ni) in a titanium base material by adding Ru and Ni without adding a large amount of Ru. However, there is a problem that the titanium alloy to which a large amount of Ni is added has poor processability such as stretch.

[0026] The present inventors have examined for a novel additive element that promotes an alloy base material to be melted at an initial stage after a Ti-Ru alloy is immersed in an acid solution in order to enable Ru to be precipitated immediately and uniformly on a surface to be condensed. It is considered that the addition of such a novel additive element to the Ti-Ru alloy causes the alloy base material to be melted in the initial stage in an active state area after being immersed in the acid solution. Accordingly, the Ru ion concentration is increased in the solution near the surface of the alloy, and a sufficient amount of Ru is immediately precipitated and condensed on the surface of the alloy so as to make the alloy have a potential in a passivation area. Hereinafter, such precipitation of such an amount of Ru on the surface of the alloy is referred to as "Ru precipitation condensation". Even if the content of Ru is low in the alloy, when the Ru precipitation condensation occurs, it becomes possible to decrease the hydrogen overvoltage of the Ti-Ru alloy immediately so as to make the Ti-Ru alloy have a potential that is more noble and stable (a potential in the passivation area).

[0027] In the Ti-Ru alloy having a low content of Ru, when the alloy base material is immediately melted in the initial active state by such a novel additive element being added, the Ru ion concentration and Ti ion concentration near the surface become higher than in a case in which the additive element is not added. Accordingly, the Ru precipitation condensation occurs. Thus, it can be considered that the hydrogen overvoltage of the alloy is immediately decreased and that the potential can be kept in the passivation area.

[0028] On the other hand, in the Ti-Ru alloy having a high content of Ru and containing this novel additive element, in a case in which a damage such as a scratch is generated on the surface of the alloy in a usage environment, the Ru precipitation condensation propagates more immediately on a fresh surface generated by the damage than in a case of a conventional titanium alloy. Accordingly, it can be considered that the hydrogen overvoltage of the alloy reaches the passivation area, and the damage will be repaired. Therefore, corrosion starting from the damage is unlikely to propagate.

[0029] As shown in Non-Patent Document 3, in a bromine-containing environment, pitting or crevice corrosion is generated on pure titanium. It has been considered that crevice corrosion may not occur in a Ti-Pd-based titanium alloy, but crevice corrosion may sometimes be generated in an environment of a chloride containing bromine ions. The present inventors have intensively studied this problem, and have found out that the resistance to corrosion caused by bromine is increased by condensing Ru on the surface.

[0030] On the basis of such assumption and knowledge, the present inventors have performed experiment to examine for an element that promotes an alloy base material to be melted in an initial stage after the alloy is immersed in a solution, that is, an element that promotes Ru precipitation condensation on the Ti-Ru alloy surface (the above described "novel additive element").

[0031] Accordingly, the present inventors have found out that rare earth elements correspond to such an element,

and that the resistance to corrosion caused by bromine is further increased by a synergetic effect of adding, in addition to Ru and a rare earth element, one or more selected from the group consisting of Ni, Co, Mo, Cr, V, and W. Note that the description is made on the basis of Ru; however, another platinum group element such as Pd is also considered to increase the resistance to corrosion caused by bromine in a similar manner.

[0032] The rare earth element itself does not have an effect of increasing corrosion resistance of an alloy. In this light, the rare earth element has a different function from the additive element disclosed in each of Patent Documents 2 to 4 and Non-Patent Document 1 above.

[0033] The usage of the alloy and the function of the element in Patent Documents 5 and 6 are different from those in the present invention. That is, the function of the rare earth element in Patent Documents 5 and 6 are compared with that in the present invention as below (the content is weight%).

[0034] Patent Documents 5 and 6: The titanium alloy has high solid solubility of oxygen. The rare earth element is added in order to fix oxygen as an oxide so as to prevent dissolved oxygen from being dispersed in the alloy and to prevent its release to a vacuum atmosphere in a gas state when being used in a high vacuum usage. To obtain this effect, the lower limit of the rare earth element is set to 0.02%. When the added amount exceeds 0.5%, ductility is decreased by the precipitated oxide. Accordingly, the upper limit of the rare earth element is set to 0.5%.

[0035] The present invention: When being immersed in an environment of a chloride aqueous solution, the titanium alloy containing a platinum group element is melted in an active state area, and the platinum group element is precipitated to be condensed on the surface, so that the potential of the alloy as a whole is shifted to be in a passivation area (the potential becomes noble). The rare earth element has a function of shortening the time for the potential to become noble and a function of increasing the condensing degree of the platinum group element on the surface. To obtain this effect, the rare earth element is desirably in a dissolving range of the titanium alloy. The lower limit is 0.001% and the upper limit is 0.1% in order to obtain this effect. When the amount exceeds 0.1%, a compound of titanium and the rare earth element is produced, which may degrade corrosion resistance.

[0036] The role of the rare earth element in Patent Documents 5 and 6 is to react with oxygen dissolved in the titanium alloy to produce an oxide. In contrast, in the present invention, the rare earth element has a largely different role of promoting the platinum group element to be condensed on the surface of the titanium alloy in a wet corrosion environment. Further, in the present invention, a desirable rare earth element component is within the dissolving range, which is a content lower than that in Patent Documents 5 and 6.

[0037] The present invention has been made on the basis of this knowledge and provides titanium alloys as described in (1) to (7) below.

(1)

[0038] A titanium alloy to be used in a bromine-ion-containing environment, the titanium alloy consisting of, in mass%, a platinum group element: greater than or equal to 0.01% and less than or equal to 0.10%, a rare earth element: greater than or equal to 0.001% and less than 0.02%, O: greater than or equal to 0% and less than 0.1%, and the balance: Ti and impurities.

(2)

[0039] The titanium alloy according to (1), wherein the titanium alloy contains, instead of part of Ti, one or more selected from the group consisting of Ni, Co, Mo, V, Cr, and W, the content of Ni is less than or equal to 1.0 mass%, the content of Co is less than or equal to 1.0 mass%, the content of Mo is less than or equal to 0.5 mass%, the content of V is less than or equal to 0.5 mass%, the content of Cr is less than or equal to 0.5 mass%, and the content of W is less than or equal to 0.5 mass%.

(3)

[0040] The titanium alloy according to (1) or (2), consisting of, in mass%, the platinum group element: greater than or equal to 0.01% and less than or equal to 0.05%.

(4)

[0041] The titanium alloy according to any one of (1) to (3), wherein the platinum group element is Ru.

(5)

[0042] The titanium alloy according to any one of (1) to (4), wherein the rare earth element is Y.

(6)

[0043] The titanium alloy according to any one of (1) to (5), wherein the content of O is less than 0.05 mass%.

(7)

[0044] The titanium alloy according to any one of (1) to (6), wherein the titanium alloy is used in a chemical plant apparatus.

[Effect(s) of the Invention]

[0045] The titanium alloy according to the present invention has high corrosion resistance, the corrosion resistance particularly in a bromine-ion-containing environment. Further, in a case of using Ru, which is an inexpensive platinum group element, the raw material cost of the titanium alloy becomes low. In a case in which the content of the platinum group element is high (for example, higher than 0.05 mass%), when a damage such as a removal of a passivation film is generated on the surface by a scratch or the like, corrosion starting from the damage is unlikely to propagate.

[0046] In a case in which the titanium alloy contains, instead of part of Ti, one or more selected from the group consisting of Ni, Co, Mo, Cr, V, and W, the resistance to a high-concentration chloride environment containing bromine is also obtained.

[0047] In a case in which the content of O is less than 0.05 mass%, favorable processability is obtained.

[0048] Y is inexpensive among rare earth elements. In a case in which Y is contained as the rare earth element, the raw material cost becomes low.

