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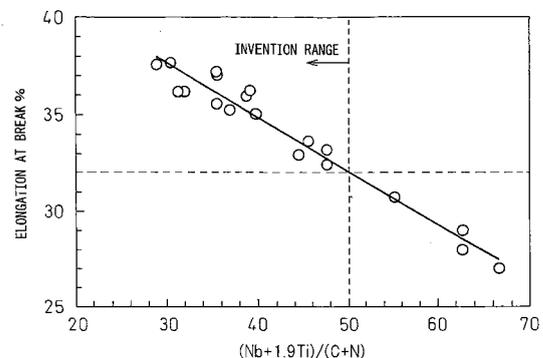
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(54) **Cr-CONTAINING STEEL EXCELLENT IN THERMAL FATIGUE CHARACTERISTICS**

(57) The present invention provides Cr-containing steel superior in heat fatigue characteristics, that is, Cr-containing steel superior in heat fatigue characteristics, **characterized by** containing, by mass%, C: 0.01% or less, N: 0.015% or less, Si: 0.8 to 1.0%, Mn: 0.2 to 1.5%, P: 0.03% or less, S: 0.01% or less, Ni: 0.2% or less, Cu: 0.2% or less, Cr: 13 to 15%, Mo: 0.1% or less, Nb: 0.3 to 0.5%, Ti: 0.05 to 0.2%, V: 0.01 to 0.2%, Al: 0.015 to 1.0%, and B: 0.0002 to 0.0010%, satisfying $(Nb+1.9 \times Ti)/(C+N) \leq 50$, and having a balance of Fe and unavoidable impurities, wherein a 0.2% yield strength at 800°C after aging at 800°C for 100 hours or more is 20 MPa or more and a drawability value at 200°C is 35% or more and wherein a soluble Nb amount+soluble Ti amount after aging at 800°C for 100 hours or more is 0.08% or more.

Fig.1



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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a Cr-containing steel superior in heat fatigue characteristics optimal for use for exhaust system parts etc. particularly requiring high temperature strength and oxidation resistance.

BACKGROUND ART

10 **[0002]** Exhaust manifolds, front pipes, center pipes, and other exhaust system parts of automobiles carry high temperature exhaust gas discharged from engines, so the materials forming the exhaust parts are required to have oxidation resistance, high temperature strength, heat fatigue characteristics, and various other characteristics.

15 **[0003]** In the past, cast iron has generally been used for automobile exhaust parts, but from the viewpoint of toughening of emission controls, improvement of engine performance, reduction of the weight of chasses, etc., stainless steel exhaust manifolds have come to be used. Further, in recent years, the exhaust gas temperatures have become the higher 800 to 900°C or so, so materials having oxidation resistance, high temperature strength, and heat fatigue characteristics at high temperatures and long usage environments are required.

20 **[0004]** Among stainless steels, austenitic stainless steel is superior in heat resistance and workability, but is large in coefficient of heat expansion, so when applied to a part repeatedly subjected to heating and cooling like an exhaust manifold, heat fatigue breakage easily occurs.

25 **[0005]** On the other hand, ferritic stainless steel has a smaller coefficient of heat expansion compared with austenitic stainless steel, so is superior in heat fatigue characteristics. Further, to increase the high temperature strength in accordance with the exhaust gas temperature, steel adjusted in amounts of addition of alloy elements such as Cr, Mo, and Nb is used. Along with the increase in exhaust gas temperatures, the amounts of these alloy elements added are increasing. The most important characteristic, that is, the heat fatigue life, does not necessarily become longer. Further, excessive increase of the amount of addition of alloy elements leads to an increase in costs, so sometimes has the defect of not being economical.

30 **[0006]** Japanese Patent Publication (A) No. 7-145453 discloses ferritic stainless steel superior in oxidation resistance, high temperature strength, and heat fatigue characteristics for automobile exhaust manifolds. It is art for the case where the Cr amount is a relatively low Cr content of 11 to 14% and adding Si to improve the oxidation resistance, high temperature strength, and heat fatigue characteristics at 900°C or more. Among these, the heat fatigue characteristics are the characteristics under the conditions of 50% restraint at 200 to 900°C. The invention steels became longer in heat fatigue life, but when the restraint ratio became longer, the temperature becomes about 800°C, and the cycle imparted becomes longer, sufficient properties could not be obtained. As the reason for this, it is believed that the high temperature strength and high temperature ductility were insufficient under conditions of long term exposure to the usage environment, that is, aging of the material. Further, in the above Japanese Patent Publication (A) No. 7-145453, there is an example of combined addition of Ti and Nb, but in this case the phenomenon arose of cracks forming in the middle of working the actual shaped part (secondary working cracks), the parts could not be shaped, or the fine cracks resulted in remarkable deterioration of the heat fatigue characteristics.

