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(54) **FERRITE HEAT RESISTANT STEEL**

(57) There is provided a heat resistant ferritic steel, excellent in the weld crack resistance of the HAZ and creep strength. A high-Cr heat resistant ferritic steel is **characterized by** consisting of, by mass%, Si: more than 0.1% and not more than 1.0%, Mn: 2.0% or less, Co: 1 to 8%, Cr: 7 to 13%, V: 0.05 to 0.4%, Nb: 0.01 to 0.09%, either one or both of Mo and W: 0.5 to 4% as a total, B: 0.005 to 0.025%, Al: 0.03% or less, and N: 0.003 to 0.06%, and containing C in an amount satisfying Expression (1), the balance being Fe and impurities, and O, P

and S as impurities being such that O: 0.02% or less, P: 0.03% or less, and S: 0.02% or less, respectively,

$$0.005 \leq C \leq (-5/3) \times B + 0.085 \dots (1)$$

in which C and B represent the content of each element (mass%). Furthermore, the high-Cr heat resistant ferritic steel may contain one or more kinds selected from the group consisting of Nd, Ta, Ca and Mg.

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**Description**

## Technical Field

5 **[0001]** The present invention relates to a heat resistant ferritic steel excellent in the high-temperature strength and weld crack resistance in a weld heat-affected zone, which is used as members for high temperature services, such as thermal power generation boilers.

## Background Art

10 **[0002]** In recent years, in the thermal power generation, efforts are being made toward higher temperatures and higher pressure steam conditions in order to improve thermal efficiency. Also a new plant will be opened under ultra super critical pressure conditions of 650°C and 350 atmospheric pressures. Heat resistant ferritic steels are widely used because they are inexpensive compared to austenitic stainless steels and have small coefficients of thermal expansion, which is the advantage for heat resistant steels.

15 **[0003]** For heat resistant ferritic steels, efforts have been made to increase strength in order to cope with severer steam conditions in the future. In Patent Document 1 and Patent Document 2, for example, it has been proposed to optimize the W and Mo contents and to add Co and B to the steels. Patent Document 3 proposes a steel strengthened by a fine intermetallic compound phase with the addition of W and Mo. Patent Document 4 proposes a steel having improved strength by using the phase of  $M_{23}C_6$ -based carbides and intermetallic compounds which precipitate at the martensite lath interface.

20 **[0004]** However, when these heat resistant ferritic steels are used in welded structures, the creep strength may be significantly decreased in a weld heat-affected zone (hereinafter referred to as the "HAZ") subjected to a thermal cycle due to welding, as shown, for example, in Non-Patent Document 1. For this reason, the problem is that the advantage of steels whose strength is increased cannot be adequately made use of. Hence, steels have been proposed which are intended to increase not only the strength of the steel itself, but also to increase the creep strength of HAZ subjected to a weld thermal cycle.

25 **[0005]** For example, Patent Document 5 discloses a steel whose long-time creep strength of joints is improved by producing Ti-, Zr- and Hf-based nitrides which are stable in spite of weld heat input; Patent Document 6 discloses a steel similarly improved by adding W and causing (Nb, Ta) carbo-nitrides to finely precipitate. Patent Document 7 and Patent Document 8 disclose steels similarly improved by suppressing the formation of Cr carbides and increasing the long-time stability of fine carbo-nitrides, such as V and Nb. Although various methods for improving the strength of the HAZ by making use of carbo-nitrides have been proposed as described above, a further improvement of HAZ strength is desired in terms of practical use.

30 **[0006]** Furthermore, Patent Document 9 proposes a method that involves suppressing the grain refinement in the HAZ by adding 0.003 to 0.03% of B, thereby improving the creep strength in the HAZ. Although B is known well as an element having such an effect, B is also known well as an element that increases the susceptibilities of the solidification cracking in a weld metal and also of the liquation cracking in its HAZ. For this reason, the problem is that when the steel is used as thick wall members in main steam pipes for boilers, pressure vessels and the like, this steel does not have sufficient weldability (weld crack resistance).

**[0007]**

[Patent Document 1] JP4-371551A

[Patent Document 2] JP4-371552A

45 [Patent Document 3] JP2001-152293A

[Patent Document 4] JP2002-241903A

[Patent Document 5] JP8-85848A

[Patent Document 6] JP9-71845A

50 [Patent Document 7] JP2001-279391A

[Patent Document 8] JP2002-69588A

[Patent Document 9] JP2004-300532A

[Non-Patent Document 1] Science and Technology of Welding and Joining, 1996, Vol. 1, No. 1, pp. 36-42

## Disclosure of the Invention

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## Problems to be Solved by the Invention

**[0008]** Since heat resistant ferritic steels have the advantage of small coefficients in thermal expansion in addition to

inexpensiveness as described above, it is expected that these steels are used in welded structures in thermal power generation boilers and the like for which efforts are being made toward higher temperature and higher pressure steam conditions.

