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(54) **Titanium alloy excellent in intergranular corrosion resistance**

(57) A titanium alloy contains Ni in a content of 0.35% to 0.55%; Pd in a content of 0.01% to 0.02%; Ru in a content of 0.02% to 0.04%; and Cr in a content of 0.1% to 0.2%, with the remainder including titanium and inevitable impurities, in which the titanium alloy includes nickel-rich phases, each nickel-rich phase being a phase (other than titanium alpha phase) locally containing Ni in a content of 10 times or more the average Ni content of the titanium alloy, the nickel-rich phases are aligned along a rolling direction to form a row, and a multiplicity of the rows are aligned substantially in parallel in a cross direction. The titanium alloy minimizes the proceeding of intergranular corrosion even in specific environments where the intergranular corrosion may easily proceed.

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Description

[0001] The present invention relates to a titanium alloy which excels in corrosion resistance, particularly in intergranular corrosion resistance, in specific environments.

[0002] Titanium is known to show satisfactory corrosion resistance in chloride solutions such as seawater and in oxidizing acids such as nitric acid. Titanium, however, may not exhibit its satisfactory corrosion resistance when exposed to a non-oxidizing environment such as hydrochloric acid or sulfuric acid in a high concentration at high temperatures.

[0003] For improving the corrosion resistance in such specific environments, Ti-Pd alloys containing palladium (Pd) in a content of about 0.12% to 0.25% (Japanese Industrial Standards (JIS) H 4650 Types 11 to 13; ASTM Grade 7 and Grade 11) have been employed.

[0004] To overcome the drawback of expensiveness of the Ti-Pd alloys, there have been recently developed corrosion-resistant titanium alloys containing Pd, which is an expensive platinum-group element, in a less content; and corrosion resistant titanium alloys corresponding to the Ti-Pd alloys, except for replacing part of Pd typically with a more inexpensive element such as Ru, Ni, or Cr (hereinafter these titanium alloys are also referred to as "inexpensive corrosion-resistant titanium alloys") (e.g., Japanese Examined Patent Application Publication No. H04-57735, Japanese Unexamined Patent Application Publication No. S61-127844, and Japanese Unexamined Patent Application Publication No. H04-308051).

[0005] The inexpensive corrosion-resistant titanium alloys include Ti-0.4Ni-0.015Pd-0.025Ru-0.14Cr alloys (nominal composition; hereinafter these alloys are also referred to as "Ti-Ni-Pd-Ru-Cr alloys") newly standardized typically as JIS Type 14 and Type 15 (JIS H4650), and ASTM Grade 33 and Grade 34.

[0006] Such novel inexpensive corrosion-resistant titanium alloys (Ti-Ni-Pd-Ru-Cr alloys) are known to develop corrosion resistance according to a mechanism different from that of existing inexpensive corrosion-resistant titanium alloys (e.g., "Tetsu-to-Hagane (in Japanese; Iron and Steel)", vol. 80, No. 4 (1994), p.353-358). Specifically, the novel inexpensive corrosion-resistant titanium alloys contain chromium (Cr) unlike the existing inexpensive corrosion-resistant titanium alloys. When the novel alloys are exposed to a corrosive environment, chromium selectively dissolves out during early stages of the exposure to allow Pd and Ru to be concentrated on the surface, in which Pd and Ru are platinum-group elements contained in less contents than those of the existing inexpensive corrosion resistant titanium alloys. As a result, the novel alloy exhibits satisfactory corrosion resistance even though they contain platinum-group elements in less contents.

[0007] The Ti-Ni-Pd-Ru-Cr alloys have been widely used typically in the chemical industry and in heat exchangers using seawater because of their inexpensiveness and satisfactory corrosion resistance. However, even the Ti-Ni-Pd-Ru-Cr alloys undergo corrosion in the form of intergranular corrosion in certain specific environments. Exemplary specific environments include severe use environments such that the Ti-Ni-Pd-Ru-Cr alloys are disable to maintain their passive state and that the Ti-Ni-Pd-Ru-Cr alloys have to be exchanged every several years; and environments typically in parts attached around electrodes of electrolysis tanks such that an anode current also passes through the Ti-Ni-Pd-Ru-Cr alloys.

[0008] Such corrosion-resistant titanium alloys are originally excellent in intergranular corrosion resistance, and even pure titanium is resistant to intergranular corrosion in regular environments. However, intergranular corrosion may proceed in the specific use environments. The intergranular corrosion is abominated by users because it may cause rapid fracture of apparatuses, unlike general corrosion which is a regular corrosion form. Accordingly, demands are made to provide a Ti-Ni-Pd-Ru-Cr alloy that can minimize the proceeding of intergranular corrosion even in the specific corrosive environments.

[0009] The present invention has been made under these circumstances, and an object thereof is to provide a titanium alloy that may minimize the proceeding of intergranular corrosion even in specific environments where the intergranular corrosion may easily proceed.

[0010] The present invention has achieved the object and provides, in an aspect, a titanium alloy which contains nickel (Ni) in a content of 0.35 to 0.55 percent by mass (hereinafter contents will be simply expressed in"%"); palladium (Pd) in a content of 0.01% to 0.02%; ruthenium (Ru) in a content of 0.02% to 0.04%; and chromium (Cr) in a content of 0.1% to 0.2%, with the remainder including titanium and inevitable impurities, in which the titanium alloy includes nickel-rich phases, each nickel-rich phase being a phase (other than titanium alpha phase) locally containing Ni in a content of 10 times or more the average Ni content of the titanium alloy, the nickel-rich phases are aligned along a rolling direction to form a row, and a multiplicity of the rows are aligned substantially in parallel in a cross direction.