[Brief Description of the Drawing(s)]

[0049]

[FIG. 1] FIG. 1 is a schematic diagram showing a mechanism by which corrosion resistance of a Ti-Pd(-Co) alloy is expressed.

[FIG. 2] FIG. 2 is schematic diagrams showing a test piece for a crevice corrosion resistance test, and (a) shows a plan view and (b) shows a side view.

[FIG. 3] FIG. 3 is a schematic diagram showing a state of a test piece used in a crevice corrosion resistance test (ASTM G78).

[FIG. 4] FIG. 4 is a graph showing a relation between a Y content of a Ti alloy containing 0.02% Pd in Example 2 and a corrosion speed (96 hours average).

[FIG. 5] FIG. 5 is a graph showing a change in a surface Pd concentration after a boiling hydrochloric acid test of a Ti alloy containing 0.02% Pd in Example 2.

[Mode(s) for Carrying out the Invention]

[0050] As described above, the titanium alloy according to the present invention consists of, in mass%, a platinum group element: greater than or equal to 0.01% and less than or equal to 0.10%, a rare earth element: greater than or equal to 0.001% and less than 0.02%, O: greater than or equal to 0% and less than 0.1%, and the balance: Ti and impurities. The present invention will be described below in detail.

1. Platinum group element

[0051] Platinum group elements have an effect of decreasing a hydrogen overvoltage of a titanium alloy and of maintaining a natural potential in a passivation area. Among the platinum group elements, the titanium alloy according to the present invention contains Ru, for example. Ru is less expensive than other platinum group elements and is preferable to secure economic efficiency. The market price of Ru was about 1/6 of that of Pd as of January in 2012.

[0052] According to the present inventors' study, by adding the platinum group element and the rare earth element to the titanium alloy, an effect of preventing corrosion of the titanium alloy can be obtained even in a bromine-ion-containing environment, although the mechanism thereof has not been revealed. In the present invention, the content of the platinum group element is 0.01 to 0.10 mass%. In a case in which the content of the platinum group element is less than 0.01 mass%, corrosion resistance of the titanium alloy may be insufficient and corrosion may occur in a high-temperature and high-concentration chloride aqueous solution. On the other hand, even if the content of the platinum group element is higher than 0.10 mass%, an increase in corrosion resistance is not expected, and in addition, the raw material cost

becomes high and processability becomes poor.

[0053] Considering the balance between processability and corrosion resistance, the content of the platinum group element having a β -stabilizing function, such as Ru, is preferably set to 0.01 to 0.05 mass%, for example. This is because the titanium alloy according to the present invention, in which the content of the platinum group element is in this range, has corrosion resistance as high as a conventional titanium alloy in which the content of the platinum group element is higher than 0.05 mass%. Note that, in a case in which a scratch or the like generates a damage on the titanium alloy, such as a removal of a passivation film, the Ru precipitation condensation propagates more immediately on a fresh surface generated by the scratch or the like as the content of Ru is higher in the titanium alloy, as described above by taking the Ti-Ru alloy as an example. Accordingly, since a potential of a portion where a scratch or the like is generated reaches the passivation area immediately and the surface is repaired (the passivation film is repaired), as the Ru content is higher, corrosion starting from the damage is more unlikely to occur. In a case in which the Ru content is higher than 0.05 mass%, the titanium alloy according to the present invention is suitable for a usage in a harsh environment where a damage can be generated in the passivation film.

2. Rare earth element

2-1. Reason of containing rare earth element

[0054] The present inventors have considered to add, to a Ti-0.04 mass% Ru alloy, a minute amount of various elements that are likely to be melted in an environment of a high-temperature and high-concentration chloride aqueous solution. A titanium alloy containing such elements was immersed in a chloride aqueous solution to be melted in the active state area. Then, the present inventors have investigated whether an effect of shifting the potential of the entire alloy to the passivation area is obtained by promoting the Ru precipitation condensation on the surface of the titanium alloy. As a result, rare earth elements are confirmed as elements having this effect.

[0055] A further investigation has revealed that the same effect can be obtained not only in a case in which the Ru content is 0.04 mass%, but also in a case in which the Ru content is in a range of 0.01 to 0.05 mass% or greater than 0.05 mass% in the Ru-containing titanium alloy. That is, it is found out that the addition of the rare earth element to the titanium alloy, in which the Ru content is in a range of 0.01 to 0.10 mass%, enables Ti and Ru to be melted immediately after the titanium alloy is subjected to a corrosion environment. In other words, it is found out that the Ru ion concentration can be increased (the Ru precipitation condensation can be generated) immediately in a solution near the surface of the titanium alloy. As compared with a titanium alloy containing Ru and not containing the rare earth element, the titanium alloy containing Ru and the rare earth element can efficiently precipitate Ru on the surface. Even when a melted amount (corrosion amount) of the entire titanium alloy is small, and the titanium alloy containing Ru and the rare earth element can efficiently precipitate Ru and has high corrosion resistance. Note that although the description is made on Ru, another platinum group element such as Pd is similarly considered to have an effect of increasing the resistance to corrosion caused by bromine.

[0056] Rare earth elements include Sc, Y, light rare earth elements (La to Eu), and heavy rare earth elements (Gd to Lu). According to the present inventors' study, any of the rare earth elements has the above described effect. Further, it is not necessary to add only one element as the rare earth element. The above described effect has been confirmed also in a case of using a mixture or compound of rare earth elements, such as a mixture of rare earth elements (also referred to as mischmetal or "Mm" below) before separation purification or a didymium alloy (alloy including Nd and Pr).

[0057] Considering the above description, in terms of economic efficiency, it is preferable to use La, Ce, Nd, Pr, Sm, Mm, a didymium alloy, Y (Y is particularly preferable), which are easily obtained and relatively inexpensive among rare earth elements. Any Mm and didymium alloy that are commercially available can be used for the present invention regardless of the component ratio of rare earth element(s).

2-2. Content of rare earth element(s)

[0058] The range of the content of the rare earth element(s) in the titanium alloy according to the present invention is greater than or equal to 0.001 and less than 0.02 mass%. When the content of the rare earth element(s) is 0.001 mass% or more, in a passivation area of a Ti- alloy, it is possible to melt Ti, the platinum group element, and the rare earth element(s) simultaneously in a chloride aqueous solution, and to obtain a sufficient effect of promoting the precipitation of the platinum group element on the surface of the alloy.

[0059] The upper limit of the content of the rare earth element(s) is set to less than 0.02 mass% because the content of the rare earth element(s) being more than this limit does not increase the above effect, and in addition, a compound that is not produced in a case of not adding the rare earth element(s) may be produced in the Ti alloy. This compound is melted preferentially in a chloride aqueous solution, and generates pit-like corrosion in the Ti-platinum group element. Accordingly, the Ti-platinum group element alloy in which this compound is produced has lower corrosion resistance

than in a case of not adding the rare earth element(s).

[0060] The content of the rare earth element(s) in the Ti-platinum group element alloy is preferably set to the solid solubility limit or less in α -Ti, the solid solubility limit being shown in a phase diagram or the like. For example, the solid solubility limit of Y in α -Ti is 0.02 mass% (0.01 at%). Accordingly, it is preferable that the content of Y is less than 0.02 mass% in a case of adding Y. Further, the solid solubility of La in α -Ti is extremely high, which is 2.84 mass% (1 at%) according to Non-Patent Document 4 above. However, also in a case of adding La, in view of securing economic efficiency, the content of La is set to less than 0.02 mass%.