**[0009]** And as described above, in order to ensure that heat resistant ferritic steels can be used under conditions of still higher temperatures and pressures, various proposals have been made to improve the HAZ creep strength of welded joints in addition to further strength improvement. However, the problem is not only that the strength improvement of the HAZ is still insufficient, but also that sufficient weld crack resistance during welding is not obtained.

**[0010]** The present invention has been made in view of such a situation, and its objective is to provide a heat resistant ferritic steel which is excellent in the weld crack resistance of the HAZ and is also superior in creep strength.

#### Means for Solving the Problems

**[0011]** It has been found that, in order to improve the creep strength of the HAZ, it is effective to limit the Cr, Co, V and Nb contents to prescribed ranges and to add B. However, it has been found that, when B is added in an amount necessary for increasing HAZ strength, the cracking susceptibilities of the HAZ and weld metal increase, posing a problem in weld crack resistance.

**[0012]** Hence, the inventors have found that in order to improve the creep strength in the HAZ and also to ensure excellent weldability, optimizing the contents of C and B is effective as follows. The heat resistant ferritic steel, in accordance with the present invention, sets a target value of rupture time for the creep strength in the HAZ of not less than three times, and preferably not less than five times that of conventional steels.

**[0013]** As a result of examinations and investigations, it was ascertained that in a ferritic steel, having the composition ranges of Cr: 7 to 13%, Co: 1 to 8%, V: 0.05 to 0.4% and Nb: 0.01 to 0.09%, the HAZ strength is increased by the addition of B.

**[0014]** One of the reasons why the creep strength is lowered in the HAZ rather than in the base metal is that grain refinement occurs due to a weld thermal cycle heating the HAZ to a temperature between the  $Ac_1$  transformation point and the  $Ac_3$  transformation point. When the ferritic phase or tempered martensitic phase, which is the original microstructure, is heated to this temperature range, new nuclei of the austenitic phase forms and grow at the grain boundaries, whereby grain refinement occurs. B is an element that is apt to segregate at the grain boundaries. When heated to this temperature range, B reduces the energy at the grain boundaries by segregating at the grain boundaries of the original ferritic phase, and B suppresses grain refinement by suppressing and retarding the nucleation of the austenitic phase. The inventors considered that this results in an improvement in the creep strength in the HAZ.

**[0015]** However, it has been found that when B is added in an amount larger than the amount at which the creep strength improving effect is obtained, the susceptibilities of the solidification cracking in a weld metal and of the liquation cracking in its HAZ increase.

**[0016]** This is caused by the addition of B. B is an element which is apt to segregate at the grain boundaries and also lowers melting points significantly. S and P are elements that are apt to undergo grain-boundary segregation and also lower melting points significantly. The inventors considered that, in the HAZ in the close vicinity of a fusion line, the grain-boundary segregation of P and S, in addition to the grain-boundary segregation of B, cause grain-boundary melting and an opening due to thermal stress or external stress, which results in liquation cracking.

**[0017]** It is possible to prevent the solidification cracking in a weld metal by adjusting the components of the welding materials. On the other hand, the liquation cracking in the HAZ is related to the composition of the steel used, and this constitutes a significant restriction in actual use. In view of these problems, the inventors earnestly examined the requirements in order to be able to prevent the liquation cracking of the HAZ and also to increase the strength of the HAZ.

**[0018]** As a result of repeated investigations, the inventors obtained the new knowledge that only the restriction of the C content within a prescribed range can prevent the liquation cracking. The inventors considered the reason for this as follows.

**[0019]** C, like B, acts as a melting point lowering element and increases the liquation cracking susceptibility in the HAZ by adding to the above-described melting point lowering action of B. For this reason, the inventors considered that it becomes possible to reduce the lowering of a melting point by lowering the C content according to the B content. From thermodynamic theoretical calculations the inventors were able to find  $(-5/3) \times [\%B] + 0.085$  for the upper limit of the C content (%) which causes the solidification brittle temperature range (BTR) in the ranges of Cr: 7 to 13%, Co: 1 to 8%, V: 0.05 to 0.4% and Nb: 0.01 to 0.09%, which are the basic alloy components of the present invention, to decrease to 100°C or less, at which liquation cracking can be sufficiently prevented in terms of practical use. In this expression, [%B] represents the B content (mass%) in steel, the same of which is applied hereinafter..

