



amarchand mangaldas

Our Ref.: DR/AKV/sg/0031206.P3016IN00

April 30, 2014

E-FILING

The Controller of Patents
The Patent Office
New Delhi

Dear Sir,

Re: New Indian Patent Application based on PCT/JP2012/078788

International Filing Date:	November 7, 2012
Applicant:	Nippon Steel & Sumitomo Metal Corporation
Title:	Seamless Austenitic Heat-Resistant Alloy Tube
Priority:	Japanese Application No. 2011-249875 dated November 15, 2011

Enclosed herewith is an application accompanied by a complete specification and supporting documents for grant of a patent under the Indian Patents Act, 1970 by:

Nippon Steel & Sumitomo Metal Corporation, a corporation organized under the laws of Japan, of 6-1, Marunouchi 2-chome, Chiyoda-ku, Tokyo 100-8071, Japan.

The requisite fee submitted in respect of making the application is as follows:

- | | |
|---|------------|
| 1. On application for patent claiming a single priority | Rs. 8,000 |
| 2. For additional sheets of specification | Rs. 10,400 |

Total	Rs. 18,400
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It is respectfully submitted that Nippon Steel & Sumitomo Metal Corporation has the right to make the present application as the surviving entity on account of a merger dated October 1, 2012 between Sumitomo Metal Industries, Ltd., of 5-33 Kitahama 4-chome, Chuo-ku, Osaka-shi, Japan, and Nippon Steel Corporation, of 6-1, Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan, with absorption of Sumitomo Metal Industries, Ltd., into the surviving entity and a name change as of that date to the name provided herein as applicant. In support, a notarially attested copy of the certified copy of the Certificate of Commercial Register in the name of the applicant along with a notarially attested copy of a sworn English translation thereof are submitted herewith.

As required by Public Notice no. CG/Public Notice/PO/2012/15 dated July 2, 2012, the applicant has refrained from submitting documents already available with the International

amarchand & mangaldas & suresh a. shroff & co.

advocates & solicitors

amarchand towers, 216, okhla industrial estate, phase - III, new delhi - 110 020

tel. : (91-11) 41590700, 40606060, 41000541, 26920500

fax : (91-11) 26924900, 26922900

email : am.delhi@amarchand.com

other offices : mumbai, bangalore, kolkata, ahmedabad, hyderabad, chennai



amarchand mangaldas

Bureau in connection with the corresponding PCT application. However, upon the Learned Controller's request, the applicant would submit any requested document (insofar as available) that is otherwise required to be furnished to the Patent Office by the International Bureau.

The Controller is respectfully requested to take the application on record.

Yours sincerely,

Dev Robinson

IN/PA-367

Enc.:

1. Form 1;
2. Verified English language translation of complete specification (in conformation with the international application), No. of pages 43, No. of claims 3;
3. Drawings, No. of sheets 1;
4. Notarized true copy of power of authority;
5. Notarially attested copy of the certified copy of the Certificate of Commercial Register in the name of the applicant along with a notarially attested copy of a sworn English translation thereof;
6. Form 3;
7. Form 5; and
8. Abstract.

Prescribed fee of Rs. 18,400/- through electronic transfer from Axis Bank Ltd.

To Follow: Proof of right

FORM 1 THE PATENTS ACT 1970 (39 of 1970) & THE PATENTS RULES, 2003 APPLICATION FOR GRANT OF PATENT <i>(See Sections 7, 54 & 135 and Rule 20(1))</i>	(FOR OFFICE USE ONLY) Application No: Filing Date: Amount of Fee Paid: CBR No: Signature:
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1. APPLICANT

Name	Nationality	Address
Nippon Steel & Sumitomo Metal Corporation	Japanese	6-1, Marunouchi 2-chome Chiyoda-ku, Tokyo 100-8071 Japan

2. INVENTORS

Name	Nationality	Address
JOUTOKU, Kana	Japanese	c/o Nippon Steel & Sumitomo Metal Corporation 6-1, Marunouchi 2-chome Chiyoda-ku, Tokyo 100-8071 Japan
ISEDA, Atsuro	Japanese	c/o Nippon Steel & Sumitomo Metal Corporation 6-1, Marunouchi 2-chome Chiyoda-ku, Tokyo 100-8071 Japan
OKADA, Hirokazu	Japanese	c/o Nippon Steel & Sumitomo Metal Corporation 6-1, Marunouchi 2-chome Chiyoda-ku, Tokyo 100-8071 Japan
HIRATA, Hiroyuki	Japanese	c/o Nippon Steel & Sumitomo Metal Corporation 6-1, Marunouchi 2-chome Chiyoda-ku, Tokyo 100-8071 Japan

YOSHIZAWA, Mitsuru	Japanese	c/o Nippon Steel & Sumitomo Metal Corporation 6-1, Marunouchi 2-chome Chiyoda-ku, Tokyo 100-8071 Japan
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3. TITLE OF THE INVENTION: "SEAMLESS AUSTENITIC HEAT-RESISTANT ALLOY TUBE"

4. ADDRESS FOR CORRESPONDENCE OF APPLICANT/AUTHORIZED PATENT AGENT IN INDIA

Amarchand & Mangaldas &
Suresh A. Shroff & Co.
Amarchand Towers
216 Okhla Industrial Estate
Phase III, New Delhi - 110020

Telephone No.: (91) (11) 26920500,
41590700
Fax No.: (91) (11) 26922900
Mobile No.: 91 98100 10435
E-mail: dev.robinson@amarchand.com

5. PRIORITY PARTICULARS OF THE APPLICATION(S) FILED IN CONVENTION COUNTRY

Country	App. Number	Filing Date	Name of the Applicant	Title of the Invention
Japan	2011-249875	November 15, 2011	Nippon Steel & Sumitomo Metal Corporation (originally Sumitomo Metal Industries, Ltd.)	Seamless Austenitic Heat-Resistant Alloy Tube

6. PARTICULARS FOR FILING PATENT COOPERATION TREATY (PCT) NATIONAL PHASE APPLICATION

International Application Number	International filing date as allotted by the receiving office
PCT/JP2012/078788	November 7, 2012

7. PARTICULARS FOR FILING DIVISIONAL APPLICATION

Original (first) application number	Date of filing of Original (first) application

8. PARTICULARS FOR FILING PATENT OF ADDITION

Main application/patent Number	Date of filing of main application

9. DECLARATIONS:

(i) Declaration by the inventor(s)

We, the above named inventors, are the true & first inventors for this invention and declare that the applicant herein is our assignee.

(a) Date _____

(b) Signature _____

(c) Name: JOUTOKU, Kana

(a) Date _____

(b) Signature _____

(c) Name: ISEDA, Atsuro

(a) Date _____

(b) Signature _____

(c) Name: OKADA, Hirokazu

(a) Date _____

(b) Signature _____

(c) Name: HIRATA, Hiroyuki

(a) Date _____

(b) Signature _____

(c) Name: YOSHIZAWA, Mitsuru

~~(ii) Declaration by the applicant in the convention country~~

~~We are the applicant in the convention country declare the applicant herein is our assignee.~~

~~a) Date _____~~

~~(b) Signature: _____~~

~~(c) Name of the Signatory: _____~~

(iii) Declaration by the applicant:

We, the applicant hereby declare that:-

- ☐ We are in possession of the above-mentioned invention. ✓
- ☐ The complete specification relating to the invention is filed with this application. ✓
- ☐ The invention as disclosed in the specification uses biological material from India and the necessary permission from the competent authority shall be submitted by us before the grant of patent to us. ×
- ☐ There is no lawful ground of objection to the grant of the patent to us. ✓
- ☐ We, Nippon Steel & Sumitomo Metal Corporation, are the surviving entity on ✓

account of a merger dated involving the original convention country applicant (Sumitomo Metal Industries, Ltd. of 5-33 Kitahama 4-chome, Chuo-ku, Osaka-shi, Japan).

- ☐ The application, particulars of which are given in Para-5 was the first application in convention country in respect of our invention. ✓
- ☐ We claim priority from the above mentioned application filed in convention country and state that no application for protection in respect of the invention had been made in a convention country before that date by us or by any person from which we derive title. ✓
- ☐ Our application in India is based on international application under Patent Cooperation Treaty (PCT) as mentioned in Para-6. ✓
- ☐ The application is divided out of our applications, particulars of which are given in Para-7 and pray that this application may be treated as deemed to have been filed on _____ under sec.16 of the Act. ×
- ☐ The said invention is an improvement in or modification of the invention particulars of which are given in Para-8. ×

10. Following are the attachments with the application:

- a) Verified English language translation of complete specification (in conformation with the international application), No. of pages 43, No. of claims 3;
- b) Drawings, No. of sheets 1;
- c) Notarized true copy of power of authority;
- d) Notarially attested copy of the certified copy of the Certificate of Commercial Register in the name of the applicant along with a notarially attested copy of a sworn English translation thereof;
- e) Form 3;
- f) Form 5; and
- g) Abstract.