3. O (oxygen)

[0061] The titanium alloy according to the present invention contains O in less than 0.1 mass%. The content of O is set to less than 0.1 mass% because corrosion resistance and favorable processability are secured. Ti has high solid solubility of oxygen, so that Ti having high solid solubility of oxygen (JIS type-2 to type-4 titanium) is intentionally used for a usage for which high strength is required. Indeed the solid solution of oxygen is effective in increasing the strength, but it may degrade processability. Accordingly, considering processability in addition to corrosion resistance and economic efficiency, the upper limit of the content of O is set to 0.1 mass%. For a usage that does not need high strength or a usage that puts much value on processability, the content of O is preferably set to less than 0.05 mass%.

4. Ni, Co, Mo, V, Cr, and W

[0062] The titanium alloy according to the present invention may contain, instead of part of Ti, one or more of Ni, Co, Mo, V, Cr, and W. In this case, in combination with the effects of the platinum group element and the rare earth element(s), the titanium alloy can have higher corrosion resistance in a bromine-ion-containing environment.

[0063] In a case of the titanium alloy containing one or more of these elements, the contents thereof are as follows: Ni: 1.0 mass% or less, Co: 1.0 mass% or less, Mo: 0.5 mass% or less, V: 0.5 mass% or less, Cr: 0.5 mass% or less, and W: 0.5 mass% or less.

5. Impurities

[0064] Examples of impurities in the titanium alloy include Fe, O, C, H, N, Al, Zr, Nb, Si, Sn, Mn, and Cu. Fe, O, C, H, and N are mixed from a raw material, a melting electrode, and an environment, and Al, Zr, Nb, Si, Sn, Mn, and Cu are mixed in a case of using scrap as a raw material. These impurities may be mixed without any problem as long as the amount thereof is as small as not to impede the effects of the present invention seriously. Specifically, the amounts of the impurities being as small as not to impede the effects of the present invention seriously are as follows: Fe: 0.3 mass% or less, O: less than 0.1 mass%, C: 0.18 mass% or less, H: 0.015 mass% or less, N: 0.03 mass% or less, Al: 0.3 mass% or less, Zr: 0.2 mass% or less, Nb: 0.2 mass% or less, Si: 0.02 mass% or less, Sn: 0.2 mass% or less, Mn: 0.01 mass% or less, and Cu: 0.1 mass% or less. The total amount of these elements is 0.6 mass% or less.

[Example 1]

[0065] To confirm crevice corrosion resistance and processability (bendability and stretch) of the titanium alloy according to the present invention, the following tests were performed and the results were evaluated.

1. Test methods

1-1. Samples

[0066] Table 1 shows samples that were used for the tests and composition thereof (analytical values are shown for elements other than Ti, and Ti is the balance (bal.)).

[Table 1]

	Sample number	Pd	Ru	Ni	Cr	Co	Mo	W	V	O	C	H	N	Fe	Y	La+Ce+Nd+Pr (Mm)	Ti
Comparative material 1	1	0.14	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.109	0.006	0.0018	0.0077	0.073	-	-	Bal.
Comparative material 2	2	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	0.006	0.0042	0.005	0.036	-	-	Bal.
Comparative material 3	3	-	0.054	0.52	0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.004	0.001	0.003	0.03	-	-	Bal.
Comparative material 4	4	-	0.052	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.006	0.0022	0.005	0.04	-	-	Bal.
Present invention example 1 (claim 1)	5	-	0.042	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.005	0.0021	0.006	0.03	0.005	-	Bal.
Present invention example 2 (claim 1)	6	-	0.049	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.08	0.006	0.0032	0.004	0.03	0.004	-	Bal.
Present invention example 3 (claim 1)	7	-	0.087	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.005	0.0022	0.006	0.04	-	0.01	Bal.
Present invention example 4 (claim 1)	8	-	0.013	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.007	0.0028	0.006	0.03	0.01	-	Bal.
Example beyond invention range 1	9	-	0.048	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.12*	0.007	0.0033	0.004	0.03	0.01	-	Bal.

(continued)

	Sample number	Pd	Ru	Ni	Cr	Co	Mo	W	V	O	C	H	N	Fe	Y	La+Ce+Nd+Pr (Mm)	Ti
Example beyond invention range 2	10	-	0.004*	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.006	0.0034	0.006	0.04	0.01	-	Bal.
Example beyond invention range 3	11	-	0.043	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.007	0.0044	0.005	0.04	-	0.12*	Bal.
Present invention example 5 (claim 2)	12	-	0.025	0.12	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.008	0.002	0.005	0.02	0.01	-	Bal.
Present invention example 6 (claim 2)	13	-	0.027	<0.01	<0.01	0.18	<0.01	<0.01	<0.01	0.04	0.007	0.003	0.006	0.03	0.01	-	Bal.
Present invention example 7 (claim 2)	14	-	0.028	<0.01	0.18	<0.01	<0.01	<0.01	<0.01	0.04	0.008	0.003	0.006	0.04	-	0.01	Bal.
Present invention example 8 (claim 2)	15	-	0.029	<0.01	<0.01	<0.01	0.11	<0.01	<0.01	0.03	0.006	0.004	0.005	0.03	0.01	-	Bal.
Present invention example 9 (claim 2)	16	-	0.028	<0.01	<0.01	<0.01	<0.01	0.14	<0.01	0.04	0.006	0.005	0.006	0.03	0.015	-	Bal.

(continued)

	Sample number	Pd	Ru	Ni	Cr	Co	Mo	W	V	O	C	H	N	Fe	Y	La+Ce+Nd+Pr (Mm)	Ti
Present invention example 10 (claim 2)	17	-	0.027	<0.01	<0.01	<0.01	<0.01	<0.01	0.19	0.03	0.007	0.004	0.005	0.03	0.01	-	Bal.
Present invention example 11 (claim 2)	18	-	0.029	<0.01	0.04	0.01	0.01	0.02	0.03	0.04	0.006	0.003	0.004	0.03	0.015	-	Bal.
In sample numbers 9 to 11, numerical values with * means being beyond the range of the present invention.																	

[0067] The following titanium alloy sheet materials were prepared as the samples used for tests: Comparative materials which are conventional materials (sample numbers 1 to 4); Present invention examples (sample numbers 5 to 8 each corresponding to claim 1, and sample numbers 12 to 18 each corresponding to claim 2); Examples beyond the range of the present invention, which are not conventional materials (hereinafter simply referred to as "Examples beyond invention range", sample numbers 9 to 12). Comparative materials 1 to 3 were obtained from the market, and the other samples (including Comparative material 4) were fabricated in a laboratory. Comparative material 4 was obtained by employing the composition of the Ti-Ru alloy disclosed in Patent Document 3 above, which is described as "having high crevice corrosion resistance and bendability".

1-1-1. Compositions of samples

[0068] Comparative material 1 is Gr. 7, Comparative material 2 is Gr. 17, and Comparative material 3 is Gr. 13. Each of Comparative materials 1 to 4 is an alloy that does not contain a rare earth element.

[0069] The samples as Present invention examples and Examples beyond invention range have the following characteristics.

[0070] Present invention example 1, 4: the Ru content is less than 0.05 mass% and the oxygen content is less than 0.05 mass%.

[0071] Present invention example 2: the Ru content is less than 0.05 mass% and the oxygen content is 0.05 mass% or more.

[0072] Present invention example 3: the Ru content is 0.05 mass% or more and the oxygen content is less than 0.05 mass%.

[0073] Present invention example 5: containing Ni.

[0074] Present invention example 6: containing Co.

[0075] Present invention example 7: containing Cr.

[0076] Present invention example 8: containing Mo.

[0077] Present invention example 9: containing W.

[0078] Present invention example 10: containing V.

[0079] Present invention example 11: containing Cr, Co, Mo, W, and V.

[0080] In Present invention examples 1 to 11, the content of the rare earth element(s) is less than 0.02 %.

[0081] Example beyond invention range 1: being beyond the range of the present invention in that the O content exceeds 0.10 mass%.

[0082] Example beyond invention range 2: being beyond the range of the present invention in that the Ru content is less than 0.01 mass%.