[0011] The present invention also provides, in another aspect, a titanium alloy which contains Ni in a content of 0.35% to 0.55%; Pd in a content of 0.01% to 0.02%; Ru in a content of 0.02% to 0.04%; and Cr in a content of 0.1% to 0.2%, with the remainder including titanium and inevitable impurities, in which the titanium alloy includes one or more nickel-rich phases, each nickel-rich phase being a phase (other than titanium alpha phase) locally containing Ni in a content of 10 times or more the average Ni content of the titanium alloy, and the nickel-rich phases contain Ti_2Ni.

[0012] As used herein the term "nickel-rich phase" includes the beta phase and precipitates as compounds between and Ni, each of which contains Ni in a content 10 times or more the average Ni content of the matrix titanium alloy. It should be noted, however, that titanium alpha phase is excluded from the "nickel-rich phase" herein, even when the alpha phase contains Ni in a large content of 10 times or more the average Ni content

[0013] The respective titanium alloys according to the present invention may be obtained by performing final annealing at a temperature in the range of 600°C to 725°C after rolling.

[0014] According to the present invention, the conditions for final annealing after rolling of Ti-Ni-Pd-Ru-Cr alloys are suitably controlled, and whereby the titanium alloys are allowed to have (1) a microstructure in which the nickel-rich phases are aligned along a rolling direction to form a row, and a multiplicity of the rows are aligned substantially in parallel in a cross direction; or (2) a microstructure in which the nickel-rich phases mainly contain Ti_2Ni. The resulting titanium alloys excel in intergranular corrosion resistance in specific environments and are thereby very useful as materials typically for apparatuses to be used in such environments which are believed to cause intergranular corrosion.

FIG. 1 depicts photographs illustrating results of electron probe microanalysis (EPMA) mapping of Ni in L-direction (longitudinal direction; rolling direction) sectional structures of titanium alloys obtained through final annealing at different temperatures;

FIGS. 2A, 2B, and 2C depict scanning electron micrographs (SEMs) illustrating how are corrosion forms of the titanium alloys obtained through final annealing at different temperatures;

FIGS. 3A, 3B, 3C, and 3D depict scanning electron micrographs illustrating how are corrosion forms of other exemplary titanium alloys obtained through final annealing at different temperatures;

FIG. 4 depicts results of EPMA mapping of Ni and Cr in L-direction sectional structures of titanium alloys obtained through final annealing at different temperatures;

FIG. 5 depicts photographs illustrating secondary electron images (SEM images) and results of mapping of a specimen; and

FIGS. 6A and 6B depict photographs illustrating exemplary results in observation of a specimen under a transmission electron microscope (TEM).

[0015] Ti-Ni-Pd-Ru-Cr alloys to which the present invention is applied are used as materials for various apparatuses in the chemical industry and for heat exchangers. They are generally in the form of hot-rolled plates or cold-rolled plates. These rolled plates are subjected to final annealing to give products. In laboratory scale, the annealing of titanium may be performed as vacuum annealing in a vacuum atmosphere or an atmosphere obtained through evacuation and argon (Ar) purge, without subsequent acid wash. However, in industrial scale where productivity is weighed, the annealing is generally performed as continuous annealing in an air atmosphere, followed by acid wash. The final annealing is generally performed at a relatively high temperature (final annealing temperature) of about 750°C to 800°C, for obtaining satisfactory formability.

[0016] The present inventors made various investigations to improve intergranular corrosion resistance of Ti-Ni-Pd-Ru-Cr alloys and, as a result, have found that titanium alloys manufactured through final annealing at a temperature in the range of 600°C to 725°C have distinct microstructures.

[0017] Specifically, the present inventors have found that the titanium alloys manufactured through final annealing at a temperature in the above-specified range include nickel-rich phases, each nickel-rich phase being a phase (other than titanium alpha phase) locally containing Ni in a content of 10 times or more the average Ni content of the titanium alloy and have (1) a microstructure in which the nickel-rich phases are aligned along the rolling direction to form a row, and a multiplicity of the rows are aligned substantially in parallel in the cross direction; or (2) a microstructure in which the nickel-rich phases contain Ti_2Ni. The present inventors have also found that the titanium alloys having these microstructures may exhibit satisfactory intergranular corrosion resistance even in specific corrosive environments where customary titanium alloys suffer from intergranular corrosion. The present invention has been made based on these findings.

[0018] Of the microstructures of the titanium alloys according to the present invention, the microstructure in which the nickel-rich phases are aligned along the rolling direction to form a row, and a multiplicity of the rows are aligned substantially in parallel in a cross direction may be verified by the mapping of the cross section in the rolling direction (cross section in the L direction) with an electron probe microanalyzer (EPMA).

[0019] The "nickel-rich phase" being a phase (other than titanium alpha phase) locally containing Ni in a content of 10 times or more the average Ni content, and the microstructure containing Ti_2Ni may be verified by observation under a transmission electron microscope (TEM) or electron diffraction analysis of the crystal structure.

