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(54) PURE TITANIUM SHEET HAVING EXCELLENT BALANCE BETWEEN PRESS FORMABILITY AND STRENGTH AND EXCELLENT CORROSION RESISTANCE, AND PROCESS FOR MANUFACTURING SAME

(57) Disclosed is a pure titanium sheet including 0.02% to 0.10% of Fe and 0.04% to 0.20% of O, with the balance being titanium and inevitable impurities. The Fe and O contents satisfy a condition specified by Expression (1). Regions having Schmidt factors of {11-22}<11-23> twins of 0.45 or more are present in an area percentage of 43% or more, which Schmidt factors of the twins are determined at a depth of one-fourth the gage of the pure titanium sheet with a rolling direction as an axis. The pure titanium sheet has a beta phase volume fraction of 0.3% or less. Expression (1) is expressed as follows:

$$[\text{Oxygen content (in mass percent)}]+0.12\times[\text{Iron content (in mass percent)}]\geq 0.050 \quad (1)$$

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Description

Technical Field

[0001] The present invention relates to a pure titanium sheet and a manufacturing method therefor, which pure titanium sheet is excellent in balance between press formability and strength at room temperature and in corrosion resistance. Specifically, the present invention relates to a pure titanium sheet and a manufacturing method therefor, which pure titanium sheet has, even at room temperature, a strength (tensile strength) of 343 MPa or more and exhibits press formability and crevice corrosion resistance both at satisfactory levels. The present invention also relates to a method for manufacturing a heat-exchanging member for a plate type heat exchanger through press forming of the pure titanium sheet.

Background Art

[0002] Titanium has corrosion resistance, press formability, specific strength, and lightness in weight at satisfactory levels and, with the help of these properties, are widely used in various fields and applications such as aircraft parts, chemical plant members, coast structural materials (particularly bay-coast structural materials whose corrosion is accelerated by the contact with seawater), automobiles, and building materials.

[0003] Titanium, even though rated as being lightweight and strong, requires a further higher strength. This is because further reduction in environmental load and energy consumption has been recently required in various fields, and titanium materials for use in such applications should have a further lighter weight and a smaller wall thickness. In addition, titanium requires further better formability. This is because titanium is also used in or as bodies typically of cellular phones, mobile personal computers, and cameras; eyeglass frames; plate type heat exchanger components; fuel cell separators; household electric appliance exterior trim parts; and transportation equipment members.

[0004] Pure titanium sheets heavily used in these applications are prescribed in Japanese Industrial Standard (JIS) H4600 and are categorized typically into JIS Grade 1, Grade 2, and Grade 3 by the contents of impurities such as iron (Fe) and oxygen (O), and by the strength. With an increasing grade number, a pure titanium sheet has an increasing minimum strength, and different grades of pure titanium sheets are used in accordance with purposes.

[0005] JIS Grade 1 pure titanium sheets have been used in members requiring high formability, because such pure titanium sheets typically of JIS Grade 1, which have low iron and oxygen contents, have high ductility although having a low strength.

[0006] Typically, one of applications in which pure titanium sheets are mostly used is a plate type heat exchanger (PHE). Pure titanium sheets to be adopted to this application are generally subjected to cold press forming (anisotropic bulging) into a complicated corrugated shape so as to have a larger heat exchange effective area in order to improve heat exchanger effectiveness. Specifically, they are exposed to a press forming environment which is extremely severe for the materials. A pure titanium of JIS Grade 1, which is soft and most easily formable among the grades, is used in pure titanium sheets to be used under such severe press forming conditions.

[0007] However, such pure titanium sheets require further higher strengths and more excellent formability, because improvements in heat exchanger effectiveness of a heat exchanger are performed not only based on the shape of the heat exchanger itself but also based typically on increase in flow rate of a heat medium (or cooling medium), and this requires higher pressure tightness of the pure titanium sheets.

[0008] Pure titanium sheets of JIS Grade 2 and Grade 3 having high iron and oxygen contents are used as pure titanium sheets having high strengths. According to customary techniques, however, a high strength and satisfactory formability are incompatible, because such pure titanium sheets have poorer formability with increasing iron and oxygen contents, although having higher strengths. In addition, titanium products having some manufacturing histories may disadvantageously suffer from crevice corrosion typically when used in hot and humid surroundings which readily cause corrosion.

[0009] As techniques for improving press formability of pure titanium sheets, Patent Literature (PTL) 1 proposes a technique of controlling titanium microstructure; and PTL 2 proposes a technique of alloying titanium. These techniques, however, are intended to improve the formability of a pure titanium having a strength (yield strength) corresponding to JIS Grade 1 and fail to improve the formability when applied to pure titanium sheets of higher strength levels.

[0010] PTL 3 proposes a technique of adjusting iron and oxygen contents and controlling titanium grain size so as to improve the press formability of a pure titanium sheet having a strength at high level. Mere control of iron and oxygen contents and titanium grain size, however, hardly provides good balance between press formability and strength.

[0011] Such pure titanium sheets have been applied to wider and wider applications as described above. When used in corrosive environments, the pure titanium sheets require further better crevice corrosion resistance.

[0012] PTL 4 discloses a technique of depositing a platinum-group element on a pure titanium sheet surface so as to allow the titanium sheet to have better crevice corrosion resistance. This technique, however, is difficult to be generally used because the platinum-group element is disadvantageously expensive and causes higher manufacturing cost.

[0013] PTL 5 discloses a titanium alloy sheet further containing Cu, Ni, and Mo as a technique for improving the balance between strength and press formability. This technique, however, is unsuitable for industrial-scale production, because the addition of alloy elements causes inferior productivity. In addition, this literature lacks specific disclosure about corrosion resistance.

[0014] As has been described above, there has not yet been provided a pure titanium sheet that has excellent balance between press formability and strength at room temperature and exhibits satisfactory crevice corrosion resistance.