Prescribed fee of Rs. 18,400/- through electronic transfer from Axis Bank Ltd.

We hereby declare that to the best of our knowledge, information and belief the facts and matters stated herein are correct and we request that a patent may be granted to us for the said invention.

Dated this 30th day of April, 2014.

Nippon Steel & Sumitomo Metal Corporation


(Dev Robinson)

of Amarchand & Mangaldas &
Suresh A. Shroff & Co.
Attorneys for the Applicant

The Controller of Patents
The Patent Office
New Delhi

IN THE MATTER OF
THE PATENTS ACT, 1970 (No. 39 of 1970)
AND
THE PATENTS RULES, 2003
AND
IN THE MATTER OF

Indian Patent Application titled **"Seamless Austenitic Heat-Resistant Alloy Tube"**

VERIFICATION OF ENGLISH LANGUAGE TRANSLATION
OF INTERNATIONAL APPLICATION NO. PCT/JP2012/078788

We, Nippon Steel & Sumitomo Metal Corporation, a corporation organized under the laws of Japan, of 6-1, Marunouchi 2-chome, Chiyoda-ku, Tokyo 100-8071, Japan, the applicant herein verify:

- (i) that the present application is based on International PCT Application PCT/JP2012/078788,
- (ii) that the specification attached hereto is an English language translation of International Patent Application numbered PCT/JP2012/078788 filed at the Japanese Patent Office and accorded the filing date of November 7, 2012, which application was filed in Japanese language, and
- (iii) that the English language translation attached hereto is correct, complete and faithful to the best of our knowledge and belief.

Dated this 30th day of April, 2014.

Nippon Steel & Sumitomo Metal Corporation



(Dev Robinson)

of Amarchand & Mangaldas &
Suresh A. Shroff & Co.

Attorneys for the Applicant

The Controller of Patents
The Patent Office
New Delhi

FORM 2
THE PATENTS ACT 1970
(39 OF 1970)
&
THE PATENTS RULES, 2003
COMPLETE SPECIFICATION
(See section 10 and rule 13)

1. TITLE OF THE INVENTION :

“SEAMLESS AUSTENITIC HEAT-RESISTANT ALLOY TUBE”

2. APPLICANT:

- (a) NAME: Nippon Steel & Sumitomo Metal Corporation
(b) NATIONALITY: Japanese
(c) ADDRESS: 6-1, Marunouchi 2-chome, Chiyoda-ku
Tokyo 100-8071, Japan

3. PREAMBLE TO THE INVENTION

COMPLETE

The following specification particularly describes the invention and the manner in which it is to be performed.

DESCRIPTION

TITLE OF THE INVENTION

SEAMLESS AUSTENITIC HEAT-RESISTANT ALLOY TUBE

TECHNICAL FIELD

[0001]

The present invention relates to a seamless austenitic heat-resistant alloy tube. More particularly, it relates to a seamless austenitic heat-resistant alloy tube that can be used as a high-temperature equipment member, such as a tube constituting a furnace wall of power generation boiler (hereinafter, referred to as a "water wall tube"), by allowing direct fillet-welding of the outer surface of the tube. Still more particularly, it relates to a seamless austenitic heat-resistant alloy tube excellent in weld crack resistance and capable of restraining the generation of cracks in a HAZ at the time of welding among seamless alloy tubes that are excellent in high temperature strength, have sufficient stress corrosion cracking resistance, and are produced using an austenitic heat-resistant alloy having a low thermal expansion coefficient as a starting material.

BACKGROUND ART

[0002]

In recent years, concerning the power generation boilers, "ultra-supercritical pressure boilers", in which the temperature and pressure of steam are raised to increase the boiler efficiency, have been newly built in the world. Further, the practical use of "next-generation ultra-supercritical pressure boilers", in which the steam temperature, which was so far about

600°C, is raised to 650°C or higher, further 700°C or higher, has been planned. This is because the effective use of energy and resources and the reduction in CO₂ gas emissions for environmental conservation have been one of solutions to energy problem and have become an important industrial policy. This is also because, in the power generation boiler in which fossil fuels are burnt, higher temperature and higher pressure of steam is advantageous in increasing the efficiency of boiler.

[0003]

The higher temperature and higher pressure of steam raise the temperature at the time when a tube constituting a boiler, for example, a heat-transfer tube such as a superheater tube and a resuperheater tube and a main steam tube is in operation. Therefore, the material that is used in such a severe environment for a long period of time is required to have a high temperature strength and corrosion resistance at high temperatures, above all, long-term stability of metal micro-structure and high creep properties.

[0004]

Non Patent Document 1 (Fujimitu Masuyama: Journal of The Iron and Steel Institute of Japan, Vol.80 (1994) No.8, pp.587-592) shows a graph in which the abscissas represent the Cr content of material and the ordinates represent the temperature at an allowable stress of 49 MPa for a practicable heat-resistant material, and describes that, with the increase in Cr content, the temperature on the ordinates, and therefore, the creep strength as a high temperature strength increases.

[0005]

Also, Non Patent Document 2 (Masamichi Koiwa: Metal Corrosion Damage and Anticorrosion Technique (1983, Agune Syoufuusha Corp.), pp.452-453) shows a graph in which the abscissas represent the Ni content of

material and the ordinates represent the crack susceptibility for a practicable heat-resistant material, and describes that, with the increase in Ni content, the crack susceptibility on the ordinates decreases, and the corrosion resistance (stress corrosion cracking resistance) at high temperatures increases.

[0006]

Patent Documents 1 to 3 (JP60-100640A, JP64-55352A and JP2-200756A) disclose heat-resistant alloys in which by increasing the contents of Cr and Ni, and moreover, by containing one or more kinds of Mo and W, an attempt is made to improve creep rupture strength as a high temperature strength.

[0007]

Further, to meet the requirement for the high temperature strength properties, which has become increasingly severer, especially, the requirement for the creep rupture strength, Patent Documents 4 to 7 (JP7-216511A, JP7-331390A, JP8-127848A and JP8-218140A) disclose heat-resistant alloys in which 28 to 38% of Cr and 35 to 60% of Ni are contained, and by utilizing the precipitation of α -Cr phase of body-centered cubic structure consisting mainly of Cr, an attempt is made to further improve creep rupture strength.

[0008]

On the other hand, Patent Documents 8 and 9 (JP51-84726A and JP51-84727A) disclose Ni-based alloys in which by containing Mo and/or W, solid-solution strengthening is attempted, and also by utilizing the precipitation strengthening of γ' phase, which is an intermetallic compound containing Al and Ti, specifically $\text{Ni}_3(\text{Al}, \text{Ti})$, the use in the severe high-temperature environment is made possible.

[0009]

Also, Patent Document 10 (JP9-157779A) proposes a high-Ni austenitic heat-resistant alloy in which by controlling the content ranges of Al and Ti and by precipitating γ' phase, the creep strength is improved.

[0010]

Generally, the austenitic heat-resistant alloys are assembled into various structures by welding, and the structures are used at high temperatures. However, as reported in Non Patent Document 3 (Edited by Japan Welding Society: Welding and Joining Handbook 2nd edition (2003, Maruzen), pp.948-950), if the amounts of alloying elements of the austenitic heat-resistant alloy increase, when welding is performed, there arises a problem of cracks generated in a welding heat affected zone (hereinafter, referred to as a "HAZ"), above all, in the HAZ adjacent to a fusion boundary.

[0011]

Therefore, the austenitic heat-resistant alloy used as a member of various structures is required to achieve both of prevention of cracks in the HAZ at the welding time and provision of weld joint performance.

[0012]

Patent Document 11 (JP2011-63838A) discloses an austenitic heat-resistant alloy in which by containing a specific amount of Fe and by controlling the effective B amount range, the assurance of workability at high temperatures and the prevention of cracks in the HAZ at the butt welding time are made possible.

[0013]

Further, Patent Document 12 (JP2010-150593A) discloses an austenitic heat-resistant alloy in which by controlling the contents of impurity elements such as Sn and Pb in addition to P and S, cracks in the HAZ can be prevented

when butt welding is performed and when a welded structure is used for a long period of time, and moreover, the alloy is also excellent in creep strength.