[0083] Example beyond invention range 3: being beyond the range of the present invention in that the content of the rare earth element(s) is 0.02 mass% or more.

1-1-2. Raw materials used for fabrication of samples

[0084] Raw materials used for the fabrication of the titanium alloys were commercially available pure Ti sponge (JIS type-1) for industrial use, ruthenium (Ru) powder (purity 99.9 mass%) produced by Kishida chemical Co., Ltd., turning yttrium (Y) (purity 99.9 mass%) produced by Kishida chemical Co., Ltd., and a massive form Mm (mixed rare earth elements). The ratio of rare earth elements in Mm was as follows: La: 28.6 mass%, Ce: 48.8 mass%, Pr: 6.4 mass%, and Nd: 16.2 mass%.

1-1-3. Method for fabricating samples

[0085] The raw materials were measured to be in the predetermined ratio for each sample to be fabricated, and were melted (molten) in an argon atmosphere by an arc melting furnace to fabricate five ingots (each of which weighs 80 g). Then, all the five ingots were re-melted together to fabricate square ingots each having a thickness of 15 mm. Each of the square ingots was re-melted for homogenization to fabricate square ingots each having a thickness of 15 mm again. That is, melting was performed three times in total.

[0086] Since each square ingot contained a minute amount of Pd and rare earth element(s), in order to reduce segregation of the elements and homogenize the elements in the alloy, heat treatment was performed under the following conditions.

Atmosphere: vacuum ($< 10^{-3}$ Torr)

Temperature: 1100 °C

Time: 24 hours

[0087] The square ingot subjected to heat treatment was rolled under the following conditions to obtain a sheet material

having a thickness of 2.5 mm.

β -phase region hot rolling: rolling was performed with a heating temperature of 1000 °C to reduce the thickness from 15 mm to 9 mm.

α + β -phase region hot rolling: rolling was performed on the sheet material, subjected to the β -phase region hot rolling, with a heating temperature of 875 °C to reduce the thickness from 9 mm to 2.5 mm.

[0088] The sheet material obtained by rolling was annealed in vacuum at 750 °C for 30 minutes to remove strain.

[0089] From the thus obtained hot-rolled sheet, test pieces to be used for the following tests were obtained by machining.

1-2. Crevice corrosion resistance tests

[0090] Crevice corrosion resistance tests were performed by using the thus obtained test pieces.

1-2-1. Test pieces for crevice corrosion resistance tests

[0091] FIG. 2 is schematic diagrams showing a test piece for a crevice corrosion resistance tests, and (a) shows a plan view and (b) shows a side view. As shown in the figures, this test piece has a thickness of 2 mm, a width of 30 mm, and a length of 30 mm. A hole having a diameter of 7 mm was formed in the center of the test piece. Further, on one surface (front surface) of the test piece was polished using an emery paper with a grit of 600.

[0092] FIG. 3 is a schematic diagram showing a state of a test piece used in a crevice corrosion resistance test. A test piece 1 was interposed between clevises (spacers) 2 formed of poly-trifluoroethylene. A hole was formed in the center of each of the clevises so as to correspond to the hole in the test piece 1. On one surface of the clevis 2, a plurality of trenches were formed, and the surface including the trenches were made to be in contact with the test piece 1. The trench formed a crevice between the test piece 1 and the clevis 2.

[0093] A bolt 3 was inserted into the hole of the test piece 1 and the clevis 2, and a nut 4 was attached to the bolt 3, so that the test piece 1 and the clevises 2 were tightened. The bolt 3 and the nut 4 were obtained by oxidizing the surface of a bolt and a nut which were made of pure titanium, by heat treatment in air. The torque at the time of tightening was 40 kgf · cm.

1-2-2. Crevice corrosion resistance tests in environment not containing bromine ions substantially

[0094] By use of the test piece in the above state shown in FIG. 3, crevice corrosion resistance tests based on a multi-clevis test regulated in ASTM G78 were performed. Specifically, the test piece was immersed in a 250 g/L NaCl aqueous solution (pH = 2, pH was adjusted by hydrochloric acid), and the test was performed in a manner that the aqueous solution maintained an air-saturated liquid state at 150 °C by using an autoclave apparatus. The test time was 500 hours.

[0095] After the test, the number of portions in which crevice corrosion occurred in the test piece was counted, and an increase or decrease in the weight of the test piece due to the test (the value obtained by subtracting the weight of the test piece before the test from the weight of the test piece after the test) was measured. The weight per test piece before the test was about 7 g.

1-2-3. Crevice corrosion resistance tests in bromine-ion-containing environment

[0096] The same tests and evaluation were performed as in "Crevice corrosion resistance tests in environment not containing bromine ions substantially" except that, instead of the NaCl aqueous solution used in the above "Crevice corrosion resistance tests in environment not containing bromine ions substantially", an aqueous solution obtained by adding sodium bromide reagent to set the bromine ion concentration to 0.01 mol/L was used for corrosion tests.

1-3. Evaluation of processability

[0097] The processability of a material was evaluated by bending tests and tension tests. The test conditions were as follows.

1-3-1. Bending tests

[0098] The test piece was obtained in the following manner. A sheet material having a thickness of 2.0 mm to 2.5 mm was extended to a thickness of 0.5 mm by rolling and then was annealed. From this sheet material, a fragment having a size and a shape which are based on JIS Z 2204 (a width of 20 mm and a length of 60 mm) was cut out, and a surface of the fragment was polished by an emery paper with a grit of 600 in the rolling direction and the perpendicular direction.

[0099] The bending tests were performed by a method based on JIS Z 2248, and T-direction adhesion bendability

was evaluated.

1-3-2. Tension tests

[0100] From each of the test pieces 1 for the above crevice corrosion resistance tests, which were not used in the crevice corrosion resistance tests, two test pieces each having half the size of ASTM with a thickness of 2 mm were cut out in a direction parallel to the rolling longitudinal direction. The cut out test pieces were subjected to tension tests by using an autograph tension tester manufactured by Shimadzu Cooperation. The tension rate was 0.5%/min up to the bearing force, and was 5 mm/min thereafter. An average value of breaking extension measured for the two test pieces was set as a stretch of that test piece in an L direction.

2. Test results

2-1. Crevice corrosion resistance

[0101] Table 2 shows results of the crevice corrosion resistance tests. In Table 2, results of the crevice corrosion resistance tests in an environment not containing bromine ions substantially are shown in cells with "250 g/L-NaCl, pH = 2, 150°C". Results of the crevice corrosion resistance tests in a bromine-ion-containing environment are shown in cells with "250 g/L - NaCl, Br 0.01 mol/L, pH = 2, 150°C".