Citation List

Patent Literature

[0015]

PTL 1: Japanese Unexamined Patent Application Publication (JP-A) No. 2004-285457
PTL 2: JP-A No. 2002-317234
PTL 3: JP-A No. 2009-228092
PTL 4: Japanese Examined Patent Application Publication (JP-B) No. S49-31610
PTL 5: JP-A No. 2010-236067

Summary of Invention

Technical Problem

[0016] The present invention has been made in consideration of the problems in customary techniques, and an object thereof is to provide a pure titanium sheet and a manufacturing method therefor, which pure titanium sheet has excellent balance between press formability and strength and exhibits satisfactory corrosion resistance (crevice corrosion resistance). Specifically, the object of the present invention is to provide a pure titanium sheet and a manufacturing method therefor, which pure titanium sheet has a tensile strength of 343 MPa or more at room temperature, has excellent press formability (ductility in anisotropic bulging and in isotropic bulging), and also exhibits satisfactory crevice corrosion resistance.

Solution to Problem

[0017] The present invention can achieve the object and provides a pure titanium sheet which has excellent balance between press formability and strength and excellent corrosion resistance. The pure titanium sheet contains iron (Fe) in a content of from 0.02% to 0.10%; and oxygen (O) in a content of from 0.04% to 0.20%, in mass percent, with the balance being titanium and inevitable impurities; in which the iron and oxygen contents satisfy a condition specified by Expression (1); regions are present in an area percentage of 43% or more, the regions having Schmidt factors of {11-22} <11-23> twins of 0.45 or more, the Schmidt factors of the twins determined at a depth of one-fourth the gage of the pure titanium sheet with a rolling direction as an axis; and the pure titanium sheet has a beta phase volume fraction of 0.3% or less, Expression (1) expressed as follows:

$$[\text{Oxygen content (in mass percent)}] + 0.12 \times [\text{Iron content (in mass percent)}] \geq 0.050 \quad (1)$$

[0018] The pure titanium sheet which has excellent balance between press formability and strength and excellent corrosion resistance may be desirably manufactured by a method which includes the steps of hot rolling, process annealing, cold rolling, and final annealing and further includes the step of descaling pure titanium sheet surface after the step of process annealing, in which the step of cold rolling is performed to a rolling reduction of 70% or more after the step of descaling; and the step of final annealing is performed, after the step of cold rolling, in such conditions as to allow a value H as specified by Expression (2) to be positive, Expression (2) expressed as follows:

[0019] [Math.1]

$$H = \frac{1}{B \cdot X_0}\left(1 - \frac{T}{A}\right) - t^n \cdots (2)$$

wherein:

- T represents a heating temperature (°C) in the final annealing;
- t represents an annealing time (second) in the final annealing,
- X_0 represents an iron content (in mass percent) in the pure titanium sheet;
- A is 891;
- B is 0.428; and
- n is 0.135.

[0020] The pure titanium sheet can also be obtained by another manufacturing method. This manufacturing method includes the steps of hot rolling; cold rolling; and final annealing and further includes the step of descaling pure titanium sheet surface after the step of hot rolling without performing process annealing, in which the step of cold rolling is performed to a rolling reduction of 20% or more after the step of descaling; and the step of final annealing is performed, after the step of cold rolling, in such conditions as to allow a value H as specified by Expression (2) to be positive, Expression (2) expressed as follows:

[0021] [Math. 2]

$$H = \frac{1}{B \cdot X_0}\left(1 - \frac{T}{A}\right) - t^n \cdots (2)$$

wherein:

- T represents a heating temperature (°C) in the final annealing;
- t represents an annealing time (second) in the final annealing;
- X_0 represents an iron content (in mass percent) in the pure titanium sheet;
- A is 891;
- B is 0.428; and
- n is 0.135.

Advantageous Effects of Invention

[0022] The present invention strictly specifies a chemical composition in consideration among respective elements and specifies the Schmidt factors of specific twins and the beta phase in a pure titanium sheet to specific percentages. The present invention can thereby give a pure titanium sheet which not only has a high tensile strength even at room temperature, but also exhibits press formability and crevice corrosion resistance at satisfactory levels. The pure titanium sheet can exhibit good processability/formability and have further better corrosion resistance even when a high strength at room temperature is required in wide variety of fields as mentioned above.

[0023] In addition, the present invention enables inexpensive manufacturing of the pure titanium sheet.

Brief Description of Drawings

[0024]

[Fig. 1] Fig.1 is a perspective view illustrating a titanium sheet for use in a plate type heat exchanger (PHE).

[Fig. 2] Figs. 2(a) and 2(b) are a plan view and a schematic cross-sectional view along the line F-F in Fig. 2(a), respectively, of a press forming die to illustrate how to evaluate the press formability.

Description of Embodiments

[0025] It is known that a pure titanium sheet has better press formability with increasing susceptibility to twin deformation (plastic deformation by twinning), because not only slip deformation, but also twin deformation significantly contribute to the material deformation. It is also known that a pure titanium is more susceptible to twin deformation and has better press formability with an increasing softness; but becomes less susceptible to twin deformation and has inferior press formability with an increasing strength

[0026] The present inventors made various investigations on the metal structure (metal microstructure) of a pure titanium sheet to allow the pure titanium sheet to have better press formability while having a strength maintained at a high level (tensile strength of 343 MPa or more) and to exhibit satisfactory crevice corrosion resistance. As a result, they have found as follows.

[0027] Specifically, a pure titanium sheet, when cold-rolled in one direction, undergoes strength anisotropy and has a lower strength in the rolling direction than that in the width direction, because the pure titanium sheet has high ductility in the rolling direction but low ductility in the width direction. When this pure titanium sheet is subjected to press forming, deformation in the rolling direction with a lower strength preferentially proceeds. To improve the press formability, therefore, such structure control as to accelerate the activation of twin deformation is effective because the twin deformation contributes to deformation in the rolling direction acting as a main deformation direction. Specifically, the formation of such a crystal orientation is important as to readily invite twin deformation even at a tensile strength level of 343 MPa or more.

[0028] Based on these, the present inventors made investigations on a Schmidt factor, which affects the easiness in occurrence of twin deformation. As a result, they have found that a pure titanium sheet can have better press formability while maintaining its strength at a high level by controlling, within specific ranges, the Schmidt factors of twin deformation and a distribution percentage (area percentage) thereof, in which the Schmidt factors are determined when a tensile load is applied in the rolling direction in a rolling plane at a depth of one-fourth the gage of the pure titanium sheet. The present invention has been made based on these findings.

[0029] Specifically, main-phase grains in the pure titanium sheet each have a hexagonal crystal structure, of which {11-22}<11-23> twins mainly act upon bulging. To improve the formability with deformation mainly in the rolling direction, activation of {11-22}<11-23> twins upon application of a load in the rolling direction is effective. For this purpose, Schmidt factors of the {11-22}<11-23> twins are effectively increased.