35 **[0007]** Japanese Patent Publication (A) No. 9-279316 discloses an invention controlling the Si/Mn to make the yield strength at 900°C 15 MPa or more and improve the high temperature characteristics. In this case as well, just defining the tensile yield strength of the final sheet at 900°C was insufficient in a long usage environment. Further, Mn is added in an amount of 0.7 to 1.3%, so the ductility is low, and the formability when working a part and the high temperature ductility drop and thereby the heat fatigue life drops.

40 **[0008]** Japanese Patent Publication (A) No. 2002-105605 discloses the technical idea of adjusting the ingredients to make the 0.2% yield strength after holding at 900°C for one hour 18 MPa or more. Here, holding at a high temperature for one hour or more improves the strength in the usage environment, but when being subjected to a thermal cycle, sometimes just the improvement of the high temperature strength is not enough for improvement of the heat fatigue life.

45 **[0009]** Japanese Patent Publication (A) No. 9-279312, Japanese Patent Publication (A) No. 2000-169943, and Japanese Patent Publication (A) No. 10-204590 disclose steels containing B as ferritic stainless steels superior in high temperature characteristics, but B is added from the viewpoint of improvement of the workability. In prior discoveries, the effect on the high temperature characteristics was not clear. The role of B in the improvement of the workability is the improvement of the grain boundary strength through grain boundary precipitation and improvement of the secondary workability, but in the present invention, the addition of B makes the precipitate finer and improves the high temperature strength. Further, the above three patents describe the addition of V, but V was not added from the viewpoint of improvement of the corrosion resistance of the weld zone and the improvement of the workability due to the C and N being fixed.

DISCLOSURE OF THE INVENTION

[0010] The present invention provides, as a material able to handle exhaust temperatures near 800°C, a relatively inexpensive Cr-containing steel having superior oxidation resistance, high temperature strength, and heat fatigue characteristics in an environment where it is used at a high temperature for a long time or is repeatedly subjected to heating and cooling.

[0011] To solve this problem, the inventors investigated the relationship between the ingredients and high temperature deformation characteristics in relation to the oxidation resistance, high temperature strength, and heat fatigue characteristics of Cr-containing steel. Among these, considering in particular environments subjected to a thermal cycle, they carefully investigated how the deformation characteristics in the high temperature region and also the deformation characteristics in the low temperature region act on the heat fatigue life. Further, the inventors engaged in repeated studies to achieve the above object and as a result obtained the following discoveries. The invention features adding Cr and Si from the viewpoint of mainly the oxidation resistance, adding Nb and Ti in combination from the viewpoint of improving the high temperature characteristics, and further adjusting the ingredients in the novel ingredients in addition of V and B so as to secure strength and ductility at the time of long term use and greatly improve the heat fatigue characteristics. The gist of the present invention is as follows:

(1) Cr-containing steel superior in heat fatigue characteristics, characterized by containing, by mass%,

C: 0.01% or less,
 N: 0.015% or less,
 Si: 0.8 to 1.0%,
 Mn: 0.2 to 1.5%,
 P: 0.03% or less,
 S: 0.01% or less,
 Ni: 0.2% or less,
 Cu: 0.2% or less,
 Cr: 13 to 15%,
 Mo: 0.1% or less,
 Nb: 0.3 to 0.55%,
 Ti: 0.05 to 0.2%,
 V: 0.01 to 0.2%,
 Al: 0.015 to 1.0%, and
 B: 0.0002 to 0.0010%,

satisfying $(Nb+1.9 \times Ti)/(C+N) \leq 50$, and having a balance of Fe and unavoidable impurities.

(2) Cr-containing steel superior in heat fatigue characteristics as set forth in (1), **characterized in that** a 0.2% yield strength at 800°C after aging at 800°C for 100 hours or more is 20 MPa or more and a drawability value at 200°C is 35% or more.

(3) Cr-containing steel superior in heat fatigue characteristics as set forth in (1) or (2), **characterized in that** a soluble Nb amount+soluble Ti amount after aging at 800°C for 100 hours or more is 0.08% or more.

(4) Cr-containing steel superior in heat fatigue characteristics as set forth in any one of (1) to (3), characterized by satisfying $Mn/Ti \geq 3$.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIG. 1 is a view showing the relationship between the $(Nb+1.9Ti)/(C+N)$ and the elongation at break at ordinary temperature.

FIG. 2 is a view showing the effects of Ti addition on the heat fatigue life.

FIG. 3 shows the yield strength at 800°C after aging at 800°C.

