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(54) TITANIUM PLATE

(57) An object of the present invention is to provide a titanium plate having high strength and excellent workability. In order to achieve the above object, there is provided a titanium plate having, by mass, an iron content of more than 0.10% and less than 0.60%, an oxygen content of more than 0.005% and less than 0.10%, a carbon content of less than 0.015%, a nitrogen content of less than 0.015%, a hydrogen content of less than 0.015%, with the balance being titanium and unavoidable impurities, wherein a two-phase structure of an α-phase and a β-phase is formed, and the β-phase is formed so as to have a circle-equivalent average grain size of 3 μm or less.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a titanium plate, and more particularly to a titanium plate excellent in workability.

RELATED ART

[0002] Conventionally, titanium materials such as titanium alloys and pure titanium have been widely used for sports and leisure equipment, medical devices, various members for plants, aviation and space related equipment, and the like because titanium materials are generally light and high in strength compared with iron-based materials such as iron and alloys thereof.
In addition, since titanium materials are also excellent in corrosion resistance and the like, they are used, for example, for plate materials of plate heat exchangers, muffler members of motorcycles, and the like.
For producing such products, a plate formed from a titanium material (titanium plate) is subjected, for example, to various workings involving plastic deformation such as bending and drawing.
Therefore, a titanium plate is required to have excellent workability in fabrication such as drawing, in order to be subjected to such various applications.
[0003] However, recently, as a result of requirements for the reduction in the thickness of a titanium plate to reduce material cost or the like, improvement in strength has increasingly been required.
That is, simultaneously satisfying formability and strength, which are the properties in a trade-off relation, is increasingly required.
[0004] Titanium sponge used as a raw material of the titanium plate or the like is produced by the Kroll process, and for example, pure titanium is produced by a method of subjecting the titanium sponge obtained by the Kroll process to arc melting or the like to obtain an ingot.
Pure titanium is classified according to the content of elements other than titanium such as iron and oxygen in the Japanese Industrial Standard (JIS), in which JIS class 1, JIS class 2, JIS class 3, JIS class 4, and the like are specified.
With respect to the material properties thereof, JIS class 1 titanium in which the content of iron and the like is low has the lowest strength and excellent formability.
It is known that JIS class 2 titanium has higher strength than JIS class 1 titanium, and JIS class 3 titanium has higher strength than JIS class 2 titanium.
On the other hand, JIS class 2 titanium has lower formability than JIS class 1 titanium, and JIS class 3 titanium has lower formability than JIS class 2 titanium, and it is not easy to obtain a good formed article by subjecting a titanium plate of JIS class 2 or 3 to drawing or the like.
[0005] With respect to the above subject, the following Patent Documents 1 to 3 describe that formability is improved by controlling the content of components other than titanium such as iron in a titanium material to the range below a predetermined level.
However, sufficient strength cannot be expected in the titanium materials described in these Patent Documents.
Further, since the reduction reaction in the Kroll process as described above is typically performed discontinuously (batch wise) in a carbon steel or iron alloy vessel, the resultant titanium sponge contains higher amount of iron in the region close to the wall of the vessel than in the region close to the central part of the vessel.
Because of this, if the iron content is limited, for example, to a range of 0.035% to 0.100% as described in Patent Document 3, the titanium in the central part of the vessel must be used, which limits a material to be used and poses a risk of cost increase.
[0006] Note that in the following Patent Documents 4 and 5, a higher content of iron is permitted compared with the inventions described in Patent Documents 1 to 3, but it cannot be said that the materials in Patent Documents 4 and 5 have sufficient formability.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0007]

Patent Document 1: Japanese Patent Application Laid-open No. Sho-63-60247
Patent Document 2: Japanese Patent Application Laid-open No. Hei-9-3573
Patent Document 3: Japanese Patent Application Laid-open No. 2006-316323
Patent Document 4: Japanese Patent Application Laid-open No. 2008-127633

Patent Document 5: Japanese Patent Application Laid-open No. 2002-180166

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008] An object of the present invention is to provide a titanium plate having high strength and excellent workability.