[0030] After further investigations, the present inventors have found that the twins should each have a Schmidt factor of 0.45 or more to facilitate twin deformation activity.

[0031] However, grams each having a Schmidt factor at a specific level or more, if present in an excessively low percentage, do not significantly contribute to better press formability of the entire material titanium, even though facilitating twin deformation activity. To prevent this, regions each having a Schmidt factors of 0.45 or more should be present in an area percentage of 43% or more, and preferably 45% or more, of the entire area. The specific regions, when present in an area percentage of 43% or more, help the pure titanium sheet to have significantly excellent press formability while having a strength maintained at a level of 343 MPa or more. An upper limit of the area percentage is not critical.

[0032] Miller indices indicate crystal planes, in which negative integers (negative indices) are generally written with an upper bar. Such negative Miller indices, however, are written herein with a "-" (minus) sign for the sake of convenience. For example, the index "-2" in {11-22} represents a negative index.

[0033] As is described above, the present invention employs the Schmidt factor as an index for better press formability. The magnitude of a critical resolved shear stress (τ) necessary for dislocation migration along a specific crystal plane is known to vary generally depending on the crystal plane and crystal orientation and is given by the expression: $\tau=\sigma\cos\varphi\cos\lambda$ wherein σ represents a tensile stress in a tension axis direction; φ represents an angle formed between the slip plane normal line and the tension axis; and λ represents an angle formed between the slip direction and the tension axis.

[0034] The [$\cos\varphi\cos\lambda$] in the expression is called a "Schmidt factor" and indicates the percentage of force to be utilized to move the dislocation based on the total of external force applied in the tension axis. A metal sheet (titanium sheet), when including slip/twin systems having high Schmidt factors, readily plastically deforms, because the slip/twin systems having high Schmidt factors act at smaller external force when the external force is applied to the titanium sheet. A pure titanium sheet satisfying the conditions in Schmidt factor, when a tensile load is applied in the rolling direction, undergoes accelerated twin deformation and can have significantly better press formability (particularly anisotropic-bulging formability) with the rolling direction as a main strain direction.

[0035] Such a pure titanium sheet is known to generally have a higher strength, to be less susceptible to twin deformation, and to thereby have inferior press formability, with increasing contents of impurity elements. However, the present invention strictly specifies the chemical composition and controls the Schmidt factor so as to readily invite twin deformation as described later, thereby enables activation of twin deformation, and exhibits better press formability even when having high impurity element contents and thereby having a high tensile strength.

[0036] The present inventors have also found that suppression of beta phase precipitation is important for better crevice corrosion resistance, particularly for better crevice corrosion resistance in hot and humid surroundings. In such hot and humid surroundings, crevice corrosion readily occurs. Specifically, titanium for use in the present invention desirably has a metal structure mainly including alpha phase (hexagonal crystal). The pure titanium sheet may have inferior crevice corrosion resistance with a high beta phase (body-centered cubic crystal) volume fraction (volume percentage). To prevent this, the beta phase volume fraction is controlled to 0.3% or less, preferably 0.2% or less, and more preferably 0% in terms of its upper limit.

[0037] In the pure titanium sheet according to the present invention, suitable control of iron Fe and oxygen O is important, because these elements affect the press formability and tensile strength. The contents of the respective elements in the pure titanium sheet according to the present invention are specified for reasons as follows.

Iron (Fe) content: 0.02% to 0.10%

[0038] Iron (Fe) element contributes to higher strength of the pure titanium sheet. To exhibit such effects, the iron content is 0.02% or more, and preferably 0.03% or more. However, iron in an excessively high content may cause the formation of the beta phase in a large amount to impair the crevice corrosion resistance even when annealing conditions are optimized. To prevent this, the iron content is controlled to 0.10% or less, preferably 0.08% or less, and more preferably 0.07% or less.

Oxygen (O) content: 0.04% to 0.20%

[0039] Oxygen (O) element effectively helps the pure titanium sheet to have a strength at certain level. To exhibit such effects, the oxygen content is 0.04% or more, preferably 0.045% or more, more preferably 0.050% or more, and furthermore preferably 0.07% or more. Oxygen in an excessively high content, however, may cause the pure titanium sheet to have an excessively high strength to thereby have inferior press formability contrarily or to suffer from edge cracking or rupture during cold rolling. To prevent this, the oxygen content is controlled to 0.20% or less, preferably 0.18% or less, and more preferably 0.15% or less.

[0040] In addition, the relationship between the iron and oxygen contents is importantly specified in the present invention. This is because iron and oxygen are added herein so as to suppress the beta phase precipitation and to provide better crevice corrosion resistance while maintaining good balance between a higher strength and satisfactory press formability. Specifically, the iron and oxygen contents are controlled within the above-specified ranges so as to satisfy the condition: [Oxygen content (in mass percent)]+0.12×[Iron content (in mass percent)]≥0.050 (Expression (1)). If the left side value derived from the iron and oxygen contents according to Expression (1) is less than 0.050, the pure titanium sheet may have an insufficient strength. For further better effects obtained by the addition of iron and oxygen, the iron and oxygen contents are desirably controlled so that the left hand value of Expression (1) be preferably 0.055 or more, more preferably 0.060 or more, and furthermore preferably 0.080 or more.

[0041] The remainder of the pure titanium sheet according to the present invention other than the above elements is titanium and inevitable impurities. The "inevitable impurities" include impurity elements inevitably contained in the material sponge titanium, which are represented by N, C, H, Si, Cr, and Ni; and elements possibly incorporated into the product during manufacturing process, such as H (hydrogen).

[0042] Of these inevitable impurities, nitrogen (N) element, for example, also contributes to higher strength of the pure titanium sheet. Nitrogen in an excessively high content, however, may adversely affect the cold rolling performance contrarily. To prevent this, the nitrogen content is controlled to preferably 0.02% or less, and more preferably 0.01% or less. In contrast, although the nitrogen content may be controlled to 0%, excessive reduction in the content may cause higher cost contrarily. To prevent this, the nitrogen content is preferably 0.001% or more, and more preferably 0.002% or more.