FIG. 4 is a view showing the drawability value at 200°C after aging at 800°C.

FIG. 5 is a view showing the drawability at 200°C after aging at 800°C.

FIG. 6 is a view showing the relationship between the Mn/Ti and the Cr_2O_3 thickness when running a continuous oxidation test at 900°C for 200 hours.

BEST MODE FOR CARRYING OUT THE INVENTION

[0013] Below, the reasons for limitation of the present invention will be explained.

[0014] C degrades the formability and corrosion resistance and lowers the high temperature strength, so the smaller the content the better, so the content was made 0.015% or less. However, excessive reduction leads to an increase in the refining costs, so further 0.001 to 0.005% is preferable.

[0015] N, like C, degrades the formability and corrosion resistance and causes a drop in the high temperature strength, so the smaller the content the better, so the content was made 0.015% or less. However, excessive addition leads to an increase in the refining costs, so further 0.001 to 0.010% is preferable.

[0016] Si is an element important for improving the oxidation resistance and high temperature characteristics in the present invention. The oxidation resistance and the high temperature strength are improved along with the increase of the Si amount. The effect appears with 0.8% or more. Further, Si promotes the precipitation of intermetallic compounds mainly comprised of Fe and Nb called a "Laves phase" at a high temperature. If the Laves phase excessively precipitates, the amount of soluble Nb required for securing high temperature strength ends up being reduced. Further, if excessively adding Si, the ordinary temperature workability deteriorates and also the ductility during long term use is reduced and a drop in the heat fatigue life is caused. From these viewpoints, the upper limit was made 1.0%, further preferably 0.8 to 0.9%.

[0017] Mn is an element added as a deoxidizing agent and improving the high temperature strength. Its effects are manifested from 0.2% or more. Further, in steel in which it is added combined with Ti, it is learned that the addition of Mn suppresses the oxidation of Ti at the time of continuous oxidation and improves the oxidation resistance. On the other hand, addition over 1.5% lowers the ductility and also forms MnS to reduce the corrosion resistance. Further, excessive addition causes deterioration of the oxidation resistance. Therefore, the content was made 0.2 to 1.5%. Furthermore, considering the high temperature ductility and the scale adhesion, 0.3 to 1.0% is preferable.

[0018] P is a solution strengthening element like Mn and Si, so in terms of material quality, the lower the content the better, so an upper limit of 0.03% is preferable. However, excessive reduction leads to an increase in the refining costs, so a lower limit of 0.01% is preferable. Furthermore, if considering the refining costs and corrosion resistance, 0.012 to 0.025% is preferable.

[0019] S is an element degrading the corrosion resistance and oxidation resistance, but the effect of bonding with Ti or C to improve the workability is expressed from 0.0001%, the lower limit was made 0.0001%. On the other hand, excessive addition causes the S to bond with the Ti and C to reduce the amount of soluble Ti and increase the coarseness of the precipitates, whereby the high temperature strength falls, so the upper limit was made 0.01%. Furthermore, if considering the refining costs and the high temperature oxidation characteristics, 0.0010 to 0.0090% is preferable.

[0020] Cr is an element essential for securing the oxidation resistance in the present invention. If less than 13%, this effect is not manifested, while if over 15%, it reduces the workability and degrades the toughness, so the content was made 13 to 15%. Furthermore, if considering the high temperature ductility and manufacturing costs, 13.2 to 14.5% is preferable.

[0021] Ni is effective for improvement of toughness and improvement of the high temperature salt corrosion resistance. However, it is an austenite forming element, has a detrimental effect on the oxidation resistance, and is expensive, so the content was made 0.2% or less.

[0022] Cu is effective for improvement of the high temperature strength, but lowers the ductility and has a detrimental effect on the oxidation resistance, so the content was made 0.2% or less.

[0023] Mo improves the corrosion resistance, suppresses high temperature oxidation, and is effective for improvement of the high temperature strength through solution strengthening. However, it causes a drop in high temperature ductility and also is expensive, so was made 0.2% or less, more preferably 0.1% or less.

[0024] Nb is an element necessary for improving the high temperature strength through solution strengthening and strengthening by increased fineness of the precipitate. Further, it has the role of fixing C and N as carbonitrides and contributing to the formation of a recrystallized texture having an effect on the corrosion resistance and r value of the product sheet. These effects appear from 0.3% or more. On the other hand, when this precipitates as a Laves phase due to the temperature in the usage environment, the solution strengthening ability is lost, so even if excessively added, the effect ends up becoming saturated. Further, with excessive addition, the ductility falls and the heat fatigue life ends up becoming shorter in the low temperature region. In the present invention, by combined addition with Ti, the soluble Nb amount is secured. In this case, this action is saturated at 0.55%, so the content was made 0.3 to 0.55%. Further, if considering the formability, grain boundary corrosion, and manufacturing costs, 0.32 to 0.45% is preferable.