[0020] FIG. 1 depicts the results of EPMA mapping ofL direction sectional structures of JIS Type 14 cold-rolled plates (Ti-0.4Ni-0.015Pd-0.025Ru-0.14Cr alloys) manufactured through final annealing at different temperatures. The other conditions will be described in Experimental Examples later. In FIG.1, whitish areas indicate the presence of nickel-rich phases. The results demonstrate that rolled plates manufactured through final annealing at temperatures of 650°C and 725°C, respectively, include nickel-rich phases, in which a multiplicity of rows of the nickel-rich phases are aligned substantially in parallel in the cross direction.

[0021] The results also demonstrate that a rolled plate manufactured through final annealing at a temperature of 750°C includes nickel-rich phases which are somewhat aligned in a row, but includes not so many rows of nickel-rich phases as in the cold-rolled plates manufactured at final annealing temperatures of 650°C and 725°C; and that cold-rolled plates manufactured through final annealing at temperatures of 800°C and 830°C include nickel-rich phases, but the nickel-rich phases do not substantially form rows.

[0022] The titanium alloys according to the present invention, when manufactured through final annealing at a temperature of 725°C or lower, include at least one of the above microstructures and thereby show good intergranular corrosion resistance. The lower limit of the final annealing temperature is preferably 600°C, because titanium alloys, if manufactured through final annealing at a temperature of lower than 600°C, may undergo insufficient recrystallization and may thereby fail to have minimum required formability, although they have good intergranular corrosion resistance. The atmosphere in the final annealing is generally air atmosphere, but it is naturally understood that the atmosphere may be a vacuum atmosphere or an atmosphere which is obtained by evacuation and subsequent argon purge. The time or duration for final annealing (the time for which the article is exposed to the annealing temperature) is about 1 to 10 minutes in the case of continuous annealing (and acid wash) in an air atmosphere. It generally takes about 1 to 8 hours to attain uniform heating of the entire coil (plate) in the case of vacuum annealing.

[0023] The chemical compositions of the titanium alloys according to the present invention are basically in accordance with public specification values, and the microstructures of them are controlled based on the premise that they have these chemical compositions. Reasons why the respective contents of the compositions are specified are as follows.

[Ni in a content of 0.35% to 0.55%]

[0024] Nickel (Ni) element is relatively inexpensive as compared to Pd and, when contained in a content of 0.35% or more, is effective to impart corrosion resistance (corrosion resistance in a non-oxidizing environment in an atmosphere at high temperature and at a high concentration) to the titanium alloys even when Pd is contained in a lower content. However, Ni, if present in a content of more than 0.55%, may cause the titanium alloys to have poor workability. The lower limit of the Ni content is preferably 0.40% or more, and more preferably 0.45% or more, from the viewpoint of corrosion resistance.

[Pd in a content of 0.01% to 0.02%]

[0025] Palladium (Pd) element is a noble metal element added for improving basic corrosion resistance of the titanium alloys and is contained in a relatively small content due to synergistic effects with other elements. To exhibit the effects, Pd should be contained in a content of 0.01% or more. However, Pd, if present in an excessively high content of more than 0.02%, causes higher material cost, thus being undesirable. The lower limit of the Pd content is preferably 0.012% or more, and more preferably 0.015% or more, from the viewpoint of corrosion resistance.

[Ru in a content of 0.02% to 0.04%]

[0026] Ruthenium (Ru) element is, as with Ni, relatively inexpensive as compared to Pd and, when contained in a content of 0.02% or more, is effective to impart corrosion resistance (corrosion resistance in a non-oxidizing environment in an atmosphere at high temperature and at a high concentration) to the titanium alloys even when Pd is contained in a lower content However, Ru, if present in a content of more than 0.04%, causes excessively high material cost, thus being undesirable. The lower limit of the Ru content is preferably 0.025% or more, and more preferably 0.03% or more, from the viewpoint of corrosion resistance.

[Cr in a content of 0.1% to 0.2%]

[0027] Chromium (Cr) element contributes to improvements of corrosion resistance and crevice corrosion resistance of titanium alloys without adversely affecting the workability. By using in combination with the above-mentioned elements, Cr further improves the corrosion resistance of titanium alloys. To exhibit these effects, Cr should be contained in a content of 0.1% or more. However, the Cr content should be 0.2% or less, because Cr, if contained in excess, may adversely affect the workability. The lower limit of the Cr content is preferably 0.12% or more, and more preferably 0.15% or more, from the viewpoint of corrosion resistance.

[0028] The titanium alloys according to the present invention contain the above components with the remainder including titanium and inevitable impurities. As used herein the "inevitable impurities" refer to impurity elements inevitably contained in raw material titanium sponges. Representative examples thereof include oxygen, iron, carbon, nitrogen, hydrogen, chromium, and nickel Examples of inevitable impurities further include elements which may be incorporated into products during production process, such as hydrogen.

[0029] In this connection, amounts of elements such as oxygen, iron, nitrogen, carbon, chromium, and nickel may be intentionally controlled for controlling the strength level of titanium alloys. These elements, whose amounts are controlled for this purpose, are also included in the "inevitable impurities" herein. Contents of these inevitable impurities are approximately as follows. It should be noted, however, that the titanium alloys according to the present invention are intentionally added with, of these impurities, chromium (Cr) and nickel (Ni) in specific contents, and that their contents are total contents including the amounts of such inevitable impurities mentioned below.