[0043] Carbon (C) element contributes to higher strength Carbon in an excessively high content, however, may adversely affect the cold rolling performance contrarily. To prevent this, the carbon content is controlled to preferably less than 0.015%, and more preferably 0.012% or less. The carbon content is not critical in its lower limit and may be 0%. However, excessive reduction in the content may cause higher cost contrarily. To prevent this, the carbon content is preferably 0.002% or more, and more preferably 0.003% or more.

[0044] The pure titanium sheet according to the present invention may have a tensile strength of 343 MPa or more at room temperature (25°C). This is because such pure titanium sheet is used in various fields as described above and requires a high strength even at room temperature. The pure titanium sheet according to the present invention preferably has a tensile strength of 370 MPa or more. However, the pure titanium sheet, if having an excessively high tensile strength, may have inferior ductility and thereby have poor press formability. To prevent this, the pure titanium sheet preferably has a tensile strength of 600 MPa or less.

[0045] The strength and the ductility of a pure titanium sheet are trade-off properties as described above. However, the present invention provides, as one capable of having the two properties both at satisfactory levels, a pure titanium sheet having a tensile strength of 343 MPa or more and satisfactory press formability and exhibits excellent crevice corrosion resistance.

[0046] Next, manufacturing conditions will be illustrated below by taking the pure titanium sheet as an example. Typically, the pure titanium sheet is generally manufactured through steps mentioned below. Properties of titanium vary depending on the chemical composition of material titanium and the preset conditions of respective processes. For this reason, the process conditions should be selected and determined as a series of manufacturing processes; whereas strict setting of conditions per each process is not always appropriate.

[0047] The pure titanium sheet is generally manufactured in the following manner. Initially, a titanium ingot controlled to have a specific chemical composition is obtained by casting. The ingot is sequentially subjected to the steps of blooming and forging/rolling [Step I]; hot rolling [Step II]; process annealing [Step III]; cold rolling [Step IV]; and final annealing [Step V]] in this order to give the pure titanium sheet. Where necessary, descaling typically by blasting and/or acid wash treatment may be performed between the respective steps.

[0048] The step of blooming and forging/rolling (Step D is performed according to necessity so as to break a coarse cast structure. In this step, soaking may be performed at a temperature of from about 800°C to about 1100°C before the start of forging or rolling. This is preferred for good productivity (easiness to work).

[0049] In the step of hot rolling [Step II], the work may be held at a temperature of typically from about 700°C to 950°C and then hot-rolled to a desired gage.

[0050] The step of process annealing [Step III] is performed according to necessity. In this step, the work may be soaked at a temperature of typically from about 700°C to 850°C and then air-cooled.

[0051] When the step of process annealing is performed, descaling is performed after the step of process annealing and before the step of cold rolling [Step IV]. The step of cold rolling [Step IV] before final annealing is performed to a rolling reduction of 70% or more, and preferably 80% or more. The cold rolling, as performed to a rolling reduction of 70% or more, allows the subsequent step of final annealing [Step V] to give a pure titanium sheet having excellent press formability while having a tensile strength maintained at 343 MPa or more.

[0052] Specifically, when the pure titanium sheet according to the present invention is manufactured through the step of cold rolling [Step IV] performed to a rolling reduction of 70% or more after the process annealing, the resulting pure titanium sheet can have an area percentage of grains of 43% or more, which grains have Schmidt factors of {11-22} <11-23> twins of 0.45 or more. More specifically, in an embodiment, the step of cold rolling [Step IV] is performed to a rolling reduction of 70% or more after the step of process annealing; and the step of final annealing [Step V] is performed subsequently. The resulting pure titanium sheet can thereby have the desired crystal orientation and exhibit good press formability and a tensile strength maintained at a level of 343 MPa or more.

[0053] The press formability increases with an increasing rolling reduction. However, cold rolling, if performed at an excessively high rolling reduction, may cause the pure titanium sheet to suffer from edge cracking at edges thereof, or to break during the cold rolling, thus adversely affecting the productivity. To prevent this, the rolling reduction is controlled to preferably 95% or less, and more preferably 90% or less.

[0054] In another embodiment, the step of process annealing [Step III] is not performed. In this embodiment, descaling is performed after the step of hot rolling [Step II] and before the step of cold rolling [Step IV]. The step of cold rolling [Step IV] before the step of final annealing herein is performed to a rolling reduction of 20% or more, and preferably 25% or more. Even when the process annealing is omitted, the cold rolling and final annealing, as appropriately performed, allow the pure titanium sheet to have a high tensile strength of 343 MPa or more and to exhibit excellent press formability. These excellent properties can be obtained even at a low rolling reduction when the cold rolling is performed without process annealing. This is because a deformation structure, which has been formed in the material titanium during hot rolling, remains in the material without being canceled or broken by the process annealing. The pure titanium sheet obtained according to this embodiment can have excellent press formability even at a low rolling reduction without performing process annealing. This embodiment can therefore be applied typically to the case where the pure titanium sheet has a too large gage to ensure a high rolling reduction, or the case where the pure titanium sheet has a sufficiently small gage as a result of hot rolling. The rolling reduction is preferably 95% or less, and more preferably 90% or less.

[0055] In the step of final annealing [Step V], the work may be annealed under such conditions (heating temperature and annealing time) that the value H specified by Expression (2) be positive, and the work may be then air-cooled to room temperature. The final annealing, as performed under such conditions, can suppress the precipitation of beta phases that adversely affect the crevice corrosion resistance. The pure titanium sheet according to the present invention contains a trace amount of iron as described above. The conditions (i.e., the heating temperature and holding time) under which the beta phases precipitate depend on the iron content. Accordingly, the final annealing is performed under such conditions that the value H specified by Expression (2) be positive. Expression (2) is expressed as follows:

[0056] [Math. 3]

$$H = \frac{1}{B \cdot X_0}\left(1 - \frac{T}{A}\right) - t^n \cdot \cdot \cdot \quad (2)$$

wherein T represents a heating temperature (°C) in the final annealing; t represents an annealing time (second) in the final annealing; X_0 represents an iron content (in mass percent) in the pure titanium sheet; A is 891; B is 0.428; and n is 0.135.

[0057] Expression (2) is obtained based on experiments as follows. Specifically, the precipitation rate of beta phases varies depending on the iron content in the pure titanium sheet and on the holding temperature in the heat treatment as described above. The precipitation rate increases with an increasing iron content and an elevating holding temperature. Based on this, a relational expression (Expression (2)), as a basis for the precipitation rate, was determined using a precipitation rate expression calculated based on the atomic diffusion (migration) and content distribution. The coefficients A and B in Expression (2) were determined based on experimental data.