[0025] Ti is an element bonding with C, N, and S and improving the corrosion resistance, grain boundary corrosion resistance, and deep drawability. Further, in combined addition with Nb, addition of a suitable amount improves the high temperature strength after long term exposure to a high temperature, improves the high temperature ductility, and improves the heat fatigue characteristics. These effects are expressed from 0.05% or more, but addition over 0.2% causes the soluble Ti amount to increase and degrades the formability and also causes formation of surface defects, a

drop in toughness, and a deterioration of the oxidation resistance, so the content was made 0.05 to 0.2%. Furthermore, if considering the manufacturability, 0.05 to 0.15% is preferable.

5 **[0026]** V forms fine carbonitrides upon addition at 0.01% or more and gives rise to a precipitation strengthening action to contribute to an improvement of the high temperature strength. On the other hand, with addition over 0.2%, the low temperature ductility falls and conversely the heat fatigue life ends up falling, so the upper limit was made 0.2%. Furthermore, if considering the manufacturing costs and manufacturability, 0.08 to 0.15% is preferable.

10 **[0027]** Al is an element added as a deoxidizing element and also improving the oxidation resistance and the high temperature strength by solution strengthening and is an essential element in the present invention. This action appears from 0.015%, but addition over 1.0% causes hardening, the formation of surface defects, and the deterioration of the weldability, so the content was made 0.015 to 1.0%. Furthermore, if considering the refining costs, 0.03 to 0.7% is preferable.

15 **[0028]** B is an element improving the secondary workability at the time of press forming of a product. In particular, Ti-containing steel is susceptible to secondary work cracks, so B is an essential element in the present invention. In addition, in a system of ingredients like the present invention where Nb and Ti are added and Si is added, the inventors discovered that this contributes to improvement of the high temperature strength. In general, B is considered to form (Fe, Cr)₂₃(C, B)₆ or Cr₂B in the high temperature region and precipitate at the grain boundaries, but in a system of ingredients where Si is added, it was learned that these precipitates do not form and there is the effect of making the above-mentioned Laves phase finely precipitate. The Laves phase causes a reduction in the soluble Nb amount and usually ends up making the structure coarser, so there is almost no high temperature strengthening ability in particular after long aging, 20 but the addition of B causes fine precipitation, so B has precipitation strengthening ability and contributes to the improvement of the high temperature strength. The reason why B causes fine precipitation of the Laves phase is believed to be the drop in the interfacial energy due to grain boundary precipitation and the increased difficulty of grain boundary precipitation.

25 **[0029]** These effects are manifested at 0.0002% or more, but excessive addition causes worse hardening and grain boundary corrosion and also results in the formation of weld cracks, so the content was made 0.0002 to 0.0010%. Furthermore, if considering the formability and manufacturing costs, 0.0003 to 0.0007% is preferable. In the case of combined addition of Ti and Nb, if the two are excessively added, it is learned that the soluble Ti and soluble Nb increase and the ordinary temperature ductility is remarkably reduced.

30 **[0030]** In the present invention, as shown in FIG. 1, by making $(Nb+1.9\times Ti)/(C+N)\leq 50$, an elongation at break at ordinary temperature of 32% or more can be secured. Here, JIS No. 13B test pieces were taken from 14%Cr steels differing in amounts of Ti, Nb, C, and N and having a sheet thickness of 2 mm in the rolling direction, were subjected to a tensile test, and were measured for elongation at break. If the elongation at break is 32% or more, this is a level where no cracks or constriction will occur even if press forming the sheet material into an exhaust part or working it into a pipe shape, then bending or expanding it.

35 **[0031]** Further, the inventors discovered that for improvement of the heat fatigue life, in addition to the high temperature strength after aging, the ductility is important. Here, the heat fatigue test will be explained. The product sheet was made into a pipe by seam welding (outside diameter: 38.1 mm) and used for a heat fatigue test.

40 **[0032]** The heat fatigue test was conducted by a computer controlled electrical hydraulic controlled fatigue tester. The temperature cycle given was made a pattern of raising the temperature from 200 to 800°C in 120 sec, holding it at 800°C for 30 sec, then cooling down to 300°C for 120 sec and further cooling down to 200°C for 90 sec. The heating was performed by a high frequency induction heating coil, while the cooling was performed by feeding air into the test tube. Compressive strain was imparted so that the restraint ratio became a constant ratio with respect to the amount of free expansion. That is, for example, in the case of 50% restraint, compressive strain is mechanically imparted so as to give an amount of expansion of half the free expansion.