MEANS FOR SOLVING PROBLEMS

[0009] As a result of extensive and intensive investigations to achieve the above-described object, the present inventors have found that a titanium plate having high strength and excellent workability can be formed by forming the titanium plate so that it may have a predetermined content of iron and oxygen and crystal grains may be in a predetermined state, and such a finding has resulted in completion of the present invention.
[0010] Specifically, the present invention related to a titanium plate for achieving the above object is **characterized in that** the titanium plate has, by mass, an iron content of more than 0.10% and less than 0.60%, an oxygen content of more than 0.005% and less than 0.10%, a carbon content of less than 0.015%, a nitrogen content of less than 0.015%, a hydrogen content of less than 0.015%, with the balance being titanium and unavoidable impurities, wherein a two-phase structure of an α-phase and a β-phase are formed, and the β-phase is formed so as to have a circle-equivalent average grain size of 3 μm or less.

ADVANTAGES OF THE INVENTION

[0011] The present invention can provide a titanium plate having high strength and excellent workability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

Figure 1 is a photomicrograph showing the microstructure of the titanium plate of Example 7.
Figure 2 is a graph showing the relationship between the circle-equivalent average grain size of the β-phase and the Erichsen value.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0013] Hereinafter, a preferred embodiment of the present invention will be described.
The titanium plate in the present embodiment is formed from a titanium material containing the following components, wherein a two-phase structure of an α-phase and a β-phase is formed, and the β-phase is formed so as to have a circle-equivalent average grain size of 3 μm or less.
The titanium material has, by mass, an iron (Fe) content of more than 0.10% and less than 0.60%, an oxygen (O) content of more than 0.005% and less than 0.10%, a carbon (C) content of less than 0.015%, a nitrogen (N) content of less than 0.015%, a hydrogen (H) content of less than 0.015%, with the balance being titanium (Ti) and unavoidable impurities.
[0014] As described above, the iron (Fe) is contained in the titanium material in a content, by mass, of more than 0.10% and less than 0.60%.
Fe is a β-stabilizing element, and although a part of Fe forms a solid solution, most of Fe forms a β-phase.
Further, it is known that Fe is present as TiFe by heat treatment or the like, which suppresses crystal grain growth.
Therefore, it has been conventionally believed that when the Fe content in a titanium material is increased, the crystal grain size in the α-phase formed in the titanium plate is reduced, which can improve the strength of the titanium material and the workability of polishing work, but reduces an index showing ductility (formability) such as the Erichsen value.
[0015] However, as described below in detail, even if the Fe content in a titanium plate is increased, the reduction in ductility can be suppressed and the improvement in strength can be achieved by setting the O content to a predetermined value and adjusting the size of a β-phase to a predetermined value.
[0016] The Fe content of the titanium material forming the titanium plate of the present embodiment is more than 0.10% and less than 0.60% by mass because if the Fe content is 0.10% or less, it may be impossible to impart sufficient strength to the resultant titanium plate.
On the other hand, if the content is 0.60% or more, a reduction in ductility may occur even if the O content in the titanium material is set to a predetermined value, which may lead to reduction in the formability of the titanium plate.
[0017] Note that in the Kroll process, the titanium material having an iron content of 0.60% or more is generally formed