[Table 2]

	Sample number	250 g/L-NaCl, pH = 2, 150°C			250 g/L-NaCl, Br 0.01 mol/L, pH = 2, 150°C		
		Corrosion occurrence rate	Increase/decrease in weight	Note	Corrosion occurrence rate	Increase/decrease in weight	Note
Comparative material 1	1	0/40	3.5mg increase	No corrosion	2/40	36mg decrease	Crevice corrosion
Comparative material 2	2	0/40	2.4mg increase	No corrosion	2/40	41mg decrease	Crevice corrosion
Comparative material 3	3	0/40	2.6mg increase	No corrosion	1/40	3.6mg decrease	Crevice corrosion
Comparative material 4	4	3/40	44mg decrease	Crevice corrosion	12/40	325mg decrease	Crevice corrosion
Present invention example 1	5	0/40	2.8mg increase	No corrosion	0/40	1.5mg increase	No corrosion
Present invention example 2	6	0/40	2.9mg increase	No corrosion	0/40	3.1mg increase	No corrosion
Present invention example 3	7	0/40	3.4mg increase	No corrosion	0/40	2.7mg increase	No corrosion
Present invention example 4	8	0/40	2.6mg increase	No corrosion	0/40	1.9mg increase	No corrosion
Example beyond invention range 1	9	0/40	3.3mg increase	No corrosion	0/40	4.3mg increase	No corrosion
Example beyond invention range 2	10	5/40	108mg decrease	Crevice corrosion	6/40	469mg decrease	Crevice corrosion
Example beyond invention range 3	11	0/40	1.8mg increase	No corrosion	0/40	2.3mg increase	No corrosion

(continued)

	Sample number	250 g/L-NaCl, pH = 2, 150°C			250 g/L-NaCl, Br 0.01 mol/L, pH = 2, 150°C		
		Corrosion occurrence rate	Increase/decrease in weight	Note	Corrosion occurrence rate	Increase/decrease in weight	Note
Present invention example 5 (claim 2)	12	0/40	1.1mg increase	No corrosion	0/40	0.9mg increase	No corrosion
Present invention example 6 (claim 2)	13	0/40	1.6mg increase	No corrosion	0/40	1.1mg increase	No corrosion
Present invention example 7 (claim 2)	14	0/40	2.4mg increase	No corrosion	0/40	2.1mg increase	No corrosion
Present invention example 8 (claim 2)	15	0/40	2.9mg increase	No corrosion	0/40	2.7mg increase	No corrosion
Present invention example 9 (claim 2)	16	0/40	2.7mg increase	No corrosion	0/40	1.8mg increase	No corrosion
Present invention example 10 (claim 2)	17	0/40	3.1mg increase	No corrosion	0/40	1.9mg increase	No corrosion
Present invention example 11 (claim 2)	18	0/40	2.2mg increase	No corrosion	0/40	2.1mg increase	No corrosion

[0102] As for "Corrosion occurrence rate" in Table 2, "40" as denominators is the number of crevices formed between the test piece 1 and the clevis 2 due to the trenches of the clevis 2. The numbers as numerators are the number of portions where corrosion occurred among portions corresponding to the crevices on the surface of the test piece 1.

[0103] Results of the tests in the above "environment not containing bromine ions substantially" are as follows.

[0104] Corrosion did not occur at all in the 40 crevices in all of Present invention examples (Present invention examples 1 to 4 and 5 to 11), Comparative materials 1 to 3, and Examples beyond invention range 1 and 3. In these samples, oxidation coloring was found in a portion other than the portions corresponding to the crevices, and a minute increase in weight due to the oxidation was found.

[0105] Crevice corrosion occurred in Comparative material 4 (material described in Patent Document 3) and Example beyond invention range 2 (material having a content of Ru lower than the range of the present invention). As for these samples, white corrosion products were found in a portion corresponding to the crevices, and the weight was decreased by more than 40 mg by the corrosion.

[0106] Results of tests in the above "bromine-ion-containing environment" were as follows.

[0107] Corrosion did not occur at all in the 40 crevices in all of Present invention examples (Present invention examples 1 to 4 and 5 to 11), and Examples beyond invention range 1 and 3. In these samples, oxidation coloring was found in a portion other than the portions corresponding to the crevices, and a minute increase in weight due to the oxidation was found.

[0108] Crevice corrosion occurred in Comparative materials 1 to 4 and Example beyond invention range 2. Among

these samples, the weight was decreased particularly largely by corrosion in Comparative material 4 and Example beyond invention range 2.

[0109] It is found out that Present invention examples have high corrosion resistance (crevice corrosion resistance) both in a chloride environment that does not contain bromine ions substantially and a chloride environment containing bromine ions.

2-2. Processability

[0110] Table 3 shows results of bendability tests (sealing-bending) and tension tests.

[Table 3]

	Sample number	Sealing-bending in T-direction	Stretch in L-direction (%)
Comparative material 1	1	C	29
Comparative material 2	2	A	52
Comparative material 3	3	C	35
Comparative material 4	4	B	49
Present invention example 1	5	A	54
Present invention example 2	6	B	46
Present invention example 3	7	A	53
Present invention example 4	8	A	54
Example beyond invention range 1	9	C	43
Example beyond invention range 2	10	A	56
Example beyond invention range 3	11	C	49
Present invention example 5 (claim 2)	12	B	44
Present invention example 6 (claim 2)	13	B	45
Present invention example 7 (claim 2)	14	B	47
Present invention example 8 (claim 2)	15	A	50
Present invention example 9 (claim 2)	16	B	45
Present invention example 10 (claim 2)	17	B	47
Present invention example 11 (claim 2)	18	B	46

[0111] In Table 3, alphabetical characters in the cells of "sealing-bending in T-direction" denote the following.

A: A break was not generated.

B: A fine break was generated in any of the test pieces.

C: A break was generated in any of the test pieces.

[0112] As for Comparative materials 1 and 3, breaks were generated by sealing-bending in the T-direction and stretches in the L-direction were small. That is, the bendability of Comparative materials 1 and 3 was low. As for Comparative material 2, a break was not seen in sealing-bending in the T-direction and the stretch in the L-direction was as large as that of a JIS type-1 material. As for Comparative material 4, although the stretch in the L-direction was as high as that of a JIS type-1 material, a fine break was seen on the surface of the test piece in sealing-bending in the T-direction.

[0113] As for each of Present invention examples 1, 3, 4, and 8, a break was not seen in sealing-bending in the T-direction, and the stretch in the L-direction was as high as that of JIS type-1 titanium, which is 50 % or more. In contrast, as for Present invention examples 2, 5, 6, 7, 9, 10, and 11, the stretch in the L-direction was lower than that of the other Present invention examples, which is lower than 50 %, and fine breaks were generated on the surface in sealing-bending in the T-direction. In this manner, Present invention examples 2, 5, 6, 7, 9, 10, and 11 have lower processability than

Present invention examples 1, 3, 4, and 8. Present invention example 8 has a relatively smaller stretch in the L-direction than Present invention examples 1, 3, and 4.

[0114] As for Example beyond invention range 1, the stretch in the L-direction was poor and a break was generated in sealing-bending in the T-direction. As for Example beyond invention range 2, both results of sealing-bending in the T-direction and the stretch in the L-direction were favorable. As for Example beyond invention range 3, although the stretch in the L-direction was large, a break was generated in sealing-bending in the T-direction.

[0115] In general, the processability tends to increase as the O content is lower and the contents of Ni, Cr, Co, Mo, W, and V are lower. Each of Present invention examples 1, 3, and 4 has more favorable processability than Present invention example 2 possibly because the O content of Present invention examples 1, 3, and 4 was less than 0.05 mass% whereas the O content of Present invention example 2 was 0.05 mass% or more (however, the O content is less than 0.1 mass% and is within the region of the present invention). Each of Present invention examples 5 to 11 has lower processability than Present invention examples 1, 3, and 4 possibly because each of Present invention examples 5 to 11 contains any of Ni, Cr, Co, Mo, W, and V.

[0116] The content of the rare earth element(s) of Example beyond invention range 3 exceeded the range of the content of the rare earth element(s) in the present invention (0.01 to 0.10 mass%), and a compound containing a rare earth element was produced in this sample. The break generated by sealing-bending in the T-direction of Example beyond invention range 3 was assumed to have started from this compound.

3. Overall evaluation

[0117] The overall evaluation of each sample was performed by taking into consideration the above test results and economic efficiency.

[0118] Table 4 shows calculation results of cost of a platinum group element in the price of raw materials, based on the ratio of the platinum group element contained in the samples. In calculation, the price of the bare metal of the platinum group element was set to ¥1905/g for Pd and ¥300/g for Ru.