LIST OF PRIOR ART DOCUMENT(S)

[Patent Documents]

[0014]

[Patent Document 1] JP60-100640A

[Patent Document 2] JP64-55352A

[Patent Document 3] JP2-200756A

[Patent Document 4] JP7-216511A

[Patent Document 5] JP7-331390A

[Patent Document 6] JP8-127848A

[Patent Document 7] JP8-218140A

[Patent Document 8] JP51-84726A

[Patent Document 9] JP51-84727A

[Patent Document 10] JP9-157779A

[Patent Document 11] JP2011-63838A

[Patent Document 12] JP2010-150593A

[Non Patent Documents]

[0015]

[Non Patent Document 1] Fujimitu Masuyama: Journal of The Iron and Steel Institute of Japan, Vol.80 (1994) No.8, pp.587-592

[Non Patent Document 2] Masamichi Koiwa: Metal Corrosion Damage and Anticorrosion Technique (1983, Agune Syoufuusha Corp.), pp.452-453

[Non Patent Document 3] Edited by Japan Welding Society: Welding and Joining Handbook 2nd edition (2003, Maruzen), pp.948-950

[Non Patent Document 4] Shinichi Takano et al.: IHI Technical Review, vol.49 No.4 (2009), pp.185-191

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0016]

As described before, the austenitic heat-resistant alloys are generally assembled into various structures by welding. In recent years, there has been a movement to use the austenitic heat-resistant alloy tubes as water wall tubes of power generation boilers.

[0017]

As the starting material for the water wall tube, conventionally, from the various viewpoints such as workability, a carbon steel or a 1%Cr steel, which need not be subjected to both of preheating and postheating, has generally been used.

[0018]

However, in the before-mentioned "next-generation ultra-supercritical pressure boilers", in which the steam temperature is raised to 700°C or higher, for the carbon steel or the 1%Cr steel having been used conventionally, the high temperature strength is insufficient. Therefore, neither the carbon steel nor the 1%Cr steel can be used as a starting material for the water wall tube of the "next-generation ultra-supercritical pressure boilers".

[0019]

On the other hand, the ordinary austenitic stainless steel, which has been used so far as a superheater tube or a resuperheater tube, is subjected to stress corrosion cracking in the environment in which high-temperature water flows therein, such as a furnace wall, because of low content of Ni. Therefore,

the ordinary austenitic stainless steel as well cannot be used as a starting material for the water wall tube of the "next-generation ultra-supercritical pressure boilers"

[0020]

In addition, the austenitic stainless steel has a high linear thermal expansion coefficient as shown in one example in Non Patent Document 4 (Shinichi Takano et al.: IHI Technical Review, vol.49 No.4 (2009), pp.185-191). Therefore, for the austenitic stainless steel, the heat deformation becomes large when welding is performed, and there arises a problem when the furnace wall is manufactured.

[0021]

The furnace wall is formed by a panel in which a plurality of water wall tubes are arranged in parallel, and are welded to fin plates or fin bars for connecting the water wall tubes to each other. Therefore, unlike the butt welding in which machined groove faces are welded, it is necessary to fillet-weld the outer surface of the as-produced tube directly to the fin plates or the fin bars.

[0022]

In the case where the outer surface of the tube is directly fillet-welded (hereinafter, sometimes referred simply to as "the outer surface of the tube is directly welded") as described above, as compared with the case of butt welding in which welding is performed in the groove, in terms of shape, the stress concentration in an excess weld metal toe portion increases. As a result, in the case where the outer surface of the tube is directly welded, as compared with the case of butt welding, cracks are liable to be generated in the HAZ during welding.

[0023]

Therefore, an immediate challenge is the development of an austenitic heat-resistant alloy tube having an increased Ni content that can be used suitably as the water wall tube of the "next-generation ultra-supercritical pressure boilers ", that is, the development of a seamless austenitic heat-resistant alloy tube having an increased Ni content that is excellent in weld crack resistance and capable of restraining the generation of cracks in a HAZ at the time of welding among seamless alloy tubes that are excellent in high temperature strength, have sufficient stress corrosion cracking resistance, and are produced using an austenitic heat-resistant alloy having a low thermal expansion coefficient as a starting material.

[0024]

The Patent Documents 1 to 10, described before, disclose austenitic heat-resistant alloys having an improved creep rupture strength. In these Patent Documents, however, studies are not conducted from the viewpoint of "weldability" at the time when a structure is assembled, and moreover, to weld the outer surface of tube directly is not considered at all. Therefore, the tubes produced by using the austenitic heat-resistant alloys proposed in these Patent Documents as starting materials cannot at all be used as the water wall tubes of the "next-generation ultra-supercritical pressure boilers ".

[0025]

The austenitic heat-resistant alloy proposed in the Patent Document 11 by the present inventors is suitable for being used as a product, such as a tube, plate, bar, and forgings, that is used as a heat-resistant pressure-resistant part for power generation boilers, chemical industry, or the like, especially as a large-sized product. By using this austenitic heat-resistant alloy, the high-temperature workability, the resistance to weld crack susceptibility, and further the decrease in ductility caused by high-temperature aging at the time

when the product is produced and at the time when actual equipment is used can be improved remarkably.

[0026]

Likewise, for the austenitic heat-resistant alloy proposed in the Patent Document 12 by the present inventors, cracks in the HAZ can be prevented, and a defect attributable to welding workability, which is formed during the welding work, can also be prevented. Further, this austenitic heat-resistant alloy is excellent in creep strength at high temperatures. Therefore, this austenitic heat-resistant alloy can be suitably used as a starting material for high-temperature equipment for power generation boilers, chemical industry plants, or the like.

[0027]

However, when the austenitic heat-resistant alloys proposed in the Patent Documents 11 and 12 were developed, the present inventors did not necessarily consider the direct welding of the outer surface of tube. Therefore, in the case where the outer surface of the tube produced by using the austenitic heat-resistant alloy as a starting material is directly welded, in terms of shape, the stress concentration in an excess weld metal toe portion increases. As a result, there is a possibility that, as compared with the case of butt welding, cracks are unavoidably liable to be generated in the HAZ during welding. Therefore, when the tubes produced by using these austenitic heat-resistant alloys as starting materials are used for the water wall tubes of the "next-generation ultra-supercritical pressure boilers ", the problems to be solved have remained.

[0028]

The present invention has been made in view of the above-described present situation, and accordingly an objective thereof is to provide a seamless

austenitic heat-resistant alloy tube that can be used as a high-temperature equipment member, such as a water wall tube of power generation boiler, by allowing direct fillet-welding of the outer surface of tube, that is, a seamless austenitic heat-resistant alloy tube excellent in weld crack resistance and capable of restraining the generation of cracks in a HAZ at the time of welding among seamless alloy tubes that are excellent in high temperature strength, have sufficient stress corrosion cracking resistance, and are produced using an austenitic heat-resistant alloy having a low thermal expansion coefficient as a starting material.

MEANS FOR SOLVING THE PROBLEMS

[0029]

To solve the above-described problems, the present inventors conducted various examinations.

[0030]

As a result, first, it could be confirmed that by containing a proper amount of B, a sufficient high temperature strength can be given to the austenitic heat-resistant alloy.

[0031]

Next, the present inventors prepared seamless tubes of various austenitic heat resistant alloys containing B (hereinafter, sometimes referred simply to as "austenitic heat-resistant alloy tubes"), fillet-welded the outer surfaces of these alloy tubes directly to a plate compared to a fin plate, specifically, an alloy plate of 6 mm thick, 15 mm wide, and 200 mm long having the chemical composition given in Table 2 of Examples, described later, and conducted detailed examination of the cracks formed in the HAZ when welding is performed.

[0032]

As the result, the following items (a) to (d) were clarified.

[0033]

(a) The contents of the Non Patent Document 3 such that, when welding is performed, cracks are generated at the grain boundary of HAZ close to a fusion boundary could be confirmed.

[0034]

(b) As the amount of B contained in the austenitic heat-resistant alloy tube increases, and as the grain diameter of the austenitic heat-resistant alloy tube increases, the cracks in the HAZ are generated more easily. Further, as the toe angle of excess weld metal becomes larger, the cracks in the HAZ are generated more easily.

[0035]

(c) On the fracture surface of the crack generated in the HAZ, a fusion trace is recognized. Also, on the fracture surface, the concentration of B occurs. As the grain diameter of the austenitic heat-resistant alloy tube increases, the concentration of B becomes more remarkable.

[0036]

(d) As the thickness of the oxide layer formed on the outer surface of the austenitic heat-resistant alloy tube increases, the toe angle of excess weld metal becomes larger.

[0037]

From the clarified items (a) to (d), the present inventors reached the following conclusions (e) and (f).

[0038]

(e) The cracks generated in the HAZ when welding is performed are affected strongly by B existing at the grain boundary in metallurgical terms,

and the behavior at the grain boundary of B is affected indirectly by the grain diameter of the austenitic heat-resistant alloy tube.