**[0020]** In addition, C has an effect on the free energy in the formation of sulfides and phosphides through its interaction with them. That is, at high temperatures, the solubility of sulfides or phosphides of Cr, Nd and the like decreases with increasing C content, and when the C content further increases, the solubility of these sulfides or phosphides has a tendency to increase again. When the solubility of sulfides and phosphides increases, the amounts of S and P increase,

which segregate at the grain boundaries due to the thermal effect of welding and the like, and the liquation cracking susceptibility increases. For this reason, in the case of the C content range of the present invention in which the amount of C is reduced, the solubility of sulfides and phosphides decreases and stable compounds are formed. The inventors considered that as a result, the amounts of S and P at the grain boundaries decrease and the liquation cracking of the HAZ is prevented by the synergistic action of the suppression of a melting point decrease.

**[0021]** Furthermore, the inventors obtained the new knowledge that adding B and lowering content of C results in preventing liquation cracking, and also results in improving more the creep strength in the HAZ, when compared to the case of adding B but not lowered content of C.

**[0022]** The inventors considered the reason for this as follows. The lowering content of C to a prescribed range decreases the amount of carbides present at the grain boundaries. Then, the pinning effect is small even when heating is performed to a temperature between the  $Ac_1$  transformation point and the  $Ac_3$  transformation point, and the austenitic phase forms nuclei at the grain boundaries and, therefore, crystal grains are apt to coarsen readily. As a result, the grain refinement suppressing effect in the HAZ increases due to the combined effect of the nucleation suppression by the addition of B. Furthermore, since the growth rate of fine carbo-nitrides of V and Nb in the grains, which contribute to the strengthening of a ferritic steel, is suppressed, the degree of strengthening of the creep strength may increase, when compared to the case of adding B but not lowered content of C.

**[0023]** However, when the C content is extremely lowered, the amount of formed fine carbo-nitrides of V and Nb, which contribute to matrix strengthening, is small and it becomes impossible to sufficiently obtain the strengthening effect of the fine carbo-nitrides of V and Nb. Hence, the lower limit to the C content should be set at 0.005% or more in order to have the strength improving effect.

**[0024]** As a result of these investigations, in order to prevent the liquation cracking of the HAZ and in order to improve the creep strength of the HAZ, it is necessary that the B content be 0.005 to 0.025% and that the condition given by  $0.005 \leq C \leq (-5/3) \times [ \%B ] + 0.085$  be satisfied.

**[0025]** The present invention has been completed on the basis of the above-described new knowledge and the gist of the heat resistant ferritic steel in accordance with the present invention is as described in items (1) to (3) below. Hereinafter, these items are referred to as invention (1) to invention (4) respectively, and are sometimes generically referred to as the present invention.

**[0026]**

(1) A high-Cr heat resistant ferritic steel characterized by consisting of, by mass%, Si: more than 0.1% and not more than 1.0% , Mn: 2.0% or less, Co: 1 to 8%, Cr: 7 to 13%, V: 0.05 to 0.4%, Nb: 0.01 to 0.09%, either or both of Mo and W: 0.5 to 4% as a total, B: 0.005 to 0.025%, Al: 0.03% or less, and N: 0.003 to 0.06%, and containing C in an amount satisfying Expression (1), the balance being Fe and impurities, and O, P and S as impurities being O: 0.02% or less, P: 0.03% or less, and S: 0.02% or less, respectively,

$$0.005 \leq C \leq (-5/3) \times B + 0.085 \dots (1)$$

in which C and B represent the content of each element (mass%).

**[0027]**

(2) The high-Cr heat resistant ferritic steel according to item (1) above characterized by containing, by mass%, Nd: 0.08% or less in place of part of Fe.

**[0028]**

(3) The high-Cr heat resistant ferritic steel according to item (1) or (2) above characterized by containing, by mass%, Ta: 0.08% or less in place of part of Fe.

**[0029]**

(4) The high-Cr heat resistant ferritic steel according to any one of items (1) to (3) above characterized by containing, by mass%, either or both of Ca: 0.02% or less and Mg: 0.02% or less in place of part of Fe.

Advantages of the Invention

**[0030]** The heat resistant ferritic steel in accordance with the present invention is excellent in the weld crack resistance

in the HAZ and has superior creep strength in the HAZ.

#### Best Mode for Carrying Out the Invention

5 **[0031]** The claimed scope of the steel in accordance with the present invention will be described below. The symbol "%" represents mass%.