45 **[0033]** The chemical composition of the tested materials are shown in Table 1. The Steel A is steel complying with the present invention, while the Steel B is a comparative steel. Here, the Steel B is a generally used heat resistant stainless steel sheet.

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Table 1

No.	C	N	Si	Mn	P	S	Ni	Cu	Cr	Mo	Nb	Ti	V	Al	B
A	0.005	0.012	0.82	0.31	0.03	0.0012	0.11	0.03	13.8	0.01	0.35	0.14	0.08	0.05	0.0003
B	0.005	0.015	0.93	0.30	0.02	0.0009	0.15	0.02	14.1	0.01	0.45	0.005	0.08	0.03	0.0001

5 [0034] From FIG. 2, the steels of the present invention have higher lifetimes than the comparative examples at all of the restraint ratios. This is because even if imparting aging of the high temperature strength, that is, a long term thermal cycle, there is almost no drop in strength and, further, a high ductility is maintained in the low temperature region of the thermal cycle. While receiving the thermal cycle, at the high temperature, the material is given a compressive load, while
10 when held at 800°C, creep deformation or stress-relief phenomena occur, so the increase of the 0.2% yield strength at 800°C is considered effective for extension of the heat fatigue life. On the other hand, in the cooling process from 800°C to 200°C, the material is given tensile stress. This tensile stress is a stress remarkably larger than the compressive stress in the high temperature region. When damage (defects) occur in the thermal cycle, there is remarkable plastic deformation at that location. Therefore, the increase in the ductility of the material at 200°C (drawability) is believed to be effective in suppressing the progression of damage in the cooling process.

15 [0035] FIG. 3 and FIG. 4 show the tensile strength and drawability at a high temperature after aging at 800°C. In the invention steels, even with long aging at 800°C for 10 hours or more, the high temperature strength is a high strength of 20 MPa or more and the ductility is a high one of a drawability value at 200°C of 35%. This means that even if subjected to a long thermal cycle treatment in the heat fatigue process, the strength at the highest temperature is high and the ductility at the lowest temperature is high. Due to this, as shown in FIG. 2, no matter what the restraint ratio, this is believed to lead to an improvement in the heat fatigue life. In prior inventions, only improvement of the strength at the highest temperature when subjected to a thermal cycle was the technical idea, but in the present invention it was discovered that improvement of the ductility at the lowest temperature results in remarkable improvement of the heat fatigue life.

20 [0036] The improvement in the drawability value at 200°C is believed to be due to the securing of the elongation at break at ordinary temperature mentioned above and the suppression of aging deterioration. That is, the fact that the balance of addition of Ti and Nb is important became clear from the present invention. On the other hand, the soluble Nb amount and soluble Ti amount have an effect on the improvement of the high temperature strength at 800°C. FIG. 5 shows the relationship between the soluble Nb amount+soluble Ti amount after aging at 800°C and the high temperature strength at 800°C. At a soluble Nb amount+soluble Ti amount of 0.08% or more, the high temperature strength at 800°C becomes 20 MPa or more. Due to this, to obtain a high temperature strength of 20 MPa or more and improve the heat fatigue life, the soluble Nb amount+soluble Ti amount was made 0.08% or more.

25 [0037] In the present invention, a suitable amount of Ti is added in combination with Nb to improve the high temperature strength and high temperature ductility after long aging and improve the heat fatigue characteristics, but conversely acts to degrade the oxidation resistance. When continuously oxidizing steel containing Si, Cr, Mn, and Ti shown in the present invention, as scale, spinal type oxides mainly containing TiO₂, Cr, and Mn are formed at the outside layer and Cr₂O₃ is formed at the inside layer. Along with the increase the amount of Ti, the inside layer Cr₂O₃ film becomes thicker and the oxidation resistance deteriorates. The inventors studied the effects of M, whereupon they discovered that if increasing the Mn, the amount of the outside layer TiO₂ is reduced and growth of the inside layer Cr₂O₃ film is suppressed and thereby the oxidation resistance is improved. FIG. 6 shows the Ti/Mn and the film thickness of the Cr₂O₃ inside layer after continuous oxidation at 900°C for 200 hours. When the thickness of the Cr₂O₃ inside layer scale is over 5 μm, scale peeling etc. occurs and the oxidation resistance deteriorates, but when Mn/Ti≥3, the Cr₂O₃ inside layer scale becomes thinner and the oxidation resistance becomes superior. Ti diffuses outward through the inside layer Cr₂O₃, but the Mn suppresses the outward diffusion of the Ti and as a result, it is believed, the growth of the inside layer Cr₂O₃ film is suppressed. To obtain a good oxidation resistance, suppression of the growth of the inside layer Cr₂O₃ film is important. To make the thickness of the Cr₂O₃ inside layer scale formed at the time of continuous oxidation at 900°C for 200 hours in the atmosphere 5 μm or less, Mn/Ti≥3 was set.