only in a small region near the vessel.
Therefore, in the present embodiment, most of the titanium sponge obtained by the Kroll process can be used as the raw material because, in the titanium plate of the present embodiment, the upper limit of the iron content as its component is set to 0.60% by mass.
That is, the titanium plate of the present embodiment can be said to be suitable as a consumption material used for forming a formed article in that the raw material can be easily acquired.
[0018] The oxygen (O) is contained in the titanium material in a content by mass of more than 0.005% and less than 0.10%.
The O content of the titanium material forming the titanium plate of the present embodiment is more than 0.005% and less than 0.10% by mass because if the O content is 0.10% or more, the strength of the titanium plate may be excessively increased, and as a result, good formability may not be achieved even if the β-phase is adjusted.
[0019] Further, it is important that carbon (C), nitrogen (N), and hydrogen (H) are each contained in a content corresponding to JIS class 2 or less for the purpose of ensuring good workability in fabrication.
More specifically, it is important that the contents of C, N, and H are each less than 0.015% by mass.
Further, it is preferred that the content of C be 0.01% or less, the content of N be 0.01% or less, and the content of H be 0.01% or less.
Although a lower limit is not to be set for the above contents of C, N, and H from the point of view of the workability of a titanium plate, the production cost of the titanium plate may be significantly increased if the content is intended to be extremely reduced.
From the point of view of preventing such cost increase, the C content is preferably 0.0005% or more, the N content is preferably 0.0005% or more, and the H content is preferably 0.0005% or more.
[0020] Conventionally, a titanium plate for which good workability is required in fabrication generally includes only an α-phase because such a titanium plate is made from a titanium material having a low iron content corresponding to JIS class 1 or JIS class 2.
Since the larger the α-grain size, the better the workability, it is important that the titanium plate in the present embodiment has a two-phase structure of α + β, in which the β-phase has a circle-equivalent average grain size of 3 μm or less.
An index which shows workability, such as the Erichsen value, can be improved by forming a titanium plate so as to have such a structure.
[0021] If the circle-equivalent average grain size of the β-phase exceeds 3 μm, workability could be reduced with the Erichsen value lowered, for example, to less than 10 mm.
This is because cracks are likely to occur at the boundary of the coarsened β-phase and the α-phase due to stress concentration, which reduces the workability of the titanium plate.
Although the lower limit of the circle-equivalent average grain size of the β-phase is not particularly specified, but it is preferably 0.05 μm or more because the production cost will be significantly increased in obtaining a titanium plate having a circle-equivalent average grain size of less than 0.05 μm.
Note that the circle-equivalent average grain size of the β-phase can be determined by a method described in "Examples" to be described below.
[0022] Note that these findings have been found by the inventors of the present application by the following methods.
That is, cold-rolled plates each having a thickness of 0.5 mm were prepared on an experimental basis in a small-sized vacuum arc melting furnace using plural types of titanium materials each having a different iron content while changing annealing conditions. Then, the resultant cold-rolled plates (titanium plates) were evaluated for formability by the Erichsen test (details will be described in "Examples" to be described below).
Then, it was found that the grain size of the β-phase is increased by, for example, increasing the annealing time, and that the more the grain size of the β-phase is increased, the smaller the Erichsen value becomes.
A crack was discovered at the interface between the coarse β-grain and the α-phase by detailed investigation of the structure and fracture surface. Then, annealing conditions were changed to reduce the grain size of the β-phase, and it was found that the reduction in the grain size of the β-phase has increased the Erichsen value, indicating improvement in formability.
In particular, it has been found that a circle-equivalent average grain size of the β-phase of 3 μm is considered as a boundary, and that when the circle-equivalent average grain size of the β-phase is 3 μm or less, a high strength titanium plate excellent in workability can be obtained.
[0023] As shown in the description of the process for obtaining this finding, the grain size of the β-phase can be adjusted by the iron content of the titanium material, the final annealing temperature and the final annealing time during the titanium plate production, and the like.
[0024] Hereinafter, these conditions in the method for producing a titanium plate will be described.
Referring now to the conditions of the final annealing temperature and the final annealing time during the titanium plate production, the crystal grain size can be reduced by suppressing the growth of β-grains by decreasing the final annealing temperature.

Further, the crystal grain size can be reduced by suppressing the growth of crystal grains by reducing the final annealing time.

[0025] More specifically, if the final annealing temperature is less than 550°C, the worked structure after cold rolling may not be recrystallized, reducing formability.
On the other hand, if the temperature exceeds 800°C, the diffusion rate of iron in titanium may be increased, coarsening the crystal grains of the β-phase.
Accordingly, the final annealing temperature is preferably any temperature in the range of 550°C or more and 800°C or less.

[0026] Further, the final annealing time is determined by the above final annealing temperature, the thickness of a titanium plate, the capacity of an annealing furnace, and the like.
Specifically, when the final annealing temperature is 650°C or more and 800°C or less, the final annealing time is preferably longer than 0 minute and 15 minutes or less.
Note that since the structure is recrystallized during heating even in the case where the final annealing is completed immediately after the temperature of the titanium plate reached the above final annealing temperature, a risk of reducing formability is low if the final annealing time exceeds at least 0 minute.
On the other hand, the upper limit value of the final annealing time is defined as 15 minutes in the above final annealing temperature because if the final annealing is performed longer than 15 minutes, the crystal grains of the β-phase may be coarsened, reducing the workability of the titanium plate.

[0027] Note that when the final annealing temperature is 550°C or more and less than 650°C, the final annealing is preferably performed so that the following expression (1) may be satisfied, wherein t (min) represents the annealing time and T (°C) represents the annealing temperature.