[0039]

(f) The cracks generated in the HAZ are affected strongly by the toe angle of excess weld metal in mechanical terms. The toe angle is affected indirectly by the oxide layer formed on the outer surface of the austenitic heat-resistant alloy tube.

[0040]

That is, it was clarified that, in the case where the austenitic heat-resistant alloy tube, in which a proper amount of B is contained to assure a sufficient high temperature strength, is fillet-welded directly, in order to prevent cracks generated in the HAZ when welding is performed, the following two items are effective:

to control the grain diameter of the austenitic heat-resistant alloy tube, and to regulate the content of B according to the grain diameter, and

to control the thickness of the oxide layer existing on the outer surface of the austenitic heat-resistant alloy tube, and to control the shape of excess weld metal.

[0041]

The reasons for this are thought to be the following items (g) to (i).

[0042]

(g) During welding work, B is segregated at the grain boundary of HAZ near the fusion boundary by the weld thermal cycle. Since B is an element that lowers the fusion point of grain boundary, the grain boundary at which B is segregated during welding is melted locally, and the melted portion is opened by the weld heat stress; therefore, so-called "liquation cracking" occurs. In the case where the grain diameter is large, the grain boundary area per unit

volume is small. Therefore, in the case where the grain diameter is large, the grain boundary segregation of B becomes remarkable, and also the stress applied to a specific grain boundary face increases, so that cracks in the HAZ become liable to be generated.

[0043]

(h) As the toe angle of weld bead (excess weld metal) increases, the stress concentration on the HAZ occurs more easily, and therefore, cracks are liable to be generated.

[0044]

(i) In the case where a thick oxide layer is formed on the outer surface of tube, in addition to a high fusion point of oxides, the wettability with molten metal is deteriorated when the outer surface of tube is fillet-welded. Therefore, the toe angle of excess weld metal increases, and the susceptibility to cracks is enhanced.

[0045]

Accordingly, the present inventors conducted further detailed studies.

[0046]

As the result, it was clarified that even in the case where the outer surface of the austenitic heat-resistant alloy tube is fillet-welded directly to the plate compared to the fin plate (the alloy plate of 6 mm thick, 15 mm wide, and 200 mm long having the chemical composition given in Table 2 of Examples), cracks in the HAZ can be prevented by taking the following measures (j) and (k).

[0047]

(j) The average grain diameter $d(\mu\text{m})$ at the center of the wall thickness of the alloy tube is controlled so as to be 1000 μm or smaller and in the range

satisfying the following formula according to the amount of B contained in the alloy:

$$d \leq 1500 - 2.5 \times 10^5 \times B$$

in which letter B represents the content (mass%) of B.

[0048]

(k) To improve the wettability with molten metal at the time of fillet-welding, and to decrease the toe angle, the thickness of oxide layer on the outer surface of alloy tube is kept to 15 μm or smaller.

[0049]

The present invention was completed on the basis of the above-described findings, and the gist thereof is seamless austenitic heat-resistant alloy tubes described below.

[0050]

(1) A seamless austenitic heat-resistant alloy tube used by fillet-welding the outer surface thereof directly, having a chemical composition consisting, by mass percent, of

C: 0.03 to 0.15%,

Si: 1% or less,

Mn: 2% or less,

P: 0.03% or less,

S: 0.01% or less,

Ni: 35 to 60%,

Cr: 18 to 38%,

W: 3 to 11%,

Ti: 0.01 to 1.2%,

Al: 0.5% or less,

B: 0.0001 to 0.01%,

N: 0.02% or less,

O: 0.008% or less, and

at least one element selected from

Zr: 0.01 to 0.5%,

Nb: 0.01 to 0.5%, and

V: 0.01 to 0.5%,

with the balance being Fe and impurities, wherein

an average grain diameter d μm at the center of the wall thickness of the tube is 1000 μm or smaller and satisfies the following formula:

$$d \leq 1500 \cdot 2.5 \times 10^5 \times B$$

where letter B represents the content by mass percent of B;

and further,

the thickness of an oxide layer on the outer surface of the tube is 15 μm or smaller.

[0051]

(2) The seamless austenitic heat-resistant alloy tube described in the above item (1), containing, in lieu of a part of Fe, by mass percent, at least one element selected from the elements listed in following groups <1> and <2>:

<1> Mo: 1% or less, Cu: 1% or less, and Co: 1% or less

<2> Ca: 0.05% or less, Mg: 0.05% or less, and REM: 0.1% or less.

[0052]

(3) The seamless austenitic heat-resistant alloy tube described in the above item (1) or (2), wherein the tube is used as a water wall tube.

[0053]

The "impurities" mean impurity elements mixed from ore and scrap used as a raw material or a production environment when the austenitic heat-resistant alloy is produced on an industry basis.

[0054]

The "REM" is the general term of a total of seventeen elements consisting of Sc, Y, and lanthanoids, and the REM content means the total content of one kind or two or more kinds of elements of the REM.

ADVANTAGEOUS EFFECT(S) OF THE INVENTION

[0055]

The seamless austenitic heat-resistant alloy tube of the present invention is excellent in weld crack resistance and capable of restraining the generation of cracks in a HAZ at the time of welding. Therefore, among seamless alloy tubes that are excellent in high temperature strength, have sufficient stress corrosion cracking resistance, and are produced using an austenitic heat-resistant alloy having a low thermal expansion coefficient as a starting material, the seamless austenitic heat-resistant alloy tube of the present invention can be used suitably as a high-temperature equipment member such as a water wall tube of power generation boiler.

BRIEF DESCRIPTION OF THE DRAWING(S)

[0056]

Figure 1 is a schematic view for explaining a restraint weld test body simulating the fillet-welding of a water wall tube. In this figure, an alloy plate compared to a fin plate was simply written so as to be a "fin plate".

Figure 2 is a sectional view for explaining the fillet-welding of a test specimen tube to an alloy plate compared to a fin plate. In this figure, the alloy plate compared to a fin plate was simply written so as to be a "fin plate".

MODE FOR CARRYING OUT THE INVENTION

[0057]

Hereunder, the features of the present invention are explained in detail. In the following explanation, "%" representing the content of each element means "mass%".

[0058]

(A) Chemical composition of tube:

C: 0.03 to 0.15%

C (carbon) stabilizes austenite, forms fine carbides at the grain boundary, and improves the creep strength at high temperatures. In order to sufficiently achieve these effects, 0.03% or more of C must be contained. However, if C is contained excessively, the carbides become coarse, and precipitate in large amounts, so that the ductility of grain boundary is decreased, and further, the toughness and creep strength are also decreased. Therefore, the upper limit is placed, and the C content is set to 0.03 to 0.15%. The preferable lower limit of C content is 0.04%, and the preferable upper limit thereof is 0.12%.

[0059]

Si: 1% or less

Si (silicon) is an element that has a deoxidizing function, and is effective in improving the corrosion resistance and oxidation resistance at high temperatures. However, if Si is contained excessively, the stability of austenite decreases, and therefore the toughness and creep strength are

decreased. Therefore, the upper limit is placed, and the Si content is set to 1% or less. The Si content is preferably 0.8% or less.

[0060]

The lower limit of Si content need not be placed especially. However, if the Si content decreases extremely, the deoxidizing effect is not achieved sufficiently, the index of cleanliness of alloy is increased and the cleanliness is deteriorated, and also the advantageous effect of improving the corrosion resistance and oxidation resistance at high temperatures becomes less liable to be achieved. Also, the production cost increases greatly. Therefore, the preferable lower limit of Si content is 0.02%.

[0061]

Mn: 2% or less

Mn (manganese) has a deoxidizing function like silicon. Manganese also contributes to the stabilization of austenite. However, if Mn is contained excessively, embrittlement occurs, and further, the toughness and creep ductility decrease. Therefore, the upper limit is placed, and the Mn content is set to 2% or less. The Mn content is preferably 1.5% or less.

[0062]

The lower limit of Mn content also need not be placed especially. However, if the Mn content decreases extremely, the deoxidizing effect is not achieved sufficiently, the cleanliness of alloy is deteriorated, and also the austenite stabilizing effect becomes less liable to be achieved. Also, the production cost increases greatly. Therefore, the preferable lower limit of Mn content is 0.02%.

[0063]

P: 0.03% or less

P (phosphorus) is contained in the alloy as an impurity, and is an element that segregates at the grain boundary of HAZ during welding and enhances the liquation cracking susceptibility. Therefore, the upper limit is placed, and the P content is set to 0.03% or less. The P content is preferably 0.02% or less.

[0064]

The P content is preferably decreased as far as possible. However, the extreme decrease leads to the increase in production cost. Therefore, the preferable lower limit of P content is 0.0005%.