[0058] In Expression (2), T represents the heating (annealing) temperature (°C) in the final annealing and preferably falls within a range of from 550°C to 890°C [550°C≤T (°C)≤890°C]. The final annealing, if performed at an annealing temperature T of lower than 550°C, may fail to induce recrystallization and thereby cause the pure titanium sheet to have significantly poor ductility. The lower limit of the temperature necessary for recrystallization varies depending on the holding time. Typically, a higher temperature is necessary with a decreasing holding time. The heating temperature T is preferably 600°C or higher, and more preferably 700°C or higher. Annealing, if performed through heating to the beta transformation temperature or higher, the work may include an acicular structure after cooling, and this may adversely affect the press formability. To prevent this, the final annealing is preferably performed at a temperature equal to or lower than the beta transformation temperature. The heating temperature T is preferably 870°C or lower, and more preferably 850°C or lower.

[0059] The other conditions in the cold rolling and final annealing and conditions in the other steps can be common conditions.

[0060] In Expression (2), t represents the annealing time (second), i.e., the holding time within the heating temperature T (°C). It should be noted that the term "holding" as used herein refers to that the work may be held approximately within a range of [(the heating temperature T (°C))±about 5°C], as long as the range falls within the above-specified temperature range. The final annealing, if performed for an excessively short annealing time t, may be difficult to control; whereas, if performed for an excessively long annealing time t, may adversely affect the productivity. To prevent this, the annealing time t (second) preferably falls within a range of from 10 seconds to 120000 seconds [10 (seoond)≤t (second)≤120000 (second)].

[0061] The thickness (gage) of the pure titanium sheet according to the present invention is not critical and can be set in consideration typically of the required strength.

[0062] The pure titanium sheet according to the present invention has excellent ductility while having a high strength and exhibits satisfactory crevice corrosion resistance in hot and humid surroundings. The pure titanium sheet is therefore applicable to applications in wide fields where formability and mechanical strength at high levels are required. Such applications are exemplified by aircraft parts; chemical plant members; coast structural materials (particularly bay-coast structural materials whose corrosion is accelerated by the contact with seawater); automobiles; building materials; bodies typically of cellular phones, mobile personal computers, and cameras; eyeglass frames; plate type heat exchanger components; fuel cell separators; household electric appliance exterior trim parts; and transportation equipment members. Among them, the pure titanium sheet is suitable for a heat-exchanging member for a plate type heat exchanger.

EXAMPLES

[0063] The present invention will be illustrated in further detail with reference to several examples below. It should be noted, however, that these examples are never intended to limit the scope of the invention; various changes and modifications may be made without departing from the scope and spirit of the invention and all fall within the scope of the invention.

[0064] Raw materials oontaining iron and oxygen in contents as given in "Chemical composition" in Table 1 with the remainder being titanium and inevitable impurities were subjected to casting through cold crucible induction melting (CCIM) and yielded titanium ingots. The ingots were bloomed into 130 mm wide by 45 mm thick blocks, heated to 750°C, hot-rolled, and yielded hot-rolled sheets (Samples Nos. 3 to 16) about 4 mm thick. In some specimens, the gage of the hot-rolled sheet was appropriately adjusted by facing. This was performed in consideration of the final gage (0.5 mm) and the cold rolling reduction given in Table 1. Some of the hot-rolled sheets as given in Table 1 were prepared by subjecting the works sequentially to process annealing at 700°C for 5 minutes, immersion in a salt furnace, acid wash, and descaling. The others were prepared through descaling without process annealing. After the descaling, all the works were faced and acid washed to adjust their gages, cold-rolled to a "Rolling reduction" given in Table 1, and final-annealed under "Final annealing conditions" given in Table 1. Some specimens were subjected to final annealing to a rolling reduction other than 85%. After the final annealing, the works were immersed in a fluoro-nitric acid solution for descaling, and yielded pure titanium sheets 0.5 mm thick as specimens. The value H of each pure titanium sheet was calculated according to Expression (2) and indicated in "Value H in Expression (2)" in Table 1.

[0065] Each of the prepared pure titanium sheets was subjected to evaluations as follows.

Schmidt Factor Measurement Method

[0066] The texture of the pure titanium sheet surface at arbitrary points was evaluated by crystal orientation analysis using a field emission scanning electron microscope (FESEM) (JSM 5410 supplied by JEOL Ltd.) equipped with an electron backscatter diffraction pattern (EBSP) system.

[0067] Specifically, after polishing the rolling plane surface to a depth of one-fourth the gage of the pure titanium sheet, the specimen pure titanium sheet was placed in the SEM lens-barrel, a beam of electrons was applied to the specimen, an image of an electron backscatter pattern (EBSP) projected on the screen was taken with a highly sensitive camera, the image was captured into the computer, and analyzed therein to determined crystal orientations. In this process, Schmidt factors of {11-22}<11-23> twins were determined at respective measurement points with the tensile load direction agreeing with the rolling direction, and resulting orientation mapping data were collected. The measurement was performed in each field of view of 1 mm by 1 mm at a pitch of 1 μm. Adjacent measurement points, when having a difference in crystal orientations between them of within ±15°, were evaluated as belonging to the same crystal plane.

Area Percentage of Grains (Alpha Phase) Having Schmidt Factors of {11-22}<11-23> Twins of 0.45 or More

[0068] After the Schmidt factor measurement, the area percentage of grains having Schmidt factors of 0.45 or more was determined by dividing the number of measurement points having Schmidt factors of 0.45 or more by the number of entire measurement points, and multiplying the resulting value by 100. The area percentage is indicated in "Texture (%)" in Table 1.

Beta Phase Volume Fraction

[0069] The rolling plane surface of each specimen pure titanium sheet was mechanically polished to a depth of one-fourth the gage of the pure titanium sheet, subjected to buffing and chemical polishing to a mirror-smooth state, and observed on backscattered electrons (BSE). Arbitrary regions of 270 μm by 230 μm of each sample were observed at 10000-fold magnification, an average of beta phase volume fractions was determined, and the average is indicated in "Beta phase volume fraction (%)" in Table 1. In this experimental example, a sample having a beta phase volume fraction of 0.3% or less was evaluated as accepted.