[Expression 1]

$$t \geq 32.5 - 0.05 \times T \ldots (1)$$

(wherein, $550 \leq T < 650$)

[0028] A certain amount of time is required for recrystallization because recrystallization proceeds only at a slow rate in such a temperature range.
Thus, improvement in the formability by recrystallization can be achieved by selecting the conditions which satisfy the above expression (1).

[0029] However, if long-time annealing is performed in the case where the final annealing temperature is more than 630°C and less than 650°C, the crystal grains of the β-phase may be coarsened, reducing the workability of a titanium plate.
Therefore, it is preferred to perform the final annealing so that the following expression (2) may be satisfied in this temperature region.

[Expression 2]

$$t < 9277.5 - 14.25 \times T \ldots (2)$$

(wherein, $630 < T < 650$)

[0030] Further, the annealing time is preferably 300 minutes or less in the case where the final annealing temperature is in a temperature range of 550°C or more and 630°C or less.
By selecting such conditions, it is possible to suppress the coarsening of the β-phase in the structure to be formed in the titanium plate and impart good workability to the titanium plate.
Note that if a final annealing time exceeding 300 minutes is provided in this temperature range, the crystal grains of the β-phase may be coarsened, reducing the workability of the titanium plate.

[0031] By employing the production conditions illustrated in the above, the grain size of the β-phase in the titanium plate can be adjusted to a predetermined level or less, thus obtaining a titanium plate excellent in strength and workability.

[0032] Note that although not described in detail here, known matters in conventional titanium plates and titanium plate production methods can be employed in the titanium plate of the present embodiment within the range which does not significantly impair the effect of the present invention.

Examples

[0033] Next, the present invention will be described in more detail with reference to Examples, but the present invention is not limited to these.

(Examples 1 to 22, Comparative Examples 1 to 3)

(Preparation of test pieces)

[0034] An ingot (140 mm in diameter) was prepared by small-sized vacuum arc melting, and the ingot was heated to 1150°C and then forged to prepare a slab having a thickness of 50 mm.
The slab was hot-rolled at 850°C to a thickness of 5 mm and then annealed at 750°C, and the scale on the surface of the annealed slab was cut to prepare a plate material having a thickness of 4 mm.
The plate material was further cold-rolled to prepare a plate-shaped sample (titanium plate) having a thickness of 0.5 mm.
The titanium plate having a thickness of 0.5 mm was subjected to final annealing in a vacuum atmosphere to prepare a test piece for evaluation.
In the final annealing, the crystal grain size of the test piece was adjusted by adjusting the temperature (550°C or more and 800°C or less) and time (300 minutes or less).

(Measurement of components)

[0035] The amounts of iron and oxygen contained in the titanium plate were measured using the plate material having a thickness of 4 mm from which the surface scale was cut.
The iron content was measured according to JIS H1614 and the oxygen content was measured according to JIS H1620.

(Measurement of tensile strength)

[0036] Further, the tensile strength of the test piece (titanium plate) in which the crystal grain size has been adjusted as described above was measured according to JIS Z 2241.

(Evaluation of workability)

[0037] Furthermore, the Erichsen value of the test piece (titanium plate) in which the crystal grain size has been adjusted as described above was measured according to JIS Z2247 to evaluate the workability of the titanium plate.

(Investigation of structure)

[0038] The state of the microstructure of the titanium plate that was observed with a photomicrograph is shown in Figure 1 (the microstructure of Example 7).
Since the β-phase appears black and the α-phase appears white in this structural photograph, the photograph was subjected to binarization processing using image analysis software to determine the average area of the β-phase, and the diameter of a circle having the same area as the average area was determined by calculation to define a circle-equivalent average grain size.
The results of the above are shown in Table 1.
[0039]

[Table 1]

	Iron content (mass%)	Oxygen content (mass%)	Tensile strength (MPa)	Erichsen value (mm)	β-phase circle-equivalent average grain size (μm)
Example 1	0.131	0.055	390	12.4	0.7
Example 2	0.131	0.055	400	12.1	0.9
Examples 3	0.131	0.055	375	11.9	1.1
Example 4	0.131	0.055	367	11.7	1.8

(continued)