[Table 4]

	Sample number	Pd (mass%)	Ru (mass%)	Cost of platinum group element (¥/kg)	Relative cost of platinum group element
Comparative material 1	1	0.14	-	2667	100.00
Comparative material 2	2	0.06	-	1143	42.86
Comparative material 3	3	-	0.054	162	6.07
Comparative material 4	4	-	0.052	156	5.85
Present invention example 1	5	-	0.042	126	4.72
Present invention example 2	6	-	0.049	147	5.51
Present invention example 3	7	-	0.087	261	9.79
Present invention example 4	8	-	0.013	39	1.46
Example beyond invention range 1	9	-	0.048	144	5.40
Example beyond invention range 2	10	-	0.004	12	0.45
Example beyond invention range 3	11	-	0.043	129	4.84

(continued)

	Sample number	Pd (mass%)	Ru (mass%)	Cost of platinum group element (¥/kg)	Relative cost of platinum group element
Present invention example 5 (claim 2)	12	-	0.025	75	2.81
Present invention example 6 (claim 2)	13	-	0.027	81	3.04
Present invention example 7 (claim 2)	14	-	0.028	84	3.15
Present invention example 8 (claim 2)	15	-	0.029	87	3.26
Present invention example 9 (claim 2)	16	-	0.028	84	3.15
Present invention example 10 (claim 2)	17	-	0.027	81	3.04
Present invention example 11 (claim 2)	18	-	0.029	87	3.26

[0119] In Table 4, "Cost of platinum group element" means the cost (¥) of the platinum group element in 1 kg of the titanium alloy, and "Relative cost of platinum group element" means the cost ratio of the platinum group element in each sample when the cost of the platinum group element of Comparative material 1 is set to 100. On the assumption of the above price of the bare metal, the cost of the platinum group element of each Present invention example is 1/10 or less of the cost of the platinum group element of Comparative material 1, and is 1/4 or less of the cost of the platinum group element of Comparative material 2.

[0120] Table 5 shows results of the overall evaluation of Comparative materials and Present invention examples.

[Table 5]

	Crevice corrosion resistance		Processability	Economic efficiency	Overall evaluation
	Environment not containing bromine ions substantially	Environment containing bromine ions			
35	Comparative material 1	A	C	C	-
40	Comparative material 2	A	C	C	-
45	Comparative material 3	A	C	A	-
	Comparative material 4	C	C	B	A
50	Present invention examples	A	A	A to B	A

[0121] In Table 5, the evaluation is made for each evaluation item in three grades: A (excellent), B (relatively poor), and C (poor).

[0122] As described above, the processability of the present invention may become relatively poor in some cases (such as in Present invention example 2). Further, the processability is considered to become poor in a case in which the content of O is 0.05 mass% or more or in a case in which Ni, Cr, Co, Mo, W, or V is contained. Accordingly, in a case of being used in a usage that puts much value on processability, the titanium alloy according to the present invention

has the O content of less than 0.05 mass% and does not contain Ni, Cr, Co, Mo, W, and V substantially.

[0123] Other than processability, the present invention is excellent in all the items.

[0124] In contrast, Comparative materials are poor in any of the evaluation items. In particular, none of Comparative materials has crevice corrosion resistance that is high enough to be used substantially in a bromine-ion-containing environment.

[Example 2]

2.1 Composition of titanium alloy used in Example 2

[0125] In order to clarify an optimal content of the rare earth element(s) and to confirm that Ru has high corrosion resistance to bromine among platinum group elements, the following experiment was performed. Table 6 shows compositions of titanium alloys used in Example 2. In accordance with the method for manufacturing the samples shown in Example 1, alloys having the compositions shown in Table 6 were obtained.

[Table 6]

Type	Rare earth element	Platinum group element	Ni	Cr	Co	Mo	W	V	O	C	H	N	Fe	Bal.
Comparative material 5	-	Ru: 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	0.004	0.0024	0.006	0.05	Ti+Impurities
Comparative material 6	Y: 4 ppm	Ru: 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.006	0.0032	0.005	0.04	Ti+Impurities
Present invention example 12	Y: 11 ppm	Ru: 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	0.007	0.0027	0.005	0.04	Ti+Impurities
Present invention example 13	Y: 21 ppm	Ru: 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.005	0.0035	0.004	0.05	Ti+Impurities
Present invention example 14	Y: 40 ppm	Ru: 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.08	0.006	0.0038	0.006	0.05	Ti+Impurities
Present invention example 15	Y: 190 ppm	Ru: 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	0.005	0.0024	0.007	0.06	Ti+Impurities
Present invention example 16	Mm: 21 ppm	Ru: 0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.007	0.0033	0.006	0.04	Ti+Impurities
Present invention example 17	Mm: 23 ppm	Ru: 0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	0.006	0.0028	0.007	0.04	Ti+Impurities
Present invention example 18	Mm: 21 ppm	Ru: 0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.06	0.007	0.0024	0.005	0.05	Ti+Impurities
Present invention example 19	Mm: 25 ppm	Ru: 0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	0.005	0.0032	0.006	0.06	Ti+Impurities

[0126] Comparative materials 5 and 6 contain a rare earth element in less than 0.001 %, and is beyond the range of the present invention. From the materials shown in Table 6, a titanium alloy sheet for crevice corrosion tests in FIG. 2 was obtained by machining, and using the test piece, the crevice corrosion test piece shown in FIG. 3 was formed. Note that the torque at the time of tightening was 40 kgf · cm. This crevice corrosion test piece was used in each crevice corrosion test in a bromine-ion-containing environment described in 1-2-3.

[0127] Table 7 shows results obtained by performing 500-hour crevice corrosion tests. In Comparative material 5 which does not contain a rare earth element, crevice corrosion was seen in a large number of portions, and the decrease due to corrosion was 325 mg. In Comparative material 6 which does not contain a sufficient rare earth element, crevice corrosion was also seen, and the decrease due to corrosion was 32 mg. It is considered that a desirable content of rare earth element(s) is 200 ppm or less in a bromide-ion-containing environment. The content of the rare earth element in each of Present invention examples 12 to 15 was within the range of the present invention, and accordingly, crevice corrosion did not occur, and the decrease in weight thereof due to corrosion was small.

[Table 7]

			250 g/L-NaCl, Br 0.01 mol/L pH = 2, 150°C		
Type	Rare earth element	Platinum group element	Corrosion occurrence rate	Increase/decrease in weight	Note
Comparative material 5	-	Ru: 0.02	15/40	325mg decrease	Crevice corrosion
Comparative material 6	Y: 4 ppm	Ru: 0.02	3/40	32mg decrease	Crevice corrosion
Present invention example 12	Y: 11 ppm	Ru: 0.02	0/40	2.1mg increase	No crevice corrosion
Present invention example 13	Y: 21 ppm	Ru: 0.02	0/40	1.8mg increase	No crevice corrosion
Present invention example 14	Y: 40 ppm	Ru: 0.02	0/40	2.2mg increase	No crevice corrosion
Present invention example 15	Y: 190 ppm	Ru: 0.02	0/40	1.9mg increase	No crevice corrosion

[0128] Next, crevice corrosion test pieces of materials of Present invention examples 16 to 19 having different contents of Ru were used in crevice corrosion tests in the bromine-ion-containing environment shown in 1-2-3. Further, Eriksen tests based on JIS Z 2247 were performed to investigate the press formability of the materials.

[0129] For the tests, a sheet material having a thickness of 2 mm and a size of 90 mm × 90 mm was prepared, and a steel ball having diameter of 20 mm was pressed into the sheet material. When a break reaches the rear surface, the stroke of the punch at that time was set as the Eriksen value. Formation tests were performed using graphite grease for lubricating at a speed of 5 mm/min. The results are shown in Table 8.