Tensile Strength Evaluation

[0070] A No. 13 test specimen prescribed in JIS Z2201 was sampled from each pure titanium sheet so that the rolling direction agree with the load axis direction (L direction). The test specimen was subjected to a tensile test at room temperature according to JIS H4600 to measure the tensile strength. The results are indicated in "Tensile strength" in Table 1. A sample having a tensile strength of 343 MPa or more was evaluated as accepted.

Press Formability (Score).

[0071] Figs. 2(a) and 2(b) are explanatory drawings illustrating how to evaluate the press formability (anisotropic-bulging formability). Each of the prepared specimen pure titanium sheets was subjected to press forming with press forming dies using a 80-ton oil hydraulic press forming machine. Thus, the press formability of the titanium sheet was evaluated. The press forming dies simulated a heat exchanging unit of a plate type heat exchanger and had a size of 160 mm wide by 160 mm long (evaluated area: 100 mm wide by 100 mm long), in a herringbone pattern having six ridges. The six ridges were arranged at a pitch of 10 mm and a maximum height of 4 mm and had six different radii of curvature R of 0.4, 0.6, 0.8,1.0,1.4, and 1.8 (mm), respectively. The press forming was performed under such conditions that a press oil having a dynamic viscosity of 34 mm^2/s (at a temperature of 40°C) was applied to both sides of the dies to be in contact with the test specimen, and each specimen was placed on the lower die so that the rolling direction of the specimen agree with the vertical direction (top-down direction) in Fig. 2(a). The flange was fixed by a blank holder, and press forming was performed, at a press forming rate of 1 mm/second to an indentation depth of 3.4 mm.

[0072] Cracking (the presence of cracks) of the specimen was measured at 36 points as intersection points between the ridges and the dashed lines (five lines crossing the ridges and one line crossing the troughs), as illustrated in Figs. 2, in which Figs. 2(a) and 2(b) are a plan view and a cross-sectional view, respectively.

[0073] Line A (crossing the ridges), Line C (crossing the ridges), Line C' (crossing the troughs), and Line E (crossing the ridges) would act as a cracking origin. The measurement points along these lines were visually observed, and a specimen was rated as rating 2 when having no crack (no defect); rated as rating 1 when having the tendency of necking (a phenomenon in which part of the specimen become narrow and constricted rated as rating 1 when suffering from necking; and rated as rating 0 when suffered from cracking. Regarding the measurement points along Line B (crossing the ridges) and Line D (crossing the ridges), a specimen was rated as rating 2 when having no crack (no defect); rated as rating 0.5 when suffering from necking; and rated as rating 0 when suffering from cracking.

[0074] The formability score was calculated according to Expression (3) and employed as an index for press formability evaluation in the present invention. Specifically, the score was determined in the following manner. The cracking state was converted into numerical values by multiplying the respective ratings by the inverses of radii of curvature R, and the numerical values were summed up. The total value is normalized provided that the case where neither cracking nor necking was observed be rated as 100. The normalized value was multiplied by the function F (T, μ, t) and the function G (α, ρ) to give a formability score. The function F (T, μ t) depends on the temperature (T), lubricating oil viscosity (μ), and test specimen gage (t); and the function G (α, p) depends on the angle (α) and pitch (p) of the die ridge lines. In this experimental example, the temperature (T), lubricating oil viscosity (μ), test specimen gage (t), die ridge line angle (α), and pitch (p) were fixed. Accordingly, the score was calculated assuming that the product of the functions F and G be 1 for the sake of convenience. The calculated score is indicated in "Formability score" in Table 1. Expression (3) is expressed as follows:

$$\text{Formability score} = (F \times G) \times [\Sigma E(ij)/R(j)]/[(\Sigma A,C,C',E2/R(j)) + (\Sigma B,D1/R(j))] \times 100 \quad (3)$$

wherein:

For the measurement points regarding Lines A, C, C', and E, the calculation was performed provided that E (ij)=1.0×(without cracking: 2, with necking: 1, with cracking: 0); and

For the measurement points regarding Lines B and D, the calculation was performed provided that E(ij))=0.5×(without cracking: 2, with necking: 1, with cracking: 0).

A sample having a formability score of 70 or more was evaluated as having excellent formability.

Crevice Corrosion Resistance Test

[0075] A test specimen of 30 mm by 50 mm was cut out from each of the prepared pure titanium sheets, a hole 7 mm in diameter was made at the center of the test specimen, and Teflon® multi-crevice assemblies (ASTM G1671) were attached on both sides of the test specimen through the hole. The resulting work was used as a test specimen for crevice corrosion resistance evaluation. One multi-crevice assembly forms 12 crevices. In this test, two multi-crevice assemblies were attached on both sides of the test specimen and formed a total of 24 crevices. The test specimen was immersed in a boiling 10% aqueous NaCl solution for 360 hours. Whether or not the test specimen suffered from crevice corrosion was visually observed, and the number of crevice corrosion points was counted. A sample having a number of crevice corrosion points of 5 or less was evaluated as having good crevice corrosion resistance. The results are indicated in "Number of corrosion rate" in Table 1.

Assessment

[0076] As mechanical properties at room temperature, a sample having a tensile strength at room temperature of 343 MPa or more; one having a press formability score of 70 or more; and one having a number of crevice corrosion points of 5 or less were respectively evaluated as accepted. A sample evaluated as accepted in all these evaluations was evaluated as having satisfactory balance between strength and press formability and exhibiting excellent crevice corrosion resistance. The results are indicated in Table 1.