[0065]

S: 0.01% or less

S (sulfur) is, like P, contained in the alloy as an impurity, and is an element that segregates at the grain boundary of HAZ during welding and enhances the liquation cracking susceptibility. Further, S is an element that exerts an adverse influence on the toughness after long-term use. Therefore, the upper limit is placed, and the S content is set to 0.01% or less. The S content is preferably 0.005% or less.

[0066]

The S content is preferably decreased as far as possible. However, the extreme decrease leads to the increase in production cost. Therefore, the preferable lower limit of S content is 0.0001%.

[0067]

Ni: 35 to 60%

Ni (nickel) is an element effective in obtaining austenite, and also, is an element essential in assuring the structural stability at the time of long-term use. In order to sufficiently achieve the above-described effects of Ni in the range of Cr content of 18 to 38%, described later, 35% or more of Ni must be

contained. However, Ni is an expensive element, so that the containing of much Ni leads to the increase in cost. Therefore, the upper limit is placed, and the Ni content is set to 35 to 60%. The preferable lower limit of Ni content is 38%, and the preferable upper limit thereof is 55%.

[0068]

Cr: 18 to 38%

Cr (chromium) is an element essential in assuring the oxidation resistance and corrosion resistance at high temperatures. In order to achieve the above-described effects of Cr in the range of Ni content of 35 to 60%, described above, 18% or more of Cr must be contained. However, if the Cr content exceeds 38%, the stability of austenite at high temperatures is deteriorated, and the creep strength is decreased. Therefore, the Cr content is set to 18 to 38%. The preferable lower limit of Cr content is 20%, and the preferable upper limit thereof is 35%.

[0069]

W: 3 to 11%

W (tungsten) is an element that dissolves in matrix and contributes greatly to the improvement in creep strength at high temperatures exceeding 700°C. In order to sufficiently achieve this effect, 3% or more of W must be contained. However, even if W is contained excessively, the effect is saturated, and the creep strength is rather decreased in some cases. Further, W is an expensive element, so that the containing of much W leads to the increase in cost. Therefore, the upper limit is placed, and the W content is set to 3 to 11%. The preferable lower limit of W content is 5%, and the preferable upper limit thereof is 10%.

[0070]

Ti: 0.01 to 1.2%

Ti (titanium) precipitates in grains as fine carbo-nitrides, and contributes to the creep strength at high temperatures. In order to achieve this effect, 0.01% or more of Ti must be contained. However, if Ti is contained excessively, Ti precipitates in large amounts as carbo-nitrides, and decreases the creep ductility and toughness. Therefore, the upper limit is placed, and the Ti content is set to 0.01 to 1.2%. The preferable lower limit of Ti content is 0.05%, and the preferable upper limit thereof is 1.0%.

[0071]

Al: 0.5% or less

Al (aluminum) is an element having a deoxidizing function. However, if Al is contained excessively, the cleanliness of alloy is remarkably deteriorated, and the hot workability and ductility are decreased. Therefore, the upper limit is placed, and the Al content is set to 0.5% or less. The Al content is preferably 0.3% or less.

[0072]

The lower limit of Al content need not be placed especially. However, if the Al content decreases extremely, the deoxidizing effect is not achieved sufficiently, the cleanliness of alloy is inversely deteriorated, and the production cost is increased. Therefore, the preferable lower limit of Al content is 0.001%. In order to stably achieve the deoxidizing effect of Al and to assure the high cleanliness of alloy, the lower limit of Al content is further preferably set to 0.0015%.

[0073]

B: 0.0001 to 0.01%

B (boron) is an element necessary to strengthen the grain boundary by segregating at the grain boundary during the use at high temperatures and to improve the creep strength by finely dispersing the grain boundary carbides.

In addition, B has effects of improving the sticking force by segregating at the grain boundary and of contributing to the improvement in toughness. In order to achieve these effects, 0.0001% or more of B must be contained. However, if B is contained excessively, B is segregated in large amounts in the high-temperature HAZ near the fusion boundary, so that the fusing point of grain boundary is lowered, and the liquation cracking susceptibility of HAZ is enhanced. Therefore, the upper limit is placed, and the B content is set to 0.0001 to 0.01%. The preferable lower limit of B content is 0.0005%, and the preferable upper limit thereof is 0.005%.

[0074]

In the case where the average grain diameter d μm at the center of the wall thickness of the tube is large, the grain diameter of HAZ near the fusion boundary increases, in other words, the grain boundary area per unit volume decreases, so that the grain-boundary segregation of B is promoted, and the stress applied to a specific grain boundary face increases. Therefore, the liquation cracking susceptibility is enhanced.

[0075]

However, as described later, if the average grain diameter d (μm) at the center of the wall thickness of the alloy tube is regulated so as to be 1000 μm or smaller, and to be in the range satisfying the following formula according to the amount (%) of B contained in the alloy, the increase in liquation cracking susceptibility caused by the segregation of B can be restrained.

$$d \leq 1500 - 2.5 \times 10^5 \times B$$

where, letter B represents the content by mass percent of B.

[0076]

N: 0.02% or less

N (nitrogen) is an element effective in stabilizing austenite. If N is contained excessively in the range of Cr content of 18 to 38%, described above, large amounts of fine nitrides precipitate in the grains during the use at high temperatures, and the creep ductility and toughness are decreased. Therefore, the upper limit is placed, and the N content is set to 0.02% or less. The N content is preferably 0.015% or less.

[0077]

The lower limit of N content need not be placed especially. However, if the N content decreases extremely, the effect of stabilizing austenite is less liable to be achieved, and the production cost also increases greatly. Therefore, the preferable lower limit of N content is 0.0005%.

[0078]

O: 0.008% or less

O (oxygen) is contained in the alloy as an impurity. If O is contained excessively, the hot workability is decreased, and further, the toughness and ductility are deteriorated. Therefore, the upper limit is placed, and the O content is set to 0.008% or less. The O content is preferably 0.005% or less.

[0079]

The lower limit of O content need not be placed especially. However, if the O content decreases extremely, the production cost increases. Therefore, the preferable lower limit of O content is 0.0005%.

[0080]

Next, any of Zr, Nb and V combines with C or N to form carbides or carbo-nitrides, and contributes to the improvement in creep strength. Therefore, the seamless austenitic heat-resistant alloy tube of the present invention is caused to contain, in addition to the above-described elements

ranging from C to O, one or more kinds of elements of Zr: 0.01 to 0.5%, Nb: 0.01 to 0.5%, and V: 0.01 to 0.5%.

[0081]

Zr: 0.01 to 0.5%

Zr (zirconium) combines with C or N to form fine carbides or carbonitrides, and contributes to the improvement in creep strength. In order to achieve this effect, 0.01% or more of Zr must be contained. However, if Zr is contained excessively, it precipitates in large amounts as carbides or carbonitrides, and therefore the creep ductility is decreased. Therefore, the upper limit is placed, and the Zr content is set to 0.01 to 0.5%. The preferable lower limit of Zr content is 0.015%, and the preferable upper limit thereof is 0.4%.

[0082]

Nb: 0.01 to 0.5%

Nb (niobium) combines with C or N to form fine carbides or carbonitrides, and contributes to the improvement in creep strength. In order to achieve this effect, 0.01% or more of Nb must be contained. However, if Nb is contained excessively, it precipitates in large amounts as carbides or carbonitrides, and therefore the creep ductility is decreased. Therefore, the upper limit is placed, and the Nb content is set to 0.01 to 0.5%. The preferable lower limit of Nb content is 0.015%, and the preferable upper limit thereof is 0.4%.

[0083]

V: 0.01 to 0.5%

V (vanadium) combines with C or N to form fine carbides or carbonitrides, and contributes to the improvement in creep strength. In order to achieve this effect, 0.01% or more of V must be contained. However, if V is contained excessively, it precipitates in large amounts as carbides or carbonitrides, and therefore the creep ductility is decreased. Therefore, the upper

limit is placed, and the V content is set to 0.01 to 0.5%. The preferable lower limit of V content is 0.015%, and the preferable upper limit thereof is 0.4%.

[0084]

Only any one kind of Zr, Nb and V can be contained, or two or more kinds of these elements can be contained compositely. The total amount in the case where these elements are contained compositely may be 1.5%; however, the total amount is preferably 1.2% or less.

[0085]

One of the seamless austenitic heat-resistant alloy tubes of the present invention is an alloy tube having the chemical composition consisting of the above-described elements, the balance being Fe and impurities.

[0086]

As described already, the "impurities" mean impurity elements mixed from ore and scrap used as a raw material or a production environment when the austenitic heat-resistant alloy is produced on an industry basis.

[0087]

Another of the seamless austenitic heat-resistant alloy tubes of the present invention is an alloy tube having the chemical composition containing, in lieu of a part of Fe, one or more elements selected from Mo, Cu, Co, Ca, Mg and REM.