45 EXAMPLES

[0038] The steels of the compositions of ingredients shown in Table 2 were produced and formed into slabs. The slabs were hot rolled to obtain 5 mm thick hot rolled coils. After that, the hot rolled coils were annealed and pickled, were cold rolled to 2 mm thicknesses, then were annealed and pickled to obtain the product sheets. The annealing temperatures of the cold rolled sheets were made 980 to 1050°C to make the crystal grain sizes the #6 to 8 or so. From the thus obtained product sheets, high temperature tensile test pieces were taken and subjected to tensile tests at 200°C and 800°C. Further, the sheets were aged at 800°C for 100 hours, then were subjected to high temperature tensile tests similar to the above. Furthermore, the product sheets were made into pipes by seam welding (outside diameter: 38.1 mm) and used for heat fatigue tests. The temperature cycle given was made a pattern of raising the temperature from 200 to 800°C in 120 sec, holding it at 800°C for 30 sec, then cooling down to 300°C for 120 sec and further cooling down to 200°C for 90 sec. The restraint ratio was made 50%. Further, to evaluate the oxidation resistance, a width 20 mm, length 25 mm test piece was cut out from the product sheet, polished by emery paper to #600, then subjected to a continuous oxidation test at 900°C for 200 hours in the atmosphere. The thickness of the Cr₂O₃ inside layer scale was found by examination of the cross-section by an SEM (scan type electron microscope).

[0039] As clear from Table 2, when producing the steels having the compositions of ingredients defined by the present invention by the ordinary method such as described above, compared with the comparative examples, the ordinary temperature elongation is higher and the workability is superior. Further, the above range of high temperature strength is satisfied and the heat fatigue characteristics are superior. In the comparative examples, Steel Nos. 12 and 13 are high in C and N, so the elongation at break at ordinary temperature is low and the drawability value at high temperature is also low. Further, due to the formation of carbonitrides, the high temperature strength is low. Steel No. 14 is low in Si, so the high temperature strength after aging is low. Steel Nos. 15, 17, 18, 19, and 20 are respectively high in Mn, S, Ni, Cu, and Cr, so the ordinary temperature workability is poor and the drawability value after aging is low. Steel No. 16 has S outside the upper limit, has a low soluble Ti+Nb amount after aging, and has a low high temperature strength after aging. Steel Nos. 21, 22, 23, 24, 25, and 26 have Mo, Nb, Ti, V, Al, and B outside the upper limit. These contribute to high temperature strength, but the ordinary temperature workability is poor and the drawing rate at 200°C is low, so the heat fatigue life is short.

[0040] In oxidation resistance, the inside layer scale thicknesses of the present invention steels were good ones of 5 μm or less. In the comparative examples, the Si is outside the scope of the present invention. The small Mn/Ti Steel Nos. 14, 17, 23, 24, and 26 have inside layer scale thicknesses of over 5 μm and are inferior in oxidation resistance.

[0041] Note that the method of production of steel sheet is not particularly defined. The hot rolling conditions and hot rolled sheet thickness, the hot rolled sheet and cold rolled sheet annealing temperature, the atmosphere, etc. may be suitably selected. Further, it is also possible to impart patent rolling or a tension leveler after cold rolling and annealing. Furthermore, the product sheet thickness may be selected in accordance with the required part thickness.