	Iron content (mass%)	Oxygen content (mass%)	Tensile strength (MPa)	Erichsen value (mm)	β-phase circle-equivalent average grain size (μm)
Comparative Example 1	0.131	0.055	434	9.5	3.3
Example 5	0.223	0.060	402	11.7	1.5
Example 6	0.223	0.060	417	11.5	1.4
Example 7	0.223	0.060	392	10.9	1.5
Example 8	0.223	0.060	383	11.2	2.4
Example 9	0.223	0.060	395	11.4	1.5
Comparative Example 2	0.223	0.060	434	9.0	3.5
Example 10	0.253	0.038	361	12.3	1.2
Example 11	0.253	0.038	371	12.1	0.9
Example 12	0.253	0.038	349	11.4	1.3
Example 13	0.253	0.038	332	11.2	2.0
Example 14	0.253	0.038	354	12.0	1.1
Example 15	0.377	0.066	424	11.7	2.0
Example 16	0.377	0.066	429	11.3	1.9
Example 17	0.377	0.066	420	10.8	2.1
Example 18	0.377	0.066	411	10.5	2.5
Comparative Example 3	0.377	0.066	450	7.9	3.9
Example 19	0.520	0.047	459	11.3	2.2
Example 20	0.520	0.047	471	11.0	2.0
Example 21	0.520	0.047	445	10.6	2.5
Example 22	0.520	0.047	435	10.3	2.8

[0040] In Table 1, the iron content and the oxygen content in Examples 1 to 4 are the same as those in Comparative Example 1, but the circle-equivalent average grain size of the β-phase was adjusted by the difference between the annealing conditions, and the smaller the circle-equivalent average grain size of the β-phase, the larger the Erichsen value. In addition, the same tendency is observed in the other Examples and Comparative Examples, and it is understood that the present invention can provide a titanium plate having high strength and excellent workability also from Figure 2 showing the relationship between the circle-equivalent average grain size of the β-phase and the Erichsen value in Table 1.

Claims

1. A titanium plate having, by mass, an iron content of more than 0.10% and less than 0.60%, an oxygen content of more than 0.005% and less than 0.10%, a carbon content of less than 0.015%, a nitrogen content of less than 0.015%, a hydrogen content of less than 0.015%, with the balance being titanium and unavoidable impurities, wherein a two-phase structure of an α-phase and a β-phase is formed, and the β-phase is formed so as to have a circle-equivalent average grain size of 3 μm or less.