**[0032]** C: 0.005% or more and  $\{(-5/3) \times [\%B] + 0.085\}$ % or less

C (carbon) along with B is an important element in the present invention. C is an essential element because C forms carbides and contributes to ensuring high-temperature strength, and because C is an element effective in obtaining a martensitic microstructure. However, when C segregates at the grain boundaries, C promotes to lower the melting point at the grain boundaries along with the effect of B, S and P and is indirectly responsible for the formation of sulfides and phosphides in the coarse-grained HAZ. Thereby it has an exerting effect on the liquation cracking susceptibility. When the C content is lowered, in the fine-grained HAZ, C has an improved creep strength due to the effects of the promotion of crystal grain coarsening during transformation and the suppression of the growth of fine carbides. The lowering of the melting point at the grain boundaries is caused by the C itself, and it is suppressed. Stable sulfides and phosphides are formed in the coarse-grained HAZ, whereby liquation cracking is prevented by suppressing the lowering of the melting point which is caused by the grain-boundary segregation of S and P, and at the same time the creep strength of a fine-grained HAZ is improved. For this purpose, as described later, the B content is defined in a specific range and it is necessary that the C content be in the range of 0.005% or more and  $\{(-5/3) \times [\%B] + 0.085\}$ % or less. A preferred lower limit of the C content is 0.010%.

**[0033]** Si: more than 0.1% and not more than 1.0%

Si (silicon) is added in amounts exceeding 0.1 % as a deoxidizer. However, if Si is added excessively, this causes the deterioration of creep ductility and toughness, so the upper limit is 1.0%, preferably 0.8%. The Si content is more preferably in the range of more than 0.2% and not more than 0.7%.

**[0034]** Mn: 2.0% or less

Like Si, Mn (manganese) is added as an deoxidizer. However, if Mn is added excessively, this causes creep embrittlement and the deterioration of toughness. For this reason, the Mn content is 2.0% or less. The Mn content is preferably 1.8% or less. However, if the Mn content is lowered excessively, the sufficient deoxidation effect is not obtained and the cleanliness of the steel is deteriorated. In addition, this results in an increase in the manufacturing cost. For this reason, it is preferred that 0.01% or more of Mn be added, although no lower limit is set.

**[0035]** Co: 1 to 8%

Co (cobalt) is an austenite former and is an element necessary for the martensitizing of a matrix. To obtain this effect, it is necessary that 1% or more of Co be added. However, if Co is added in an amount exceeding 8%, this causes a remarkable decrease in creep ductility. The Co content is preferably in the range of over 2% and 7% or less.

**[0036]** Cr: 7 to 13%

Cr (chromium) is an element essential for ensuring oxidation resistance and high-temperature corrosion resistance in heat resistant steels and for obtaining a martensitic microstructure of a matrix in a stable manner. To obtain this effect, it is necessary that 7% or more of Cr be added. However, if Cr is added excessively, this lowers the stability of carbides caused by the formation of a large amount of Cr carbides, which results in decreases in creep strength and toughness. For this reason, it is necessary that the Cr content be 13% or less. The Cr content is preferably in the range of 8 to 12%, more preferably in the range of 8 to 10%.

**[0037]** V: 0.05 to 0.4%

V (vanadium) is an element which, along with Nb, forms fine carbo-nitrides in the grains and contributes significantly to the improvement of creep strength. To obtain this effect, it is necessary that 0.05% or more of V be added. However, if V is added excessively, this results in an increase in the growth rate of carbo-nitrides, which causes an early loss of the dispersion strengthening effect, and also results in a decrease in toughness. Therefore, it is necessary that the V content be 0.4% or less. The V content is preferably in the range of 0.10 to 0.35%.

**[0038]** Nb: 0.01 to 0.09%

Nb (niobium) is an element which, along with V, forms stable fine carbo-nitrides at temperatures up to high levels in the grains and contributes significantly to the improvement of creep strength. To obtain this effect, it is necessary that at least 0.01 % or more of Nb be added. However, if Nb is added excessively, this results in an increase in the growth rate of carbo-nitrides, which causes an early loss of the dispersion strengthening effect, and also this results in a decrease in toughness. Therefore, it is necessary that the Nb content be 0.09% or less.

**[0039]** Either one or both of Mo and W: 0.5 to 4% (as a total)

Mo (molybdenum) and W (tungsten) are elements which perform the solid-solution strengthening of a matrix and contribute to the improvement of creep strength. To obtain this effect, it is necessary that either one or both of Mo and W be added in amounts of 0.5% or more as a total. However, if these elements are added excessively in amounts exceeding 4%, this forms coarse intermetallic compounds and results in an extreme decrease in toughness. Also, when W is singly

added, it is preferred that the lower limit of the W content be 1 %.

**[0040]** B: 0.005 to 0.025%

B (boron) along with C is an important element in the present invention. B segregates at the grain boundaries in the HAZ and lowers the grain-boundary energy, thereby delaying the nucleation of the austenitic phase and suppressing grain refinement. To obtain this effect sufficiently, it is necessary that at least 0.005% or more of B be added.