Oxygen: 100 to 3000 parts by mass per million (hereinafter such contents of inevitable impurities will be simply expressed in "ppm")
Iron: 100 to 3000 ppm
Nitrogen: up to 500 ppm
Carbon: up to 800 ppm
Hydrogen: up to 150 ppm
Chromium: 10 to 300 ppm
Nickel: 10 to 300 ppm

[0030] Although the mechanism remains partially unknown, the titanium alloys according to the present invention have improved intergranular corrosion resistance by having the above-mentioned microstructures, probably because the coexistence of Ni and Cr, main added elements of the titanium alloys, affects the intergranular corrosion resistance in some manner or other.

[0031] Regular corrosion (general corrosion) of titanium alloys is known to occur according to a mechanism through the following reactions. Specifically, on the free surface of the titanium alloys, there simultaneously occur an anodic reaction represented by following Formula (1) (metal dissolving reaction) and a cathodic reaction represented by following Formula (2) (reduction reaction of dissolved oxygen in the presence of the dissolved oxygen; or reduction reaction of hydrogen ion in an acidic solution):

$$Ti \rightarrow Ti^{3+} + 3e^- \qquad (1)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (2)$$

[0032] Independently, in the case of a crevice structure, the anodic reaction and the cathodic reaction occur simultaneously inside and outside of the crevice at early stages, but dissolved oxygen or hydrogen ion is hardly fed into the crevice from the outside of the crevice, and this causes a difference in concentration of oxidizing agent between inside and outside of the crevice. Accordingly, an oxidizing-agent concentration cell is formed between the inside and outside of the crevice, in which the anodic reaction occurs inside the crevice and the cathodic reaction occurs outside the crevice. Inside the crevice, the H^+ concentration increases due to the anodic reaction, and the pH decreases. In addition, for satisfying electroneutrality with respect to H^+ ion, anions such as Cl^- migrate from the outside of the crevice to form a high-concentration hydrochloric acid. This impedes the maintenance of passive state to lead to active dissolution, namely, crevice corrosion.

[0033] As is described above, the anodic reaction and cathodic reaction are involved in general corrosion and crevice corrosion of titanium alloys. However, the grain boundary segregation of impurities and alloy elements may be probably involved in corrosion principle of intergranular corrosion. It is considered that, in the titanium alloys according to the present invention underwent annealing at relatively low temperatures, nickel-rich phases remain in the specific forms and are thus prevented from segregation at grain boundaries.

[0034] The present invention will be illustrated in further detail with reference to several working examples below. It should be noted, however, that these examples are never intended to limit the scope of the present invention; various changes and modifications may be made without departing from the scope and spirit of the invention, and it is intended in the appended claims to cover all such changes and modifications as fall within the true spirit and scope of the invention.

EXPERIMENTAL EXAMPLE 1

[0035] A commercially available Ti-Ni-Pd-Ru-Cr alloy, i.e., JIS Type 14 cold-rolled annealed plate (Ti-0.4Ni-0.015Pd-0.025R.u-0.14Cr alloy) was subjected to cold rolling at a rolling reduction of 40% to a plate thickness of 1.1 mm, the resulting plate was divided in small necessary quantities, subjected sequentially to the following air annealing (final annealing), salt immersion, and acid wash treatments simulating continuous annealing and acid wash processes, and thereby yielded corrosion specimens.

[Air Annealing]

[0036]

Temperature: 670°C, 700°C, 725°C, 750°C, 775°C, 800°C, and 830°C
Annealing Time: 165 seconds
Salt Immersion: immersion in a commercially available salt for descaling of titanium (trade name: "Kolene DGS" supplied by Nihon Parkerizing Co., Ltd.) heated at about 500°C for one minute
Acid Wash: acid wash with nitric hydrofluoric acid by a thickness of about 0.1 mm

[0037] The manufactured corrosion specimens were subjected to corrosion tests under the following conditions, and corrosion resistance of the specimens was determined. The test conditions simulate such a severe use environment that Ti-Ni-Pd-Ru-Cr alloys to which the present invention is applied do not maintain their passive state.

[Corrosion Test Conditions]

[0038] Each of the specimens was immersed in a boiling 10% hydrochloric acid for 24 hours, and a corrosion rate per year (mm/year) was calculated based on the area of the specimen before test, and the change in mass between before and after test. The results are shown as the relation between the final annealing temperature and the corrosion rate in Table 1 below.

TABLE 1

Test No.	Final annealing temperature (°C)	Corrosion rate (mm/year)
1	670	7.04
2	700	8.19
3	725	7.94
4	750	6.67
5	775	9.23
6	800	6.93
7	830	8.90

[0039] The surfaces of the specimens after the test were observed under a scanning electron microscope (SEM), and whether intergranular corrosion was present or not was determined. The corrosion forms of the specimens are shown in FIGS. 2A, 2B, 2C, 3A, 3B, 3C, and 3D (photographs). Of the photographs, FIG. 2A depicts one obtained at an annealing temperature of 670°C, FIG. 2B depicts one obtained at an annealing temperature of 700°C, FIG. 2C depicts one obtained at an annealing temperature of 725°C, FIG. 3A depicts one obtained at an annealing temperature of 750°C, FIG. 3B depicts one obtained at an annealing temperature of 775°C, FIG. 3C depicts one obtained at an annealing temperature of 800°C, and FIG. 3D depicts one obtained at an annealing temperature of 830°C, respectively.