[Table 8]

			250 g/L-NaCl, Br 0.01 mol/L pH = 2, 150°C			Eriksen value
Type	Rare earth element	Platinum group element	Corrosion occurrence rate	Increase/decrease in weight	Note	Based on JIS Z 2247
Present invention example 16	Mm: 21 ppm	Ru: 0.02	0/40	4.1mg increase	No crevice corrosion	11.4 mm
Present invention example 17	Mm: 23 ppm	Ru: 0.04	0/40	2.8mg increase	No crevice corrosion	10.6 mm
Present invention example 18	Mm: 21 ppm	Ru: 0.05	0/40	3.2mg increase	No crevice corrosion	10.1 mm

(continued)

			250 g/L-NaCl, Br 0.01 mol/L pH = 2, 150°C			Eriksen value
Type	Rare earth element	Platinum group element	Corrosion occurrence rate	Increase/decrease in weight	Note	Based on JIS Z 2247
Present invention example 19	Mm: 25 ppm	Ru: 0.06	0/40	2.9mg increase	No crevice corrosion	9.6 mm

[0130] In Present invention examples 16 to 18, crevice corrosion did not occur, and accordingly, Present invention examples 16 to 18 have high corrosion resistance in an environment of a bromide-ion-containing solution. Note that the Eriksen value representing formability was decreased slightly when the content of Ru exceeded 0.05 %. In contrast, as the content of Ru was increased, the decrease in weight due to corrosion tended to be decreased. In order to achieve both high corrosion resistance and formability, Ru is preferably set to a range of 0.01 to 0.05 %.

[0131] The thus obtained experimental facts have revealed that particularly high corrosion resistance can be obtained when the content of the rare earth element(s) is greater than or equal to 0.001 and less than 0.02 % in the present invention range. Further, when the Ru content is 0.01 to 0.05 %, high formability can also be secured.

[Industrial Applicability]

[0132] The titanium alloy according to the present invention can be applied to equipment, apparatuses, and the like that are to be used in an environment that requires corrosion resistance in a bromine-ion-containing environment (in particular, a high-temperature and high-concentration chloride environment).

Claims

1. A titanium alloy to be used in a bromine-ion-containing environment, the titanium alloy consisting of, in mass%, a platinum group element: greater than or equal to 0.01% and less than or equal to 0.10%, a rare earth element: greater than or equal to 0.001% and less than 0.02%, O: greater than or equal to 0% and less than 0.1%, and the balance: Ti and impurities.
2. The titanium alloy according to claim 1, wherein the titanium alloy contains, instead of part of Ti, one or more selected from the group consisting of Ni, Co, Mo, V, Cr, and W, the content of Ni is less than or equal to 1.0 mass%, the content of Co is less than or equal to 1.0 mass%, the content of Mo is less than or equal to 0.5 mass%, the content of V is less than or equal to 0.5 mass%, the content of Cr is less than or equal to 0.5 mass%, and the content of W is less than or equal to 0.5 mass%.
3. The titanium alloy according to claim 1 or claim 2, consisting of, in mass%, the platinum group element: greater than or equal to 0.01% and less than or equal to 0.05%.
4. The titanium alloy according to any one of claims 1 to 3, wherein the platinum group element is Ru.
5. The titanium alloy according to any one of claims 1 to 4, wherein the rare earth element is Y.
6. The titanium alloy according to any one of claims 1 to 5, wherein the content of O is less than 0.05 mass%.
7. The titanium alloy according to any one of claims 1 to 6, wherein the titanium alloy is used in a chemical plant apparatus.