However, in a coarse-grained HAZ, B that segregates at the grain boundaries promotes lowering the melting point of the grain boundaries and causes liquation cracking to occur by adding to the effect of the segregation of S and P. To prevent this, it is necessary that the C content be defined in the above-described range. However, if the B content exceeds 0.025%, the HAZ creep strength improving effect becomes saturated and it is impossible to prevent liquation cracking even when the C content is defined in the above-described range. It is preferred that the lower limit of the B content be 0.007% or more. A more preferred range of the B content is from over 0.01 % to 0.02% or less.

**[0041]** N: 0.003 to 0.06%

N (nitrogen) is an element which forms fine carbo-nitrides including V and Nb and is effective in ensuring creep strength. To obtain this effect, it is necessary that 0.003% or more of N be added. However, if N is added excessively, this results in an increase in the precipitation amount of carbo-nitrides and causes embrittlement. For this reason, the upper limit of the N content is 0.06%.

**[0042]** Al: 0.03% or less

Al (aluminum) is added as a deoxidizer. However, if Al is added excessively, this results in a decrease in creep ductility and toughness. Therefore, the upper limit of the Al content is 0.03%. The upper limit of the Al content is preferably 0.02% or less.

However, if the Al content is lowered excessively, a sufficient deoxidation effect is not obtained and the cleanliness of steel is deteriorated. In addition, this results in an increase in the manufacturing cost. For this reason, it is preferred that 0.001% or more of Al be added, although no lower limit is set.

**[0043]** O: 0.02% or less

O (oxygen) exists as an impurity. However, if a large amount of O is contained, this forms a large amount of oxides, deteriorating workability and ductility. For this reason, it is necessary that the O content be 0.02% or less.

P: 0.03% or less

P (phosphorus) is contained as an impurity. P along with S and B segregates at the grain boundaries in a coarse-grained HAZ, and this results in liquation cracking by lowering the melting point. To prevent this, it is necessary that C, Nb, S and B be defined in prescribed ranges and that the P content be 0.03% or less.

**[0044]** S: 0.02% or less

Like P, S (sulfur) is contained as an impurity. S segregates at the grain boundaries in a coarse-grained HAZ, and this results in liquation cracking by lowering the melting point. To prevent this, it is necessary that C, Nb, S and P be defined in prescribed ranges and that the S content be 0.02% or less.

**[0045]** In the steel of the present invention, the following elements can be added in prescribed amounts as required.

**[0046]** Nd: 0.08% or less

Nd (neodymium) has a strong affinity for P and S. Nd forms compounds with S and P at the grain boundaries of a coarse-grained HAZ, thereby suppressing lowering of the melting point by S and P and preventing the liquation cracking of the HAZ. At the same time, Nd is effective in improving the HAZ creep ductility by reducing the grain-boundary embrittlement by S and P during use at high temperatures. Therefore, Nd may be added as required. However, because of a strong affinity for oxygen, if Nd is added excessively, this forms extra oxides and results in a decrease in the toughness of the HAZ. For this reason, the upper limit of the Nd content is 0.08%. A desirable upper limit is 0.06%. Incidentally, to positively obtain the above-described effect of the addition of Nd, it is preferred that 0.005% or more of Nd be added. It is more preferred that 0.015% or more of Nd be added.

**[0047]** Ta: 0.08% or less

Like V and Nb, Ta (tantalum) forms stable fine carbides at temperatures up to high levels and contributes significantly to the improvement of creep strength. Therefore, Ta may be added as required. However, if Ta is added excessively, this results in an increase in the growth rate of carbides, bringing about early losing of the dispersion strengthening effect, and also this results in a decrease in toughness. Therefore, the upper limit of the Ta content is 0.08% or less.

Incidentally, to obtain the above-described effect of the addition of Ta, it is preferred that 0.005% or more of Ta be added.

**[0048]** Ca: 0.02% or less

Ca (calcium) is an element which improves the hot workability of steel, and when it is necessary to improve hot workability, Ca can be added. However, if the Ca content exceeds 0.02%, this results in the coarsening of inclusions, thereby contrastively impairing workability and toughness. Therefore, the upper limit of the Ca content is 0.02%. In order to obtain the above-described effect of the addition of Ca, it is preferred that 0.0003% or more of Ca be added. A more preferred range of the Ca content is from 0.001 % to 0.01 %.

**[0049]** Mg: 0.02% or less

Like Ca, Mg (manganese) is an element which improves the hot workability of steel, and when it is necessary to improve

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hot workability, Mg can be added in a combination with Ca or singly. However, if the Mg content exceeds 0.02%, this results in the coarsening of inclusions, thereby contrastively impairing workability and toughness. Therefore, the upper limit of the Mg content is 0.02%. In order to obtain the above-described effect of the addition of Mg, it is preferred that 0.0003% or more of Mg be added. A more preferred range of the Ca content is from 0.001 % to 0.01 %.