Table 2

No.	C	N	Si	Mn	P	S	Ni	Cu	Cr	Mo	Nb	Ti	V	Al	B	(Nb+Ti)/ (C+N)	HV/Ti	Elongation at break at ordinary temp., %	Soluble Ti+Nb amount after aging at 800°C, %	0.2% yield strength at 800°C after aging at 800°C, MPa	Drawing at 200°C after aging at 800°C, %	Heat fatigue life cycle	Inside thick. scale thick. (μm)
1	0.005	0.008	0.81	0.35	0.029	0.0012	0.11	0.03	13.5	0.01	0.30	0.11	0.05	0.05	0.0003	39	3.2	35	0.12	21	35	1198	4.5
2	0.003	0.012	0.93	0.95	0.018	0.0009	0.08	0.01	14.1	0.02	0.35	0.09	0.08	0.03	0.0012	35	10.6	36	0.13	22	37	1693	2.4
3	0.005	0.009	0.90	0.30	0.025	0.0019	0.12	0.02	13.5	0.01	0.46	0.05	0.03	0.07	0.0003	40	6.0	35	0.19	22	37	1876	2.5
4	0.004	0.013	0.85	0.64	0.013	0.0020	0.15	0.15	14.5	0.09	0.47	0.07	0.17	0.12	0.0006	35	9.1	36	0.21	23	36	1532	2.2
5	0.006	0.011	0.80	0.36	0.016	0.0015	0.13	0.02	13.8	0.01	0.39	0.12	0.13	0.25	0.0003	36	3.0	36	0.11	21	36	1264	4.8
6	0.006	0.009	0.93	0.96	0.031	0.0018	0.11	0.03	13.9	0.05	0.36	0.10	0.05	0.04	0.0010	37	9.6	36	0.14	22	38	1383	2.2
7	0.005	0.013	0.97	1.32	0.031	0.0014	0.10	0.03	13.9	0.05	0.45	0.10	0.05	0.04	0.0012	36	12.8	36	0.18	23	36	1456	2.0
8	0.008	0.014	0.91	0.45	0.025	0.0018	0.09	0.02	14.6	0.04	0.33	0.10	0.19	0.11	0.0008	24	4.5	39	0.08	20	35	1254	2.8
9	0.006	0.009	0.97	1.03	0.031	0.0014	0.10	0.03	13.9	0.05	0.45	0.10	0.05	0.04	0.0012	46	10.3	34	0.18	23	35	1756	2.1
10	0.004	0.010	0.95	1.05	0.035	0.0009	0.08	0.01	14.3	0.01	0.35	0.09	0.08	0.50	0.0008	37	11.7	34	0.13	24	36	1845	2.0
11	0.004	0.009	0.97	1.02	0.025	0.0013	0.12	0.02	13.8	0.01	0.41	0.11	0.12	0.70	0.0008	48	9.3	33	0.15	25	35	1895	2.0
12	0.016	0.011	0.85	0.53	0.021	0.0025	0.15	0.02	13.5	0.01	0.35	0.14	0.07	0.09	0.0005	23	3.8	32	0.04	13	31	836	3.8
13	0.003	0.020	0.85	0.43	0.028	0.0015	0.15	0.02	14.2	0.02	0.47	0.13	0.07	0.06	0.0005	31	3.3	32	0.04	13	31	818	4.1
14	0.005	0.008	0.90	0.20	0.029	0.0012	0.11	0.03	13.5	0.01	0.30	0.11	0.05	0.05	0.0003	39	1.8	36	0.09	18	35	940	8.5
15	0.003	0.011	0.85	1.70	0.028	0.0023	0.11	0.03	13.5	0.01	0.32	0.12	0.06	0.040	0.0005	39	14.2	32	0.10	21	33	956	1.7
16	0.006	0.009	0.90	0.30	0.040	0.0012	0.12	0.02	13.5	0.01	0.46	0.05	0.03	0.070	0.0005	37	6.0	33	0.12	23	34	922	2.5
17	0.006	0.011	0.80	0.25	0.016	0.0080	0.13	0.02	13.8	0.01	0.39	0.12	0.05	0.25	0.0003	36	2.1	36	0.03	19	36	988	5.8
18	0.004	0.013	0.83	0.36	0.025	0.0025	0.50	0.02	13.8	0.01	0.37	0.11	0.09	0.06	0.0003	34	3.3	34	0.12	22	34	964	4.5
19	0.003	0.014	0.73	0.25	0.015	0.0022	0.15	0.50	13.7	0.02	0.35	0.11	0.05	0.03	0.0004	33	2.3	33	0.11	21	33	952	10.2
20	0.004	0.011	0.85	0.45	0.025	0.0015	0.13	0.02	17.5	0.02	0.34	0.11	0.04	0.05	0.0005	37	4.1	32	0.13	21	31	816	1.7
21	0.005	0.011	0.85	0.40	0.025	0.0025	0.11	0.01	13.6	0.50	0.35	0.13	0.04	0.05	0.0005	37	3.1	31	0.18	25	33	981	4.6
22	0.003	0.009	0.92	0.45	0.029	0.0011	0.11	0.01	13.6	0.05	0.65	0.13	0.04	0.05	0.0005	35	3.5	29	0.32	25	29	864	4.2
23	0.006	0.008	0.95	0.36	0.025	0.0035	0.15	0.03	13.4	0.02	0.45	0.25	0.13	0.21	0.0005	59	1.4	29	0.38	25	29	843	6.8
24	0.003	0.014	0.83	0.33	0.015	0.0022	0.15	0.5*	13.7	0.02	0.35	0.12	0.35	0.03	0.0004	34	2.8	33	0.13	22	34	835	5.5
25	0.004	0.008	0.86	0.43	0.024	0.0023	0.11	0.02	13.3	0.05	0.31	0.09	0.13	2.00	0.0003	40	4.8	27	0.10	25	30	988	2.0
26	0.005	0.013	0.83	0.30	0.026	0.0029	0.15	0.01	14.6	0.02	0.35	0.15	0.09	0.02	0.0020	35	2.0	33	0.12	23	31	743	5.9