FIG. 1

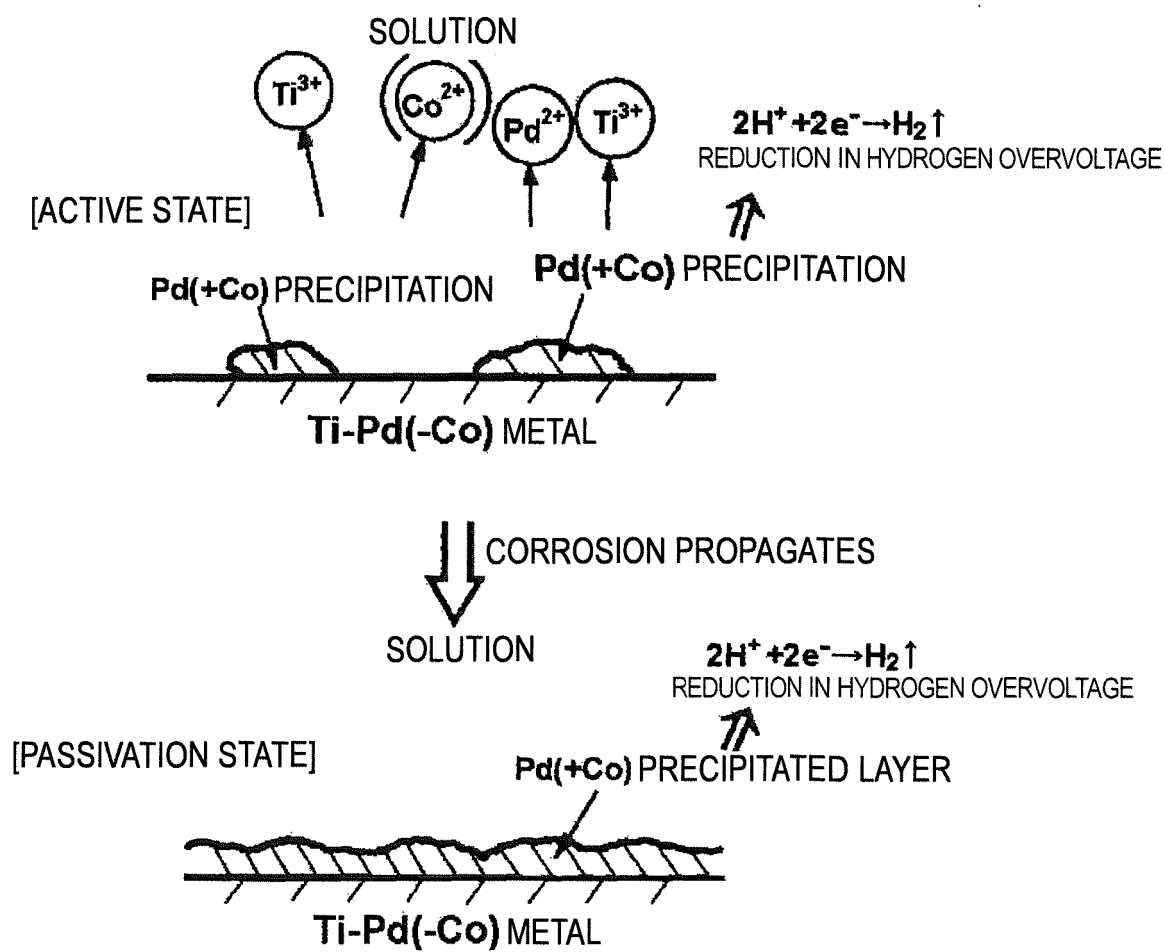


FIG. 2

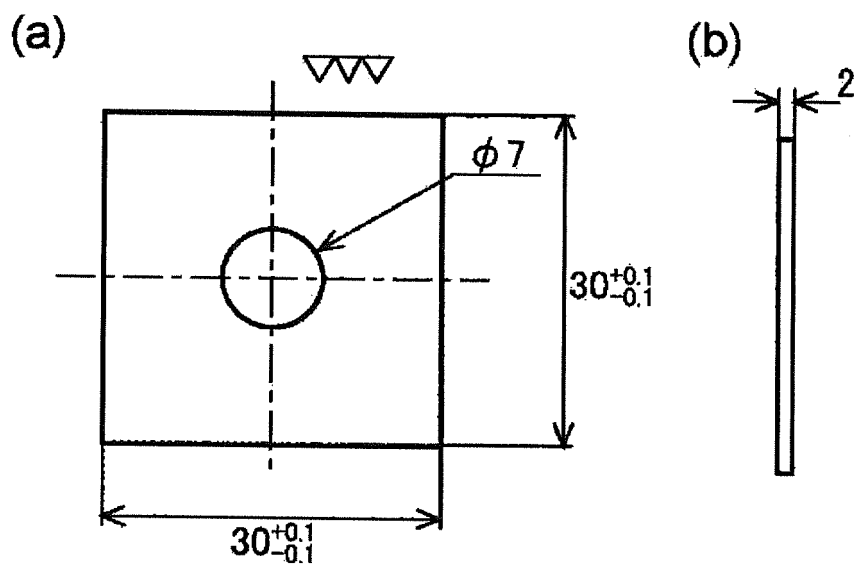


FIG. 3

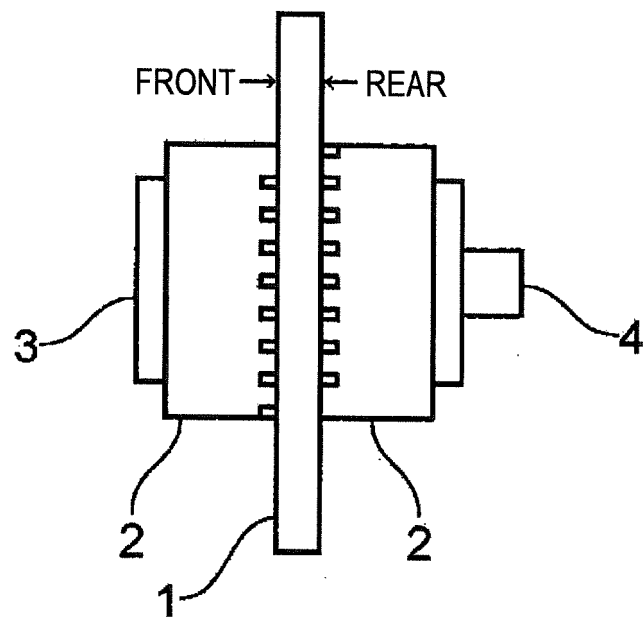


FIG. 4

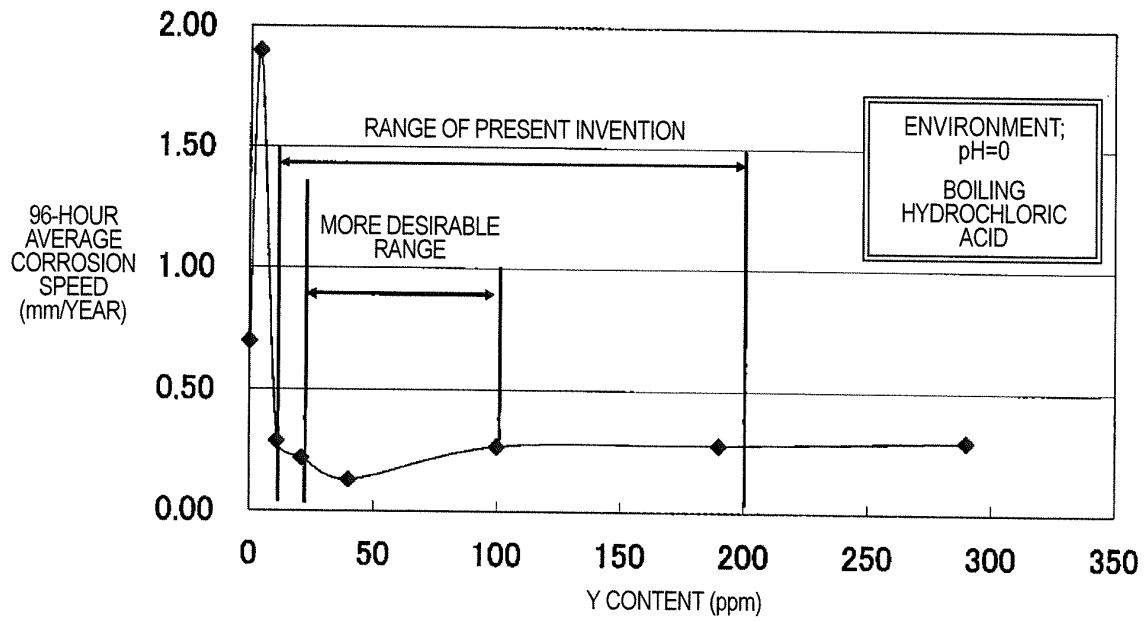
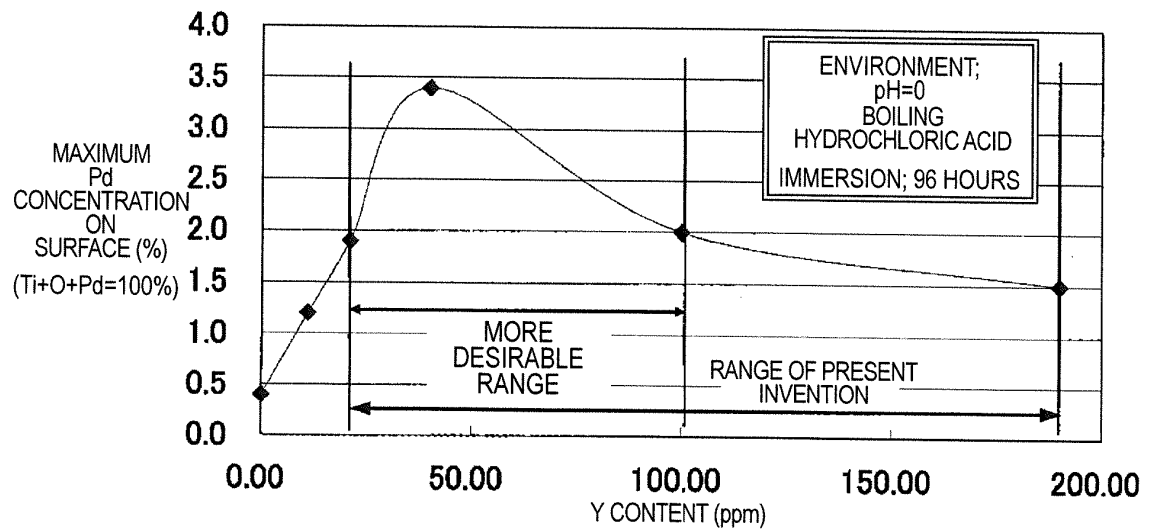


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/051550

A. CLASSIFICATION OF SUBJECT MATTER

C22C14/00(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)

C22C14/00

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 1996-2014
 Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 6-64600 A (Nissan Motor Co., Ltd.), 08 March 1994 (08.03.1994), entire text & US 5478524 A & US 5683523 A & DE 4327816 A	1-7
A	JP 2010-270360 A (Kobe Steel, Ltd.), 02 December 2010 (02.12.2010), entire text & US 2010/0322817 A1 & FR 2945822 A & CN 101892402 A & KR 10-2010-0125189 A & RU 2010120135 A	1-7

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

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Date of the actual completion of the international search
21 February, 2014 (21.02.14)Date of mailing of the international search report
11 March, 2014 (11.03.14)Name and mailing address of the ISA/
Japanese Patent Office

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/051550

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 4-36445 A (Sumitomo Metal Industries, Ltd.), 06 February 1992 (06.02.1992), entire text & US 5141566 A & EP 459909 A1 & DE 69108295 C	1-7
P, X	WO 2013/014894 A1 (Nippon Steel & Sumitomo Metal Corp.), 31 January 2013 (31.01.2013), entire text & JP 5348355 B2 & JP 2013-47369 A & JP 2013-47370 A	1-7

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

REFERENCES CITED IN THE DESCRIPTION

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