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### Example 1

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**[0050]** The sixteen kinds of steels having the chemical compositions shown in Table 1 were melted in a vacuum furnace, and were then cast and rolled. Thereafter, the steels were normalized by air cooling after being held for 1 hour at 1150°C and were tempered by air cooling after being held for 1.5 hours at 770°C, whereby the steels were heat treated. Incidentally, No. 13 denotes a steel corresponding to SUS410J3TB, which is a conventional steel. This steel was used as a comparative steel related to creep strength. Steel plates 12 mm in thickness, 50 mm in width and 300 mm in length and steel plates 10 mm in thickness, 100 to 120 mm in width and 300 to 500 mm in length were fabricated by machining. The steel plates 12 mm in thickness were used in the longitudinal V-restraint test and the liquation cracking susceptibility of the HAZ was evaluated.

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[Table 1]

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**[0051]**

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Table 1

No	Chemical composition (mass%, the balance being Fe and impurities)																		(-5/3) ×[% B] +0.085
	C	Si	Mn	P	S	Co	Cr	Ni	W	Mo	Nb	V	Ta	Nd	Al	B	O	N	
1	0.110*	0.27	0.51	0.016	0	1.0	9.0	-	3.0	-	0.07	0.20	0.04	0.03	0.002	0.008	0.005	0.009	0.072*
2	0.096*	0.25	0.61	0.013	0	3.0	9.0	-	3.0	-	0.04	0.20	0.04	0.04	0.002	0.010	0.009	0.010	0.068*
3	0.049	0.30	0.50	0.007	0	5.0	9.0	-	3.1	-	0.04	0.19	0.06	0.03	0.002	0.012	0.004	0.009	0.065
4	0.049	0.31	0.51	0.007	0	5.1	9.0	-	2.6	-	0.04	0.19	0.06	0.03	0.001	0.012	0.005	0.010	0.065
5	0.024	0.31	0.51	0.007	0	5.1	9.0	-	2.6	-	0.04	0.19	0.06	0.03	0.002	0.012	0.005	0.010	0.065
6	0.008	0.29	0.49	0.008	0	5.1	9.1	-	2.6	-	0.04	0.19	0.06	0.03	0.001	0.012	0.010	0.011	0.065
7	0.096*	0.31	0.61	0.008	0	5.0	8.9	-	2.6	-	0.04	0.20	0.05	0.04	0.001	0.0001*	0.005	0.010	0.085*
8	0.050	0.30	0.61	0.007	0	5.0	8.9	-	2.6	-	0.04	0.20	0.05	0.04	0.001	0.0001*	0.005	0.009	0.085
9	0.010	0.29	0.49	0.007	0	5.0	8.9	-	2.6	-	0.04	0.20	0.05	0.03	0.001	0.007	0.010	0.010	0.073
10	0.025	0.30	0.50	0.010	0	5.1	10.4	-	2.6	-	0.04	0.19	-	0.04	0.002	0.010	0.004	0.011	0.069
11	0.027	0.30	0.50	0.008	0	7.1	9.2	-	2.6	-	0.04	0.20	-	0.04	0.002	0.012	0.007	0.010	0.066
12	0.001*	0.25	0.61	0.010	0.01	3.0	9.0	-	3.1	-	0.04	0.20	0.05	0.02	0.001	0.006	0.005	0.023	0.075
13	0.130	0.24	0.69	0.010	0	-*	110.6	0.3	2.1	0.4	0.05	0.25	-	-	0.001	0.001*	0.005	0.050	-
14	0.070	0.30	0.50	0.008	0	5.2	9.2	-	2.6	-	0.04	0.20	0.04	0.03	0.001	0.009	0.004	0.009	0.07
15	0.061	0.31	0.49	0.009	0	5.2	9.2	-	2.6	-	0.04	0.20	0.05	0.03	0.002	0.014	0.005	0.012	0.062
16	0.050*	0.26	0.52	0.009	0	5.1	8.9	-	2.5	-	0.04	0.20	0.05	0.04	0.003	0.025	0.004	0.010	0.043*

\* out of scope of the invention

## EP 2 157 202 A1

**[0052]** The longitudinal Varestraint test is a method of evaluating the liquation cracking susceptibility of the HAZ which involves, as schematically shown in Figure 1, performing bead-on-plate welding in the longitudinal direction of a steel plate by using GTA welding, adding a strain due to bending by loading a force F at an end of the steel plate during the welding, thereby forcedly generating cracks in the HAZ, and measuring the total length of the cracks. The welding conditions were 200 A × 15 V × 10 cm/min. The amount of added strain was 4%. Steel plates in which liquation cracking did not occur in the HAZ were accepted.