[0040] These results demonstrate that the final annealing temperature does not so affect the corrosion rate but significantly affects the corrosion form. Specifically, the specimens prepared at final annealing temperatures of 725°C or lower underwent corrosion predominantly in the form of general corrosion [FIGS. 2A, 2B, and 2C]; but the specimens prepared at final annealing temperatures of 750°C or higher underwent corrosion in the form of intergranular corrosion. This demonstrates that the proceeding of intergranular corrosion may be effectively prevented by performing final annealing at a temperature of 725°C or lower. In this experimental example, the lower limit of the final annealing temperature was set to be 670°C. However, it was verified that intergranular corrosion does not occur even when final annealing is performed at a temperature equal to or lower than this temperature.

[0041] FIG. 4 depicts results of EPMA mapping ofNi and Cr in cross section (L direction cross section) of the specimens used in the corrosion tests (also see FIG. 1 regarding the Ni mapping of specimens prepared at annealing temperatures of 650°C to 830°C). The results demonstrate that the titanium alloys containing both Ni and Cr include Ni and Cr which are distributed in coexistence; and that the specimens prepared through final annealing at temperatures of 750°C or higher include Ni and Cr which are distributed in remarkable coexistence (namely, Ni and Cr are distributed in the same manner). This indicates that the coexistence of Ni and Cr adversely affects intergranular corrosion resistance.

EXPERIMENTAL EXAMPLE 2

[0042] Secondary electron images (SEM images) and results of mapping of a corrosion specimen (annealed at a final annealing temperature of 700°C) manufactured by the procedure of Experimental Example 1 are shown in FIG. 5 (photographs). White precipitation areas in the SEM images are present at positions substantially corresponding to portions with high concentrations of Ni, Cr, and Fe; and, particularly regarding Ni, the difference in concentration between the matrix (alpha phase) and precipitation areas is significant Based on these, the precipitation areas can be said as nickel-rich phases. In contrast, the data demonstrate that Pd and Ru are distributed approximately uniformly.

[0043] Independently, the specimen was subjected to observation under a transmission electron microscope (TEM), and exemplary images in 14-μm square fields of view are shown in FIGS. 6A and 6B (photographs). Precipitates with a size of 0.2 μm or more are circled in the TEM images, and by spot-spectrometry of these precipitates in TEM, the Ni content may be measured. FIG. 6A depicts an image where the nickel-rich phase is Ti_2Ni; and FIG. 6B depicts an image where the nickel-rich phase is the beta phase.

[0044] In the sample given in FIGS. 6A and 6B, the raw-material ingot for the samples had Ni contents of 0.49% and 0.43% at the top and the bottom, respectively. Accordingly, the matrix (base metal) had an average Ni content of 0.46%.

[0045] Whether the precipitates are nickel-rich phases or not could be determined by the Ni contents of the precipitates determined through spot spectrometry. It should be noted that "nickel-rich phases" defined in the present invention are phases each having a Ni content of 10 times or more the average Ni content of the matrix. In this connection, the mapping indicated that most of the precipitates are nickel-rich phases.

[0046] In addition, whether the precipitates are Ti_2Ni or the beta phase can be determined by applying electron beams to each of the precipitates, and analyzing the crystal structures of the precipitates through electron diffraction analysis. Exemplary results of the analysis of nickel-rich phases are also illustrated in FIGS. 6A and 6B.

[0047] In the above manner, specimens were manufactured through final annealing (in the air) at different temperatures of 650°C, 700°C, 725°C, 750°C, 800°C, and 830°C, and the forms or phases (Ti_2Ni or beta phase) of precipitates were examined. The results are shown in Table 2 below.

TABLE 2

Test No.	**Final annealing temperature (°C)**	**Ti_2Ni**
8	650	present
9	700	present
10	725	present
11	750	absent
12	800	absent
13	830	absent

[0048] The results demonstrate that specimens prepared through final annealing at temperatures of 650°C, 700°C, and 725°C included Ti_2Ni in nickel-rich phases; but other specimens prepared through final annealing at temperatures of 750°C, 800°C, and 830°C did not include Ti_2Ni but included the beta phase alone in nickel-rich phases. In consideration also of the results given in Table 1, the intergranular corrosion can be suppressed by allowing nickel-rich phases to contain Ti_2Ni.

Claims

1. A titanium alloy comprising:

nickel (Ni) in a content of 0.35 to 0.55 percent by mass (hereinafter contents will be simply expressed in "%");
palladium (Pd) in a content of 0.01% to 0.02%;
ruthenium (Ru) in a content of 0.02% to 0.04%; and
chromium (Cr) in a content of 0.1% to 0.2%,
with the remainder including titanium and inevitable impurities,
wherein the titanium alloy includes nickel-rich phases, each nickel-rich phase being a phase (other than titanium alpha phase) locally containing Ni in a content of 10 times or more the average Ni content of the titanium alloy, wherein the nickel-rich phases are aligned along a rolling direction to form a row, and wherein a multiplicity of the rows are aligned substantially in parallel in a cross direction.