[0088]

Hereunder, the operational advantages of these optional elements and the reasons for restricting the contents thereof are explained.

[0089]

Any of Mo, Cu and Co belonging to the <1> group has a function of improving the creep strength. Therefore, these elements may be contained.

[0090]

Mo: 1% or less

Mo (molybdenum) has a function of improving the creep strength. That is, Mo dissolves in matrix and has a function of improving the creep strength at high temperatures. Therefore, Mo may be contained. However, if Mo is contained excessively, the stability of austenite is decreased, and the creep strength is rather decreased. Therefore, the upper limit of the amount of Mo, if contained, is placed, and the Mo content is set to 1% or less.

[0091]

On the other hand, in order to stably achieve the above-described effect of Mo, the Mo content is preferably 0.1% or more.

[0092]

Cu: 1% or less

Cu (copper) has a function of improving the creep strength. That is, Cu is, like Ni, an austenite forming element, and therefore enhances the phase stability and contributes to the improvement in creep strength. Therefore, Cu may be contained. However, if Cu is contained excessively, the hot workability is decreased. Therefore, the upper limit of the amount of Cu, if contained, is placed, and the Cu content is set to 1% or less.

[0093]

On the other hand, in order to stably achieve the above-described effect of Cu, the Cu content is preferably 0.02% or more.

[0094]

Co: 1% or less

Co (cobalt) has a function of improving the creep strength. That is, Co is, like Ni and Cu, an austenite forming element, and therefore enhances the phase stability and contributes to the improvement in creep strength. Therefore, Co may be contained. However, Co is a very expensive element, so

that the excessive containing of Co leads to a significant increase in cost. Therefore, the upper limit of the amount of Co, if contained, is placed, and the Co content is set to 1% or less.

[0095]

On the other hand, in order to stably achieve the above-described effect of Co, the Co content is preferably 0.02% or more.

[0096]

Only any one kind of Mo, Cu and Co can be contained, or two or more kinds of these elements can be contained compositely. The total amount in the case where these elements are contained compositely may be 3%.

[0097]

Any of Ca, Mg and REM belonging to the <2> group has a function of improving the hot workability. Therefore, these elements may be contained.

[0098]

Ca: 0.05% or less

Ca (calcium) has a function of improving the hot workability. Therefore, Ca may be contained. However, if Ca is contained excessively, it combines with O, and remarkably decreases the cleanliness, so that the hot workability is rather deteriorated. Therefore, the upper limit of the amount of Ca, if contained, is placed, and the Ca content is set to 0.05% or less.

[0099]

On the other hand, in order to stably achieve the above-described effect of Ca, the Ca content is preferably 0.0005% or more.

[0100]

Mg: 0.05% or less

Mg (magnesium) has, like Ca, a function of improving the hot workability. Therefore, Mg may be contained. However, if Mg is contained

excessively, it combines with O, and remarkably decreases the cleanliness, so that the hot workability is rather deteriorated. Therefore, the upper limit of the amount of Mg, if contained, is placed, and the Mg content is set to 0.05% or less.

[0101]

On the other hand, in order to stably achieve the above-described effect of Mg, the Mg content is preferably 0.0005% or more.

[0102]

REM: 0.1% or less

REM (rare-earth metal) has a function of improving the hot workability. That is, REM has a strong affinity for S, and contributes to the improvement in hot workability. Therefore, REM may be contained. However, if REM is contained excessively, it combines with O, and remarkably decreases the cleanliness, so that the hot workability is rather deteriorated. Therefore, the upper limit of the amount of REM, if contained, is placed, and the REM content is set to 0.1% or less.

[0103]

On the other hand, in order to stably achieve the above-described effect of REM, the REM content is preferably 0.0005% or more.

[0104]

As described already, the "REM" is the general term of a total of seventeen elements consisting of Sc, Y, and lanthanoids, and the REM content means the total content of one kind or two or more kinds of elements of the REM.

[0105]

The REM is generally contained in a Mischmetal. Therefore, REM may be contained by being added in a form of Mischmetal so that the REM content is in the above-described range.

[0106]

Only any one kind of Ca, Mg and REM can be contained, or two or more kinds of these elements can be contained compositely. The total amount in the case where these elements are contained compositely may be 0.2%.

[0107]

(B) Average grain diameter at the center of the wall thickness of the tube:

The average grain diameter d μm at the center of the wall thickness of the tube must be 1000 μm or smaller and must satisfy the formula expressed by

$$d \leq 1500 \cdot 2.5 \times 10^6 \times B$$

according to the amount of B contained in the alloy. In this formula, letter B represents the content (mass%) of B.

[0108]

First, in the case where the average grain diameter at the center of the wall thickness of the tube is larger than 1000 μm , the toughness and ductility are decreased remarkably. Further, the grain diameter of HAZ near the fusion boundary also increases, in other words, the grain boundary area per unit volume decreases. Therefore, even if the upper limit of amount of B contained in the tube is controlled to 0.01%, the liquation cracking caused by the segregation of B cannot be prevented.

[0109]

On the other hand, even if the average grain diameter d at the center of the wall thickness of the tube is 1000 μm or smaller, in the case where the average grain diameter d does not satisfy the formula of

$$d \leq 1500 \cdot 2.5 \times 10^5 \times B,$$

B is segregated in large amounts in the high-temperature HAZ near the fusion boundary, so that the fusing point of grain boundary is lowered, and the liquation cracking susceptibility of HAZ is enhanced. Therefore, the liquation cracking cannot be prevented.

[0110]

Depending on the chemical composition of tube, for example, by subjecting the tube to solid solution heat treatment by holding the tube in the temperature range of 1150 to 1250°C for 0.5 to 5 hours, the average grain diameter d at the center of the wall thickness of the tube can be made such as to be 1000 μm or smaller and to satisfy the formula of " $d \leq 1500 \cdot 2.5 \times 10^5 \times B$ ".

[0111]

(C) Thickness of oxide layer on outer surface of tube:

The oxide film formed on the surface of the seamless austenitic heat-resistant alloy tube of the present invention, having the chemical composition described in the above item (A), has a high fusing point. Moreover, this oxide film deteriorates the wettability with molten metal when the outer surface of tube is fillet-welded. Therefore, if the thickness of oxide layer on the outer surface of tube increases, the toe angle of weld bead (excess weld metal) becomes large, so that stresses are easily concentrated on the HAZ, and liquation cracking is liable to occur. Therefore, the upper limit of the thickness of oxide layer on the outer surface of tube is placed, and the thickness is set to 15 μm or smaller. The thickness of oxide layer on the outer surface of tube is preferably 10 μm or smaller.

[0112]

For example, by performing the solid solution heat treatment, in which the tube is held in the temperature range of 1150 to 1250°C for 0.5 to 5 hours,

in a reducing gas such as hydrogen, the thickness of oxide layer on the outer surface of tube can be made 15 μm or smaller stably.

[0113]

Also, in the case where the solid solution heat treatment described in the above item (B) is performed in the atmosphere or in a combustion gas, and oxide scale (oxide layer) is formed, the thickness of oxide layer on the outer surface of tube can be made 15 μm or smaller stably by performing treatment such as pickling, grinding, or shot blasting.

[0114]

The lower limit of the thickness of oxide layer on the outer surface of tube need not be placed especially.

[0115]

For example, the thickness of oxide layer on the outer surface of tube may be made in a state close to 0 μm by performing the solid solution heat treatment in a reducing gas or by performing treatment such as pickling, grinding, or shot blasting. Also, the thickness of oxide layer may be made zero by performing mechanical grinding to remove the oxide layer on the outer surface of tube. However, an extreme decrease in thickness of oxide layer on the outer surface of tube leads to the increase in production cost. Therefore, the thickness of oxide layer on the outer surface of tube is preferably 0.1 μm or larger, further preferably 0.2 μm or larger.

[0116]

Hereunder, the present invention is explained more specifically with reference to examples; however, the present invention is not limited to these examples.

EXAMPLE(S)

[0117]

Various alloys having the chemical compositions given in Table 1 were melted using a 180-kg vacuum induction melting furnace by using the ordinary method, the molten alloys were formed into ingots, and then the ingots were hot-forged to prepare billets.

[0118]

Each of the billets thus obtained was hot piercing-rolled by using a model mill, and a seamless tube having an outside diameter of 38 mm and a wall thickness of 9 mm was produced.