**[0053]** For steel grades in which liquation cracking did not occur in the HAZ, a test material 10 mm in thickness, 10 mm in width and 100 mm in length was sampled from a 10 mm thick steel plate. A HAZ-simulated thermal cycle was given to the test material and the test material was heated to 1000°C, at which a strength decrease in the HAZ is especially remarkable, for 5 seconds. After that, the test material was subjected to post-weld heat treatment by air cooling at 740°C for 30 minutes, and creep test specimens were taken. The creep test was performed at a temperature of 650°C and stress of 117.7 MPa.

**[0054]** Table 2 shows the weld crack length (mm) in the longitudinal Varestraint test and the rupture time (hr) in the creep test.

[Table 2]

**[0055]**

Table 2

No.	Cracking length in Varestrainttest (mm)	HAZ-simulated thermal cycle material Creep rupture time (hr)
1	0.4*	-
2	0.7*	-
3	0	7327
4	0	6074
5	0	5862
6	0	3822
7	0	1584*
8	0	2211*
9	0	7207
10	0	2536
11	0	6980
12	0	2306*
13	-	829
14	0	4463 (not ruptured)
15	0	4463 (not ruptured)
16	0.6*	-
* out of scope of the invention		

**[0056]** As is apparent from Table 2, in the materials of Nos. 3 to 6, 9 to 11, 14 and 15 whose C and B contents satisfy the defined ranges of the present invention. the expression (1), the liquation cracking of the HAZ did not occur even in the severe test for cracks, such as the longitudinal Varestraint test, and the creep rupture time of the HAZ was not less than three times that of No. 13. In particular, in the materials of Nos. 3 to 5, 9, 11, 14 and 15, the creep rupture time of the HAZ was not less than five times that of No. 13.

**[0057]** However, in the materials of Nos. 1, 2 and 16, whose B contents are in the defined range of the present invention but whose C contents exceed the upper limit of Expression (1), the melting point lowering of the grain boundaries of a coarse-grained HAZ was remarkable and liquation cracking occurred in the HAZ in the longitudinal Varestraint test.

**[0058]** In contrast to this, in any of the materials of Nos. 7, 8 and 12, the creep rupture time of the HAZ did not satisfy target values although liquation cracking did not occur in the HAZ in the longitudinal Varestraint test.

[0059] That is, the material of No. 12 whose B content is in the defined range of the present invention but whose C content is less than the lower limit of Expression (1), the creep rupture time of the HAZ did not satisfy the target value. On the other hand, in the material of No. 8 whose B content does not meet the defined range of the present invention, the creep rupture time of the HAZ did not satisfy the target value although the C content satisfies Expression (1). Also, in the material of No. 7, whose B content does not satisfy the range of the present invention and also whose C content exceeds the upper limit of Expression (1), the creep rupture time of the HAZ was still lower than that of the material of No. 8.

[0060] From the above-described results it is apparent that the materials having chemical compositions satisfying the ranges of the present invention have excellent liquation cracking resistance and creep strength in the HAZ.

#### Industrial Applicability

[0061] Since the heat resistant ferritic steel, in accordance with the present invention, provides heat resistant ferritic steels, excellent in the weld crack resistance and creep strength of the HAZ, the heat resistant ferritic steel can be used in welded structures in thermal power generation boilers in which efforts are being made toward higher temperature and higher pressure steam conditions.

#### Brief Description of the Drawing

[0062] Figure 1 shows a longitudinal V restraint test method.

#### Claims

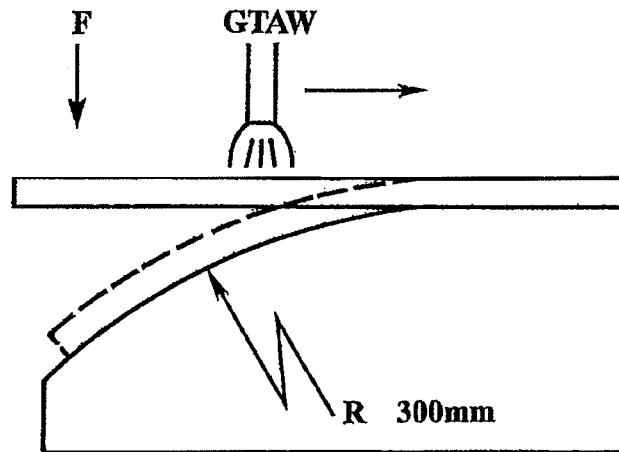
1. A high-Cr heat resistant ferritic steel **characterized by** consisting of, by mass%, Si: more than 0.1% and not more than 1.0%, Mn: 2.0% or less, Co: 1 to 8%, Cr: 7 to 13%, V: 0.05 to 0.4%, Nb: 0.01 to 0.09%, either one or both of Mo and W: 0.5 to 4% as a total, B: 0.005 to 0.025%, Al: 0.03% or less, and N: 0.003 to 0.06%, and containing C in an amount satisfying Expression (1), the balance being Fe and impurities, and O, P and S as impurities being such that O: 0.02% or less, P: 0.03% or less, and S: 0.02% or less, respectively,

$$0.005 \leq C \leq (-5/3) \times B + 0.085 \dots (1)$$

in which C and B represent the content of each element (mass%).