[Table 1]

Sample number	Chemical composition		Value of Expression (1)	Process annealing	Rolling reduction	Final annealing conditions		Texture	Beta phase volume fraction	Value H in Expression (2)		Tensile strength		Formability score		Number of corrosion points	
	Fe	○				Temperature (T)	Time (t)					L direction					
	mass percent	mass percent			%	°C	sec	%	%			MPa					
1	0.052	0.088	0.094	with	50	800	60	39	0	2.84	○	370	○	60	×	0	○
2	0.052	0.088	0.094	with	70	800	60	44	0	2.84	○	378	○	70	○	0	○
3	0.052	0.088	0.094	with	85	800	60	52	0	2.84	○	380	○	75	○	0	○
4	0.064	0.078	0.085	with	85	800	60	51	0	1.98	○	372	○	75	○	0	○
5	0.040	0.144	0.148	with	85	800	60	50	0	4.22	○	395	○	72	○	0	○
6	0.050	0.110	0.116	with	85	800	60	50	0	3.03	○	385	○	73	○	0	○
7	0.028	0.033	0.036	with	85	800	60	56	0	6.77	○	300	×	80	○	0	○
8	0.073	0.088	0.096	with	85	860	300	40	0.5	-1.05	×	385	○	60	×	7	×
9	0.073	0.088	0.096	with	85	780	120	45	0.1	2.7	○	382	○	70	○	2	○
10	0.052	0.088	0.094	with	85	750	300	45	0	4.94	○	386	○	72	○	0	○
11	0.052	0.088	0.094	without	10	800	60	35	0	2.84	○	375	○	60	×	0	○
12	0.052	0.088	0.094	without	30	800	60	54	0	2.84	○	380	○	72	○	0	○
13	0.030	0.058	0.062	without	30	780	60	56	0	7.95	○	355	○	78	○	0	○
14	0.030	0.058	0.062	with	80	830	60	58	0	3.58	○	348	○	82	○	0	○
15	0.030	0.058	0.062	with	80	800	60	57	0	6.20	○	352	○	80	○	0	○
16	0.025	0.077	0.080	with	80	800	60	60	0	7.79	○	371	○	85	○	0	○

Expression (1)=[Oxygen content (in mass percent)]+0.12×[Iron content (in mass percent)]

[0077] Table 1 indicates as follows. Specifically, pure titanium sheets of Samples Nos. 2 to 6, 9, 10, and 12 to 16 satisfied conditions specified in the present invention and excelled not only in balance between strength and press formability at room temperature, but also in crevice corrosion resistance.

[0078] By contrast, pure titanium sheets of Samples Nos.1, 7, 8, and 11 did not satisfy the conditions specified in the present invention, thereby disadvantageously failed to ensure a satisfactory strength at room temperature, or had poor press formability at room temperature and/or poor crevice corrosion resistance.

[0079] The pure titanium sheets of Samples No.1 and No. 11 underwent cold rolling to a low irolling reduction before final annealing and each had an area percentage ("Texture (%)" in Table 1) of grains having Schmidt factors of 0.45 or more of less than 43%. These pure titanium sheets thereby had poor press formability.

[0080] The pure titanium sheet of Sample No. 7 had a low oxygen content and had a value specified by Expression (1) of less than the range specified in the present invention. The pure titanium sheet thereby had a tensile strength of less than 343 MPa.

[0081] The pure titanium sheet of Sample No. 8 had a value H specified by Expression (2) of less than the range specified in the present invention. Specifically, this had a negative value H as given in Table 1. The pure titanium sheet had an area percentage ("Texture (%)" in Table 1) of grains having Schmidt factors of 0.45 or more of less than 43%, had a beta phase volume fraction of more than the range specified in the present invention, and thereby had poor press formability and poor crevice corrosion resistance.

[0082] While the present invention has been described in detail with reference to preferred embodiments thereof with a certain degree of particularity, it will be understood by those skilled in the art that various changes and modifications are possible without departing from the spirit and scope of the invention.

[0083] The present application is based on Japanese Patent Application No. 2011-120766 filed on May 30, 2011 and Japanese Patent Application No. 2012-074836 filed on March 28, 2012, the entire contents of which are incorporated herein by reference.

Industrial Applicability

[0084] The pure titanium sheets according to embodiments of the present invention are useful typically in aircraft parts; chemical plant members; coast structural materials (particularly bay-coast structural materials whose corrosion is accelerated by the contact with seawater); automobiles; building materials; bodies typically of cellular phones, mobile personal computers, and cameras; eyeglass frames; plate type heat exchanger components; fuel cell separators; household electric appliance exterior trim parts; and transportation equipment members.

Claims

1. A pure titanium sheet which has excellent balance between press formability and strength and excellent corrosion resistance, the pure titanium sheet comprising:

iron (Fe) in a content of from 0.02% to 0.10%; and
oxygen (O) in a content of from 0.04% to 0.20%,

in mass percent,
wherein:

the pure titanium sheet further comprises titanium and inevitable impurities;
the iron and oxygen contents satisfy a condition specified by Expression (1);
regions are present in an area percentage of 43% or more, the regions having Schmidt factors of {11-22}<11-23> twins of 0.45 or more, the Schmidt factors of the twins determined at a depth of one-fourth the gage of the pure titanium sheet with a rolling direction as an axis; and
the pure titanium sheet has a beta phase volume fraction of 0.3% or less, Expression (1) expressed as follows:

$$[\text{Oxygen content (in mass percent)}]+0.12\times[\text{Iron content (in mass percent)}]\geq 0.050 \quad (1)$$

2. A method for manufacturing the pure titanium sheet of claim 1 which has excellent balance between press formability and strength and excellent corrosion resistance, the method comprising the steps of:

hot rolling;
process annealing;
cold rolling; and
final annealing,

wherein:

the method further comprises the step of descabng pure titanium sheet surface after the step of process annealing;
the step of cold rolling is performed to a rolling reduction of 70% or more after the step of descaling; and
the step of final annealing is performed, after the step of cold rolling, in such conditions as to allow a value H as specified by Expression (2) to be positive, Expression (2) expressed as follows:
[Math.1]

$$H = \frac{1}{B \cdot X_0}\left(1 - \frac{T}{A}\right) - t^n \quad \cdots \quad (2)$$

wherein:

Trepresents a heating temperature (°C) in the final annealing;
$t$represents an annealing time (second) in the final annealing;
X_0represents an iron content (in mass percent) in the pure titanium sheet;
A is 891;
B is 0.428; and
n is 0.135.

3. A method for manufacturing the pure titanium sheet of claim 1 which has excellent balance between press formability and strength and excellent corrosion resistance, the method comprising the steps of:

hot rolling;
cold rolling; and
final annealing,

wherein:

the method further comprises the step of descaling pure titanium sheet surface after the step of hot rolling without performing process annealing,
the step of cold rolling is performed to a rolling reduction of 20% or more after the step of descaling; and
the step of final annealing is performed, after the step of cold rolling, in such conditions as to allow a value H as specified by Expression (2) to be positive, Expression (2) expressed as follows:
[Math. 2]

$$H = \frac{1}{B \cdot X_0}\left(1 - \frac{T}{A}\right) - t^n \quad \cdots \quad (2)$$

wherein:

Trepresents a heating temperature (°C) in the final annealing;
$t$represents an annealing time (second) in the final annealing;
X_0represents an iron content (in mass percent) in the pure titanium sheet;
A is 891;
B is 0.428; and
n is 0.135.