Fig. 1

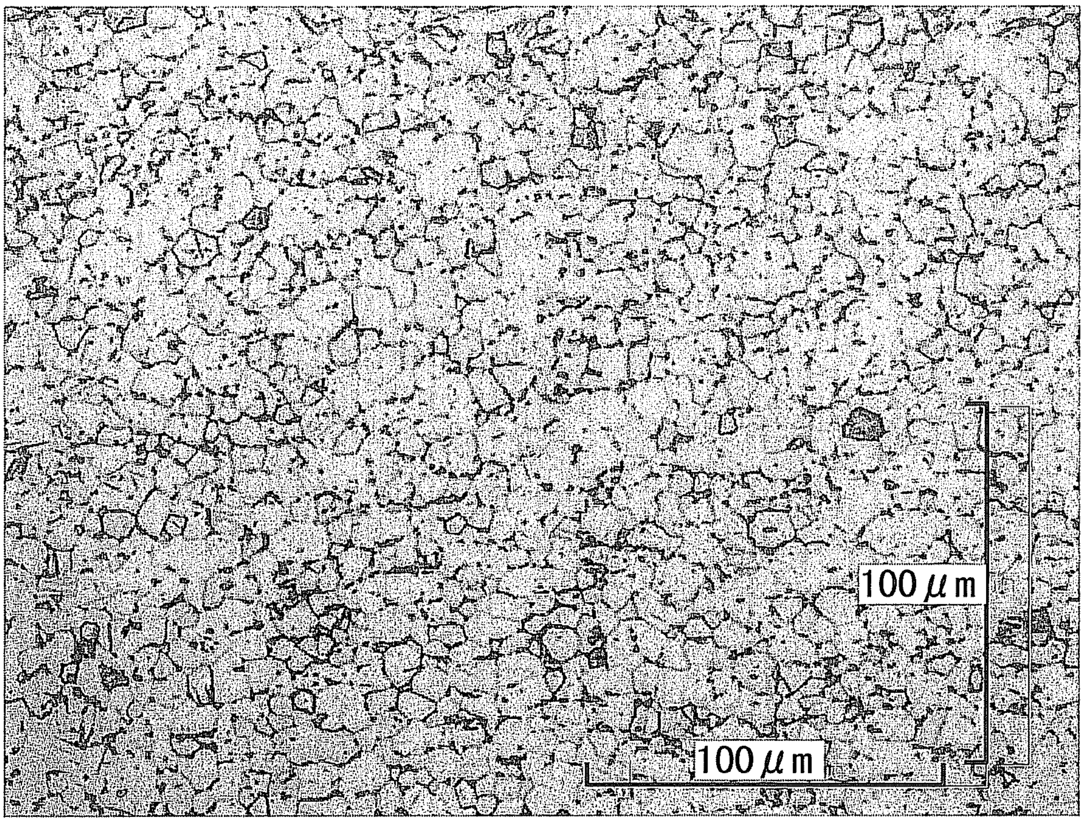
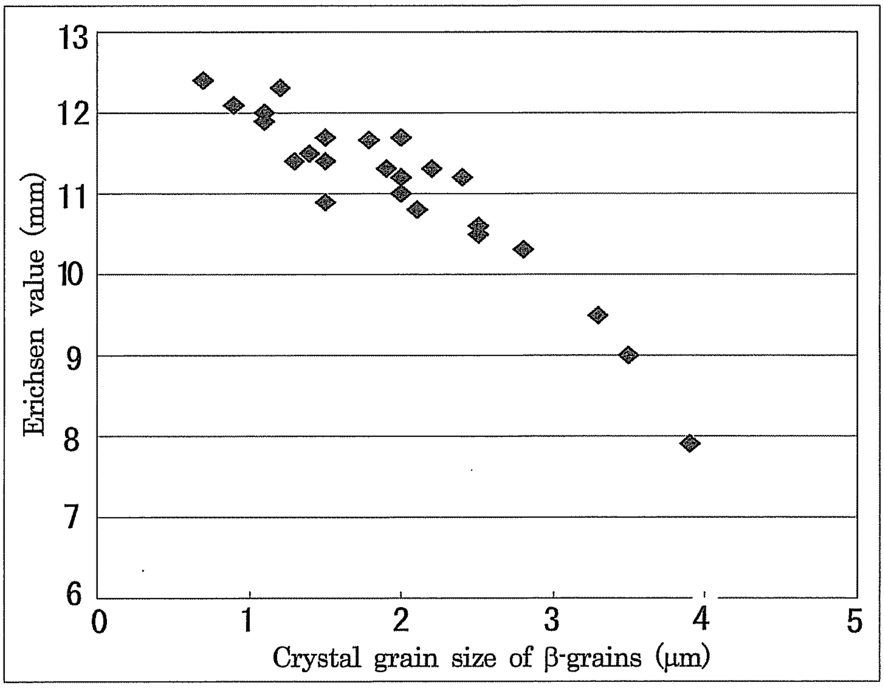

100 μm
100 μm

Fig. 2


13
12
11
10
9
8
7
6
Erichsen value (mm)
0
1
2
3
4
5
Crystal grain size of β-grains (μm)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/052084

A. CLASSIFICATION OF SUBJECT MATTER
C22C14/00(2006.01)i, *C22F1/02*(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, C22F1/000-3/02

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	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 59-179772 A (Sumitomo Metal Industries, Ltd.), 12 October 1984 (12.10.1984), (Family: none)	1
A	JP 2006-316323 A (Nippon Steel Corp.), 24 November 2006 (24.11.2006), (Family: none)	1
A	JP 63-270449 A (Nippon Steel Corp.), 08 November 1988 (08.11.1988), & US 4871400 A & GB 2204061 A	1
A	JP 2005-336551 A (Nippon Steel Corp.), 08 December 2005 (08.12.2005), (Family: none)	1

☐ 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
30 March, 2010 (30.03.10)	13 April, 2010 (13.04.10)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- JP HEI93573 B **[0007]**
- JP 2006316323 A **[0007]**
- JP 2008127633 A **[0007]**
- JP 2002180166 A **[0007]**