[0119]

TABLE 1

Alloy	Chemical Composition (mass %) Balance Fe and Impurities																
	C	Si	Mn	P	S	Ni	Cr	N	Ti	Al	B	H	O	Zr	Nb	V	Other Elements
A	0.09	0.29	0.92	0.010	0.001	44.8	22.8	8.89	0.09	0.03	0.0047	0.008	0.005	-	0.18	-	Mo:0.18
B	0.08	0.18	1.04	0.009	0.001	45.2	22.7	8.73	0.10	0.03	0.0014	0.007	0.008	-	0.23	-	-
C	0.08	0.19	1.08	0.010	0.001	45.8	22.8	7.87	0.10	0.02	0.0017	0.007	0.005	-	0.23	-	Ca:0.004
D	0.08	0.17	1.02	0.011	0.001	49.8	28.8	3.99	0.81	0.10	0.0039	0.008	0.005	0.02	0.01	-	-
E	0.08	0.17	1.01	0.012	0.001	48.9	28.8	4.07	0.51	0.10	0.0038	0.007	0.005	0.03	0.01	0.01	Ca:0.02
F	0.08	0.18	1.02	0.015	0.001	49.9	28.9	7.82	0.80	0.10	0.0038	0.008	0.005	0.03	0.02	-	Cu:0.02, REM:0.04

[0120]

The seamless tube having an outside diameter of 38 mm and a wall thickness of 9 mm was cut to a length of 200 mm, and the cut seamless tube was subjected to solid solution heat treatment, in which the temperature was set at 1150 to 1280°C, and the holding time at those temperatures was changed in the range of 0.5 to 5 hours. Thereby, various test specimen tubes, in which the average grain diameters d at the center of the wall thickness of the tube were different, were prepared.

[0121]

Next, the outer surfaces of the obtained test specimen tubes were ground to change the oxide layer thicknesses variously.

[0122]

For each of the test specimen tubes whose outer surface had been ground after the solid solution heat treatment, the average grain diameter d at the center of the wall thickness of the tube and the thickness of oxide layer on the outer surface of tube were measured by the methods as described below.

[0123]

The average grain diameter d (μm) at the center of the wall thickness of the tube was determined as described below. Five test specimens were cut out of the front and rear portions with the central portion of the 200 mm-long test specimen tube being the reference so that the surface to be measured is the transverse surface. Each of the test specimens was cut into four pieces in the circumferential direction, the surface to be measured was mirror-polished and etched with aqua regia, and the wall thickness central portion was observed under an optical microscope.

[0124]

That is, one visual field was observed at $\times 100$ magnification per one test specimen having been cut, and average grain section length of each of twenty test specimens was measured by the cutting method. The average grain section lengths of test specimens were further arithmetically averaged, and the arithmetically averaged value was multiplied by 1.128 to determine the average grain diameter d (μm).

[0125]

The thickness of oxide layer on the outer surface of tube was determined as described below. For each test specimen tube, the twenty test specimens that had been used to measure the average grain diameter d (μm) at the center of the wall thickness of the tube as described above were mirror-polished again, and in the polished state, were observed under an optical microscope.

[0126]

That is, for each test specimen tube, each of the twenty test specimens was observed at $\times 400$ magnification to measure the thickness of oxide on the outer surface of tube. Next, the values of thicknesses of oxide on the twenty test specimens were arithmetically averaged to determine the thickness of oxide layer on the outer surface of tube.

[0127]

Further, by using each test specimen tube the outer surface of which had been polished after the solid solution heat treatment and alloy plates compared to fin plates that had the chemical composition given in Table 2, and had been cut to a 200-mm length, each having a thickness of 6 mm and a width of 15 mm, a restraint weld test body simulating the fillet-welding of a water wall tube, which is shown in Figure 1, was prepared.

[0128]

As shown in Figure 2, each of the test specimen tubes and the alloy plates were fillet-welded at four places. More specifically, by using a commercially available welding wire (AWS Standard A5.14 ER NiCrCoMo-1) and bonded flux, submerged arc welding was performed at a heat input of 12 kJ/cm.

[0129]

TABLE 2

Chemical Composition (mass %) Balance: Fe and Impurities														
C	Si	Mn	P	S	Ni	Cr	W	Ti	Al	B	N	O	Nb	Mo
0.09	0.29	0.92	0.010	0.0003	44.6	22.8	6.87	0.09	0.03	0.0013	0.008	0.006	0.18	0.13

[0130]

For each of the obtained restraint weld test bodies, five test specimens were cut out of each of four fillet-welded locations so that the surface to be tested was the transverse surface, and were mirror-polished.

[0131]

Next, the test specimens were etched with aqua regia, and were examined under an optical microscope. For a total of twenty weld zones of the restraint weld test body, the presence or absence of liquation cracking in the HAZ of test specimen tube was examined, and the liquation cracking incidence rate was determined.

[0132]

The liquation cracking incidence rate was defined as "(number of cracking occurrence sections / 20) \times 100(%)", and only the test bodies in which the liquation cracking incidence rate was zero were judged to be "acceptable", and the other test bodies were judged to be "unacceptable".

[0133]

Table 3 gives the results of the tests. Table 3 additionally gives the content of B contained in the starting material alloy of test specimen tube and the value of EQU determined from the formula of " $EQU = 1500 - 2.5 \times 10^5 \times B$ ".

[0134]

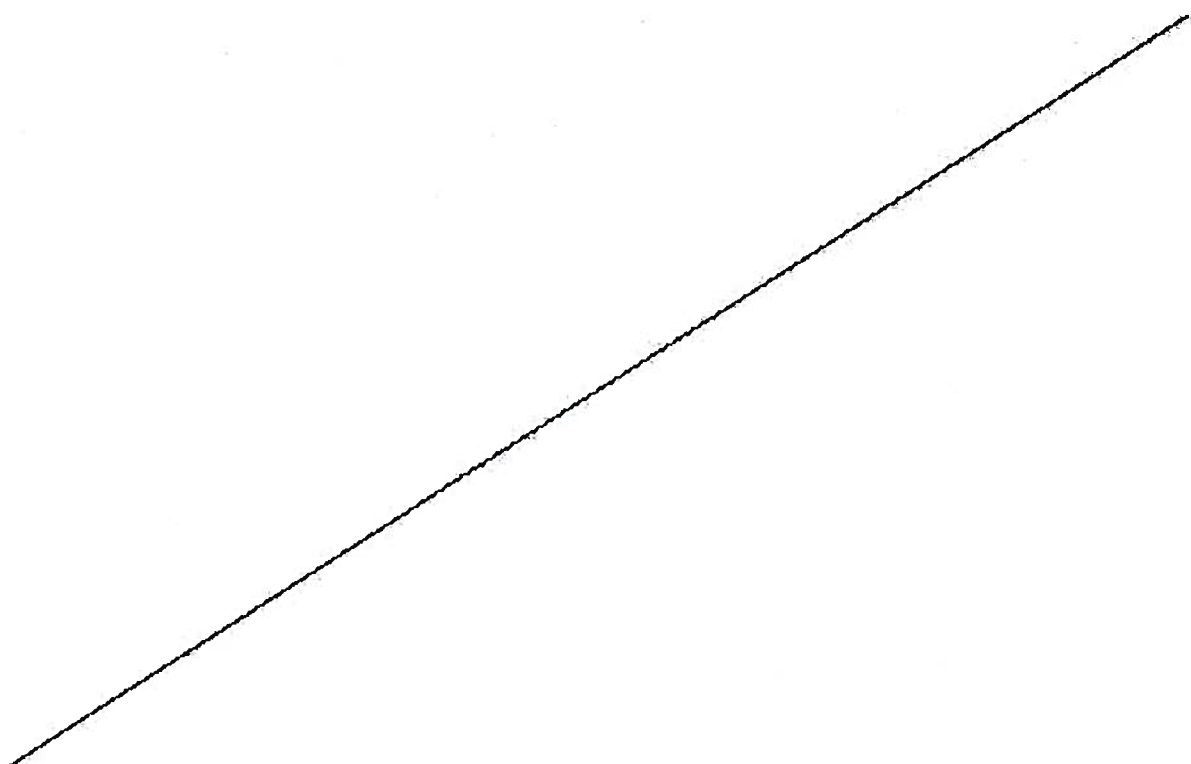


TABLE 3

Specimen Tube No.	Starting Material Alloy	Average Grain Diameter [d] (μm)	B Content of the Starting Material (%)	Value of EQU	Thickness of Oxide Layer on the Outer Surface of the Tube (μm)	Liquation Cracking Incidence Rate (%)	Evaluation	Remarks
A 1	A	275	0.0047	325	4.2	0	Acceptable	Inventive Example
A 2		* 526	0.0047	325	4.1	55	Unacceptable	Comparative Example
A 3		* 735	0.0047	325	3.8	85	Unacceptable	Comparative Example
A 4		275	0.0047	325	* 35.2	30	Unacceptable	Comparative Example
A 5		275	0.0047	325	* 20.5	15	Unacceptable	Comparative Example
A 6		275	0.0047	325	14.7	0	Acceptable	Inventive Example
A 7		275	0.0047	325	9.8	0	Acceptable	Inventive Example
B 1	B	260	0.0014	1150	3.5	0	Acceptable	Inventive Example
B 2		542	0.0014	1150	3.5	0	Acceptable	Inventive Example
B 3		794	0.0014	1150	4.2	0	Acceptable	Inventive Example
C 1	C	245	0.0017	1075	4.4	0	Acceptable	Inventive Example
C 2		503	0.0017	1075	2.9	0	Acceptable	Inventive Example
C 3		758	0.0017	1075	3.6	0	Acceptable	Inventive Example
C 4		* 1065	0.0017	1075	3.0	90	Unacceptable	Comparative Example
D 1	D	245	0.0039	525	4.0	0	Acceptable	Inventive Example
D 2		* 724	0.0039	525	3.6	80	Unacceptable	Comparative Example
E 1	E	262	0.0038	550	3.5	0	Acceptable	Inventive Example
E 2		* 741	0.0038	550	3.3	100	Unacceptable	Comparative Example
F 1	F	236	0.0038	550	2.8	0	Acceptable	Inventive Example
F 2		* 565	0.0038	550	4.1	60	Unacceptable	Comparative Example