4. A method for manufacturing a heat-exchanging member for a plate type heat exchanger, the method comprising the step of press forming the pure titanium sheet of claim 1.

5. A method for manufacturing a heat-exchanging member for a plate type heat exchanger, the method comprising the steps of:

manufacturing a pure titanium sheet by the manufacturing method of claim 2; and
press forming the manufactured pure titanium sheet.

6. A method for manufacturing a heat-exchanging member for a plate type heat exchanger, the method comprising the steps of:

manufacturing a pure titanium sheet by the manufacturing method of claim 3; and
press forming the manufactured pure titanium sheet.

FIG. 1

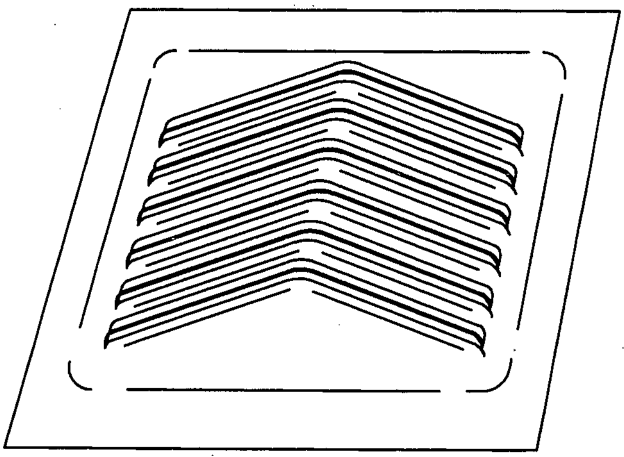
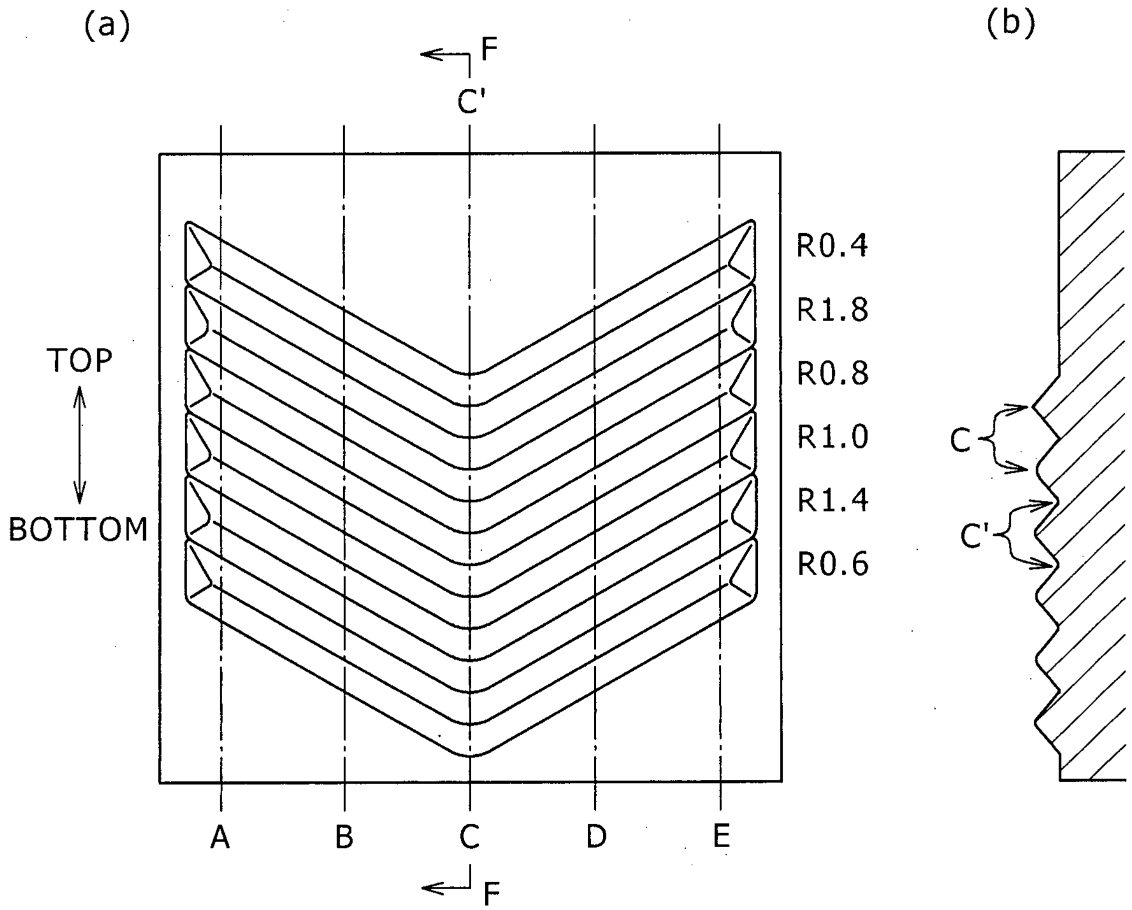


FIG.2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/063914

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

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C1/00-49/14, C22F1/00-3/02

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2011-26649 A (Kobe Steel, Ltd.), 10 February 2011 (10.02.2011), claims; paragraphs [0013], [0029] to [0031]; table 1 (Family: none)	1-6
P,A	JP 2012-72444 A (Kobe Steel, Ltd.), 12 April 2012 (12.04.2012), (Family: none)	1-6
P,A	JP 2012-82457 A (Kobe Steel, Ltd.), 26 April 2012 (26.04.2012), (Family: none)	1-6

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 June, 2012 (29.06.12)	10 July, 2012 (10.07.12)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2004285457 A **[0015]**
- JP 2002317234 A **[0015]**
- JP 2009228092 A **[0015]**
- JP S4931610 B **[0015]**
- JP 2010236067 A **[0015]**
- JP 2011120766 A **[0083]**
- JP 2012074836 A **[0083]**