2. A titanium alloy comprising:

Ni in a content of 0.35% to 0.55%;

Pd in a content of 0.01% to 0.02%;
Ru in a content of 0.02% to 0.04%; and
Cr in a oontent of 0.1% to 0.2%,
with the remainder including titanium and inevitable impurities,
wherein the titanium alloy includes one or more nickel-rich phases, each nickel-rich phase being a phase (other than titanium alpha phase) locally containing Ni in a content of 10 times or more the average Ni content of the titanium alloy, and wherein the nickel-rich phases contain Ti_2Ni.

3. The titanium alloy according to one of claims 1 and 2, which is obtained by performing final annealing at a temperature in the range of 600°C to 725°C after rolling.

FIG.1

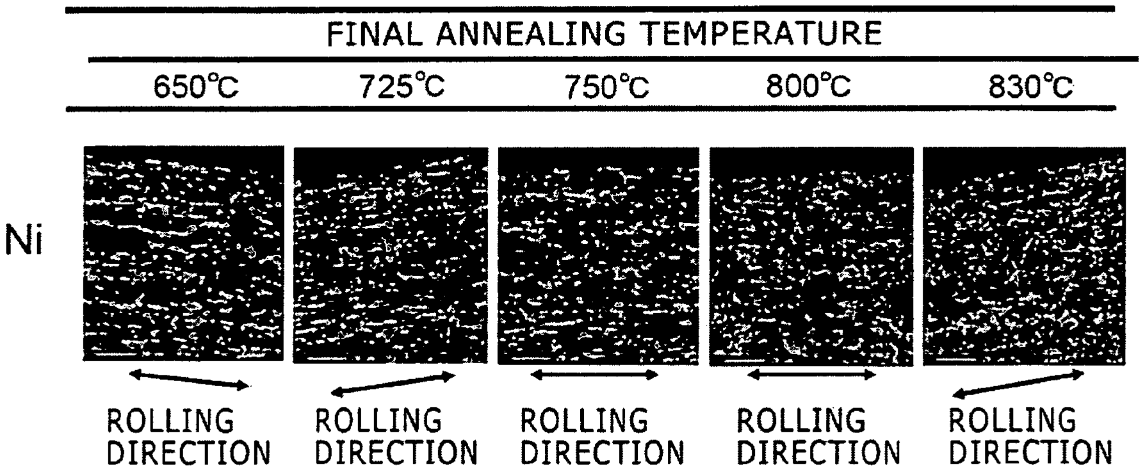

FINAL ANNEALING TEMPERATURE
650℃
725℃
750℃
800℃
830℃
Ni
ROLLING DIRECTION
ROLLING DIRECTION
ROLLING DIRECTION
ROLLING DIRECTION
ROLLING DIRECTION