“Average Grain Diameter” means an average grain diameter at the center of the wall thickness of the tube.

EQU = 1500 - 2.5 x 10⁵ x B

“*” means it does not satisfy the claimed condition.

[0135]

Table 3 reveals that, for test specimen tube signs A1, A6, A7, B1 to B3, C1 to C3, D1, E1 and F1, in which a seamless tube satisfying the claimed conditions, the liquation cracking incidence rate was zero, that is, in all

sections, the occurrence of liquation cracking in the HAZ was not recognized. Therefore, it is apparent that the seamless tube satisfying the claimed conditions had sufficient weld crack resistance even in the case of being used by allowing direct fillet-welding of the outer surface of tube as in the case of a water wall tube.

[0136]

On the other hand, even in the case where alloys A to F in which the chemical composition was within the claimed range were used as starting materials, in the case of test specimen tube signs in which the average grain diameter at the center of the wall thickness of the tube or the thickness of oxide layer on the outer surface of tube exceeded the claimed upper limit, liquation cracking occurred in the HAZ, so that such an alloy tube cannot be used as a water wall tube the outer surface of which is fillet-welded directly.

[0137]

For test specimen tube signs A2, A3, D2, E2 and F2, although the average grain diameter d at the center of the wall thickness of the tube was smaller than 1000 μm , the average grain diameter d did not satisfy the formula of

$$d \leq 1500 - 2.5 \times 10^5 \times B$$

defined according to the amount of B contained in the alloy. Therefore, liquation cracking occurred in the HAZ. Moreover, as the average grain diameter d increased, the liquation cracking incidence rate became higher.

[0138]

For test specimen tube sign C4, since the average grain diameter d at the center of the wall thickness of the tube exceeded 1000 μm , liquation cracking occurred in the HAZ.

[0139]

For test specimen tube signs A4 and A5, since the thickness of oxide layer on the outer surface of tube exceeded 15 μm , liquation cracking occurred in the HAZ. Moreover, as the thickness of oxide layer on the outer surface of tube increased, the liquation cracking incidence rate became higher.

INDUSTRIAL APPLICABILITY

[0140]

The seamless austenitic heat-resistant alloy tube of the present invention is excellent in weld crack resistance and capable of restraining the generation of cracks in a HAZ at the time of welding. Therefore, among seamless alloy tubes that are excellent in high temperature strength, have sufficient stress corrosion cracking resistance, and are produced using an austenitic heat-resistant alloy having a low thermal expansion coefficient as a starting material, the seamless austenitic heat-resistant alloy tube of the present invention can be used suitably as a high-temperature equipment member such as a water wall tube of power generation boiler.

We claim:

1. A seamless austenitic heat-resistant alloy tube used by fillet-welding the outer surface thereof directly, having a chemical composition consisting, by mass percent, of

C: 0.03 to 0.15%,

Si: 1% or less,

Mn: 2% or less,

P: 0.03% or less,

S: 0.01% or less,

Ni: 35 to 60%,

Cr: 18 to 38%,

W: 3 to 11%,

Ti: 0.01 to 1.2%,

Al: 0.5% or less,

B: 0.0001 to 0.01%,

N: 0.02% or less,

O: 0.008% or less, and

at least one element selected from

Zr: 0.01 to 0.5%,

Nb: 0.01 to 0.5%, and

V: 0.01 to 0.5%,

with the balance being Fe and impurities, wherein

an average grain diameter d μm at the center of the wall thickness of the tube is 1000 μm or smaller and satisfies the following formula:

$$d \leq 1500 - 2.5 \times 10^5 \times B$$

where letter B represents the content by mass percent of B;

and further,

the thickness of an oxide layer on the outer surface of the tube is 15 μm or smaller.

2. The seamless austenitic heat-resistant alloy tube according to claim 1 containing, in lieu of a part of Fe, by mass percent, at least one element selected from the elements listed in following groups <1> and <2>:

<1> Mo: 1% or less, Cu: 1% or less, and Co: 1% or less

<2> Ca: 0.05% or less, Mg: 0.05% or less, and REM: 0.1% or less.

3. The seamless austenitic heat-resistant alloy tube according to claims 1 and 2, wherein the tube is used as a water wall tube.

Dated this 30th day of April, 2014.

Nippon Steel & Sumitomo Metal Corporation

Dev Robinson

(Dev Robinson)

of Amarchand & Mangaldas &
Suresh A. Shroff & Co.

Attorneys for the Applicant

Figure 1

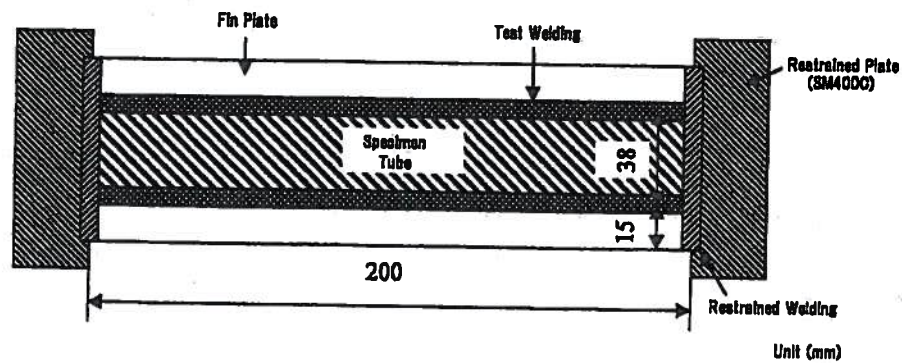
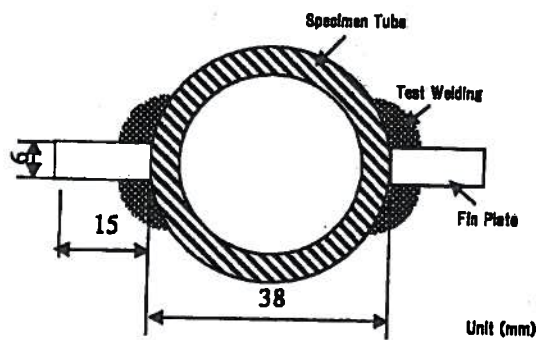


Figure 2



Dev Robinson

(DEV ROBINSON)
OF AMARCHAND & MANGALDAS &
SURESH A. SHROFF & CO.
ATTORNEYS FOR THE APPLICANT

SEAMLESS AUSTENITIC HEAT-RESISTANT ALLOY TUBE

ABSTRACT

A seamless austenitic heat-resistant alloy tube used by fillet-welding the outer surface thereof directly, having a chemical composition consisting, by mass percent, of C: 0.03-0.15%, Si \leq 1%, Mn \leq 2%, P \leq 0.03%, S \leq 0.01%, Ni: 35-60%, Cr: 18-38%, W: 3-11%, Ti: 0.01-1.2%, Al \leq 0.5%, B: 0.0001-0.01%, N \leq 0.02%, and O \leq 0.008%, and at least one element selected from Zr: 0.01-0.5%, Nb: 0.01-0.5%, and V: 0.01-0.5%, with the balance being Fe and impurities, wherein an average grain diameter d μ m at the center of the wall thickness of the tube is 1000 μ m or smaller and satisfies the formula ($d \leq 1500 - 2.5 \times 10^5 \times B$), the thickness of an oxide layer on the outer surface of the tube is 15 μ m or smaller. The tube of the present invention is excellent in weld crack resistance and capable of restraining the generation of cracks in a HAZ at the time of welding.