2. The high-Cr heat resistant ferritic steel according to claim 1 **characterized by** containing, by mass%, Nd: 0.08% or less in place of part of Fe.
3. The high-Cr heat resistant ferritic steel according to claim 1 or 2 **characterized by** containing, by mass%, Ta: 0.08% or less in place of part of Fe.
4. The high-Cr heat resistant ferritic steel according to any one of claims 1 to 3 **characterized by** containing, by mass%, either one or both of Ca: 0.02% or less and Mg: 0.02% or less in place of part of Fe.

Fig.1



INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP2008/059630

<p>A. CLASSIFICATION OF SUBJECT MATTER C22C38/00(2006.01) i, C22C38/38(2006.01) i</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>																	
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) C22C38/00, C22C38/38</p> <p>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 1996-2008                  Kokai Jitsuyo Shinan Koho 1971-2008 Toroku Jitsuyo Shinan Koho 1994-2008</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI, Science Direct, JSTPlus (JDreamII)</p>																	
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X Y</td> <td>JP 2002-317252 A (Independent Administrative Institution National Institute for Materials Science), 31 October, 2002 (31.10.02), Claims; Par. Nos. [0001] to [0006], [0018]; examples; table 1(4) &amp; CN 1461354 A &amp; EP 1382701 A1 &amp; US 2003/0188812 A1 &amp; WO 2002/086176 A1</td> <td>1 2-4</td> </tr> <tr> <td>Y</td> <td>JP 2002-235154 A (Sumitomo Metal Industries, Ltd.), 23 August, 2002 (23.08.02), Claims; Par. Nos. [0001] to [0008], [0034] to [0036]; table 1 (Family: none)</td> <td>2-4</td> </tr> </tbody> </table> <p><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p> <p>* Special categories of cited documents:                  "A" document defining the general state of the art which is not considered to be of particular relevance                  "E" earlier application or patent but published on or after the international filing date                  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)                  "O" document referring to an oral disclosure, use, exhibition or other means                  "P" document published prior to the international filing date but later than the priority date claimed                  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art                  "&amp;" document member of the same patent family</p> <table border="1"> <tr> <td>Date of the actual completion of the international search 17 July, 2008 (17.07.08)</td> <td>Date of mailing of the international search report 29 July, 2008 (29.07.08)</td> </tr> <tr> <td>Name and mailing address of the ISA/ Japanese Patent Office</td> <td>Authorized officer</td> </tr> <tr> <td>Facsimile No.</td> <td>Telephone No.</td> </tr> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X Y	JP 2002-317252 A (Independent Administrative Institution National Institute for Materials Science), 31 October, 2002 (31.10.02), Claims; Par. Nos. [0001] to [0006], [0018]; examples; table 1(4) & CN 1461354 A & EP 1382701 A1 & US 2003/0188812 A1 & WO 2002/086176 A1	1 2-4	Y	JP 2002-235154 A (Sumitomo Metal Industries, Ltd.), 23 August, 2002 (23.08.02), Claims; Par. Nos. [0001] to [0008], [0034] to [0036]; table 1 (Family: none)	2-4	Date of the actual completion of the international search 17 July, 2008 (17.07.08)	Date of mailing of the international search report 29 July, 2008 (29.07.08)	Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	Facsimile No.	Telephone No.
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INTERNATIONAL SEARCH REPORT

International application No.  
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E, X	WO 2007/091535 A1 (Babcock-Hitachi Kabushiki Kaisha), 16 August, 2007 (16.08.07), Claims; Par. Nos. [0001] to [0009], [0026], [0031]; table 1 (Family: none)	1
A	JP 2002-4008 A (Sumitomo Metal Industries, Ltd.), 09 January, 2002 (09.01.02), Full text (Family: none)	1-4
A	JP 5-311346 A (Nippon Steel Corp.), 22 November, 1993 (22.11.93), Claims; Par. Nos. [0001] to [0005]; table 1(1) (Family: none)	1-4

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**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 4371551 A [0007]
- JP 4371552 A [0007]
- JP 2001152293 A [0007]
- JP 2002241903 A [0007]
- JP 8085848 A [0007]
- JP 9071845 A [0007]
- JP 2001279391 A [0007]
- JP 2002069588 A [0007]
- JP 2004300532 A [0007]

**Non-patent literature cited in the description**

- *Science and Technology of Welding and Joining*, 1996, vol. 1 (1), 36-42 [0007]