FIG.2A

FIG.2B

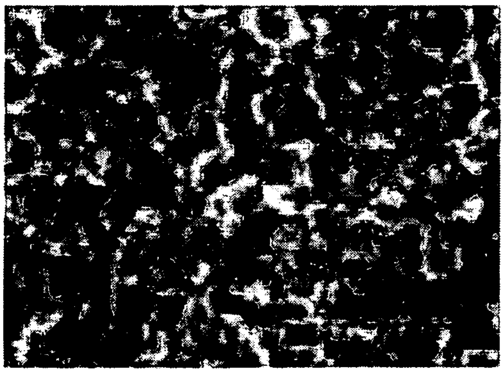


FIG.2C

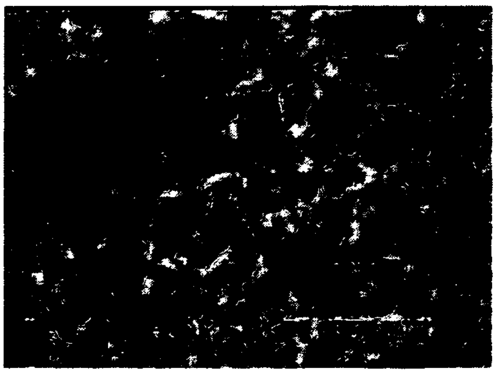


FIG.3A

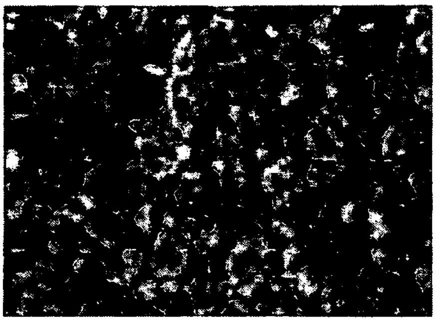


FIG.3B

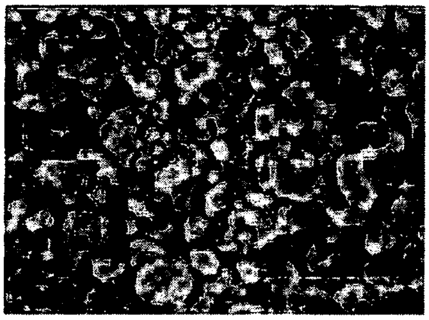


FIG.3C

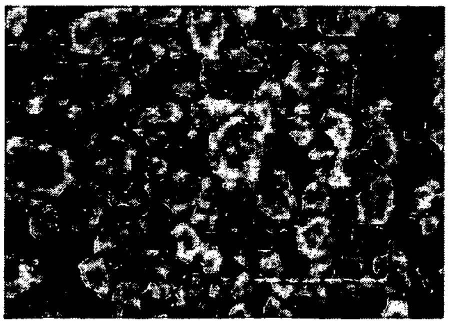


FIG.3D

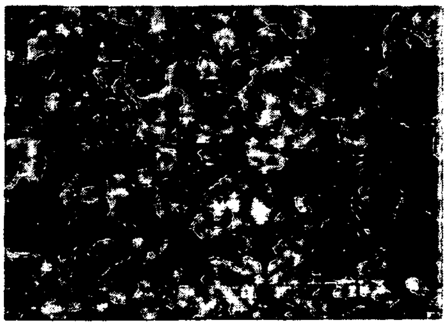


FIG.4

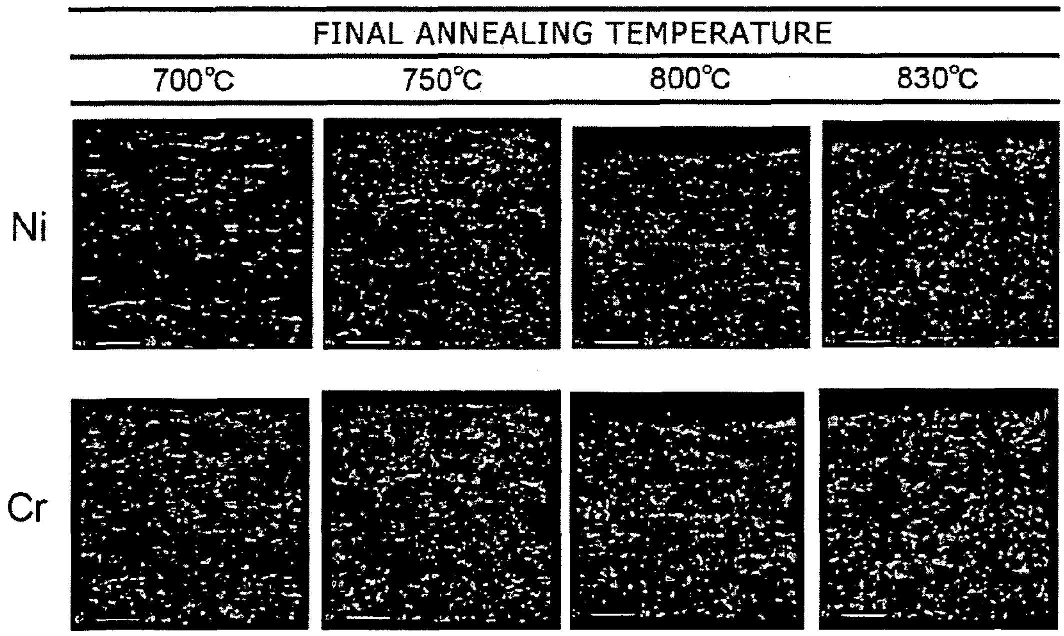


FIG.5

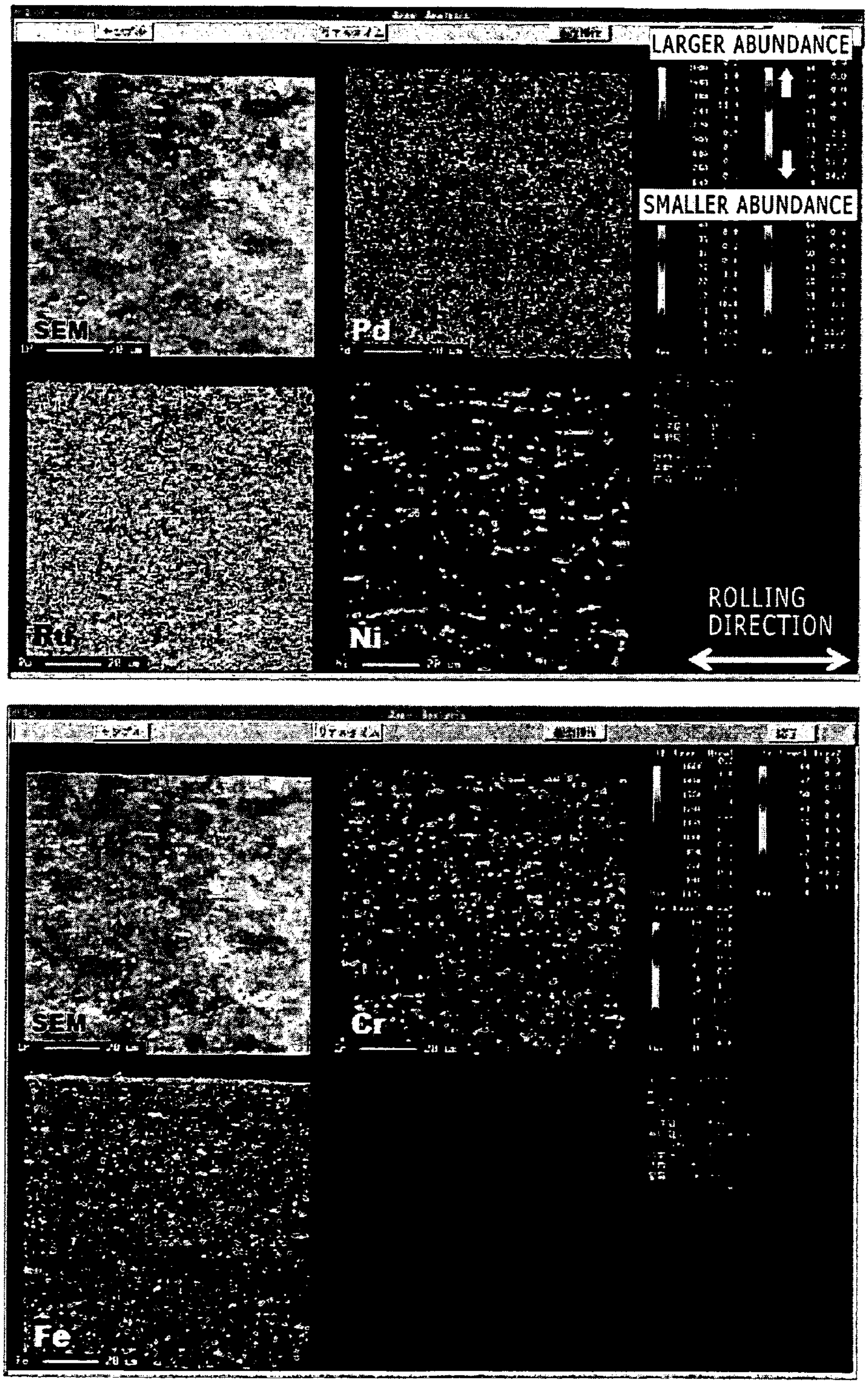

LARGER ABUNDANCE
SMALLER ABUNDANCE
SEM
Pd
Rh
Ni
ROLLING
DIRECTION
SEM
Cr
Fe

FIG.6A

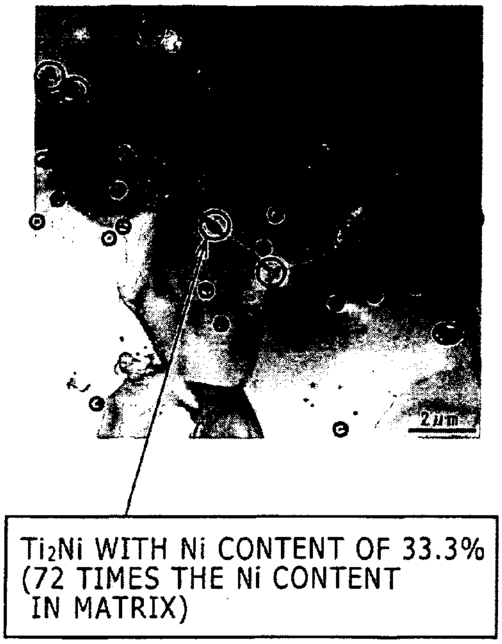
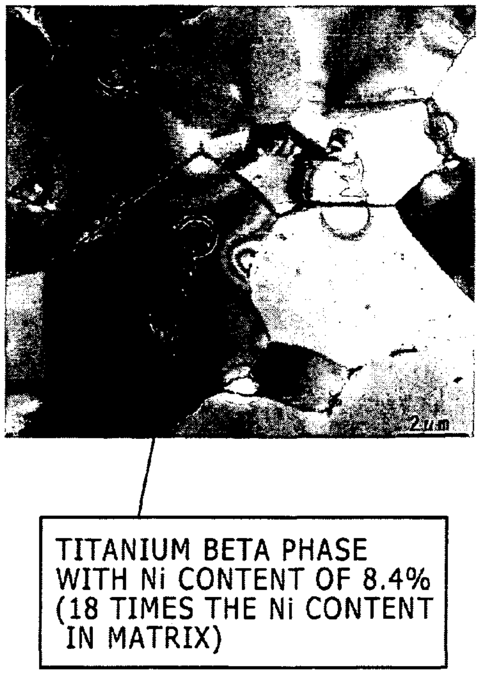

2μm
Ti2Ni WITH Ni CONTENT OF 33.3%
(72 TIMES THE Ni CONTENT
IN MATRIX)

FIG.6B


2μm
TITANIUM BETA PHASE
WITH Ni CONTENT OF 8.4%
(18 TIMES THE Ni CONTENT
IN MATRIX)

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EUROPEAN SEARCH REPORT

Application Number
EP 11 00 5263

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	Schutz ET AL: "COMPARATIVE CORROSION RESISTANCE OF Ru- AND Pd-MODIFIED C.P. TITANIUM ALLOYS", , 1 September 2001 (2001-09-01), pages 245-253, XP55006432, Retrieved from the Internet: URL:http://www.twca.com/pdf/2k1ConfProc/2001025.pdf [retrieved on 2011-09-07] * page 246 * * page 249 * -----	1-3	INV. C22C14/00 C22F1/18
A	Yashiki et al: "Corosion Resistance and Mechanical Properties of Ti-Ni-Pd-Ru-Cr Alloy" In: P.A. Blenkinsop, W.J. Evans and H.M. Flower: "Titanium '95 Science and Technology - proccedings of the 8th world conference on titanium", 22 October 1995 (1995-10-22), Institute of Materials, UK, XP000002658370, vol. 2, pages 1871-1878, * the whole document * -----	1-3	
			TECHNICAL FIELDS SEARCHED (IPC)
			C22C C22F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	7 September 2011	Brown, Andrew

CATEGORY OF CITED DOCUMENTS

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Patent documents cited in the description

- JP H0457735 B **[0004]**
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Non-patent literature cited in the description

- *Tetsu-to-Hagane,* 1994, vol. 80 (4), 353-358 **[0006]**