Underlines indicate outside the present invention

INDUSTRIAL APPLICABILITY

[0042] According to the present invention, it is possible to provide Cr-containing steel superior in heat fatigue characteristics even without adding expensive alloy elements. Particularly, by applying this to exhaust gas system parts of automobiles etc., a large effect such as environmental measures is obtained.

Claims

- Cr-containing steel superior in heat fatigue characteristics, **characterized by** containing, by mass%,
 C: 0.01% or less,
 N: 0.015% or less,
 Si: 0.8 to 1.0%,
 Mn: 0.2 to 1.5%,
 P: 0.03% or less,

S: 0.01% or less,

Ni: 0.2% or less,

Cu: 0.2% or less,

Cr: 13 to 15%,

5 Mo: 0.1% or less,

Nb: 0.3 to 0.55%,

Ti: 0.05 to 0.2%,

V: 0.01 to 0.2%,

Al: 0.015 to 1.0%, and

10 B: 0.0002 to 0.0010%, satisfying $(Nb+1.9 \times Ti)/(C+N) \leq 50$, and having a balance of Fe and unavoidable impurities.

2. Cr-containing steel superior in heat fatigue characteristics as set forth in claim 1, **characterized in that** a 0.2% yield strength at 800°C after aging at 800°C for 100 hours or more is 20 MPa or more and a drawability value at 200°C is 35% or more.

15 3. Cr-containing steel superior in heat fatigue characteristics as set forth in claim 1 or 2, **characterized in that** a soluble Nb amount + soluble Ti amount after aging at 800°C for 100 hours or more is 0.08% or more.

20 4. Cr-containing steel superior in heat fatigue characteristics as set forth in any one of claims 1 to 3, **characterized by** satisfying $Mn/Ti \geq 3$.

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Fig.1

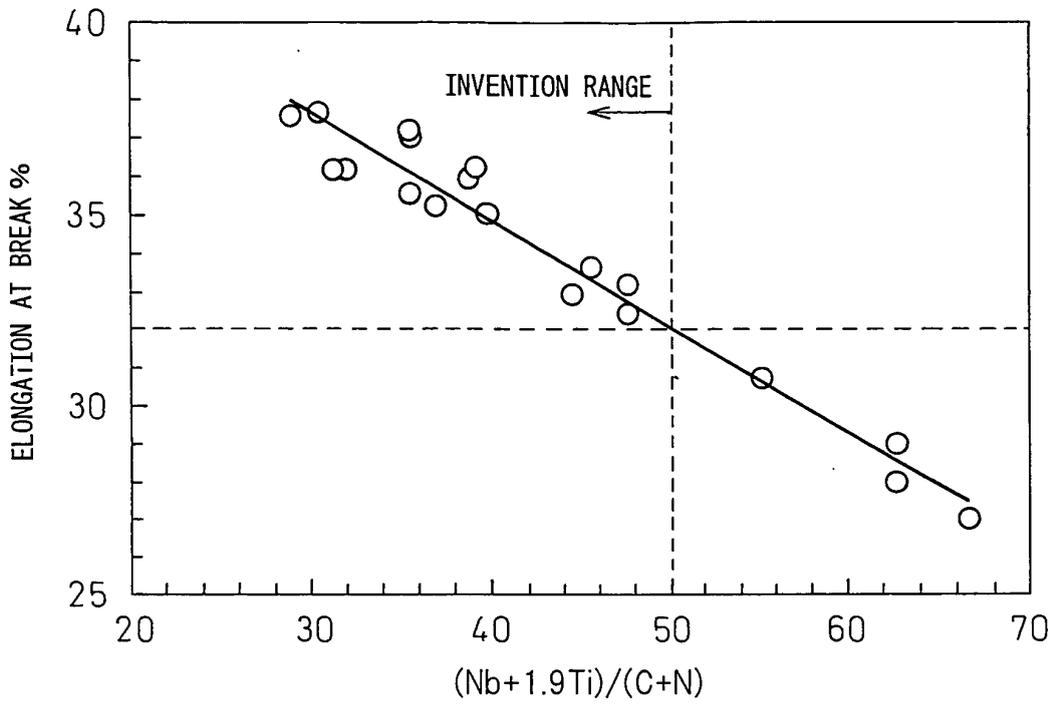


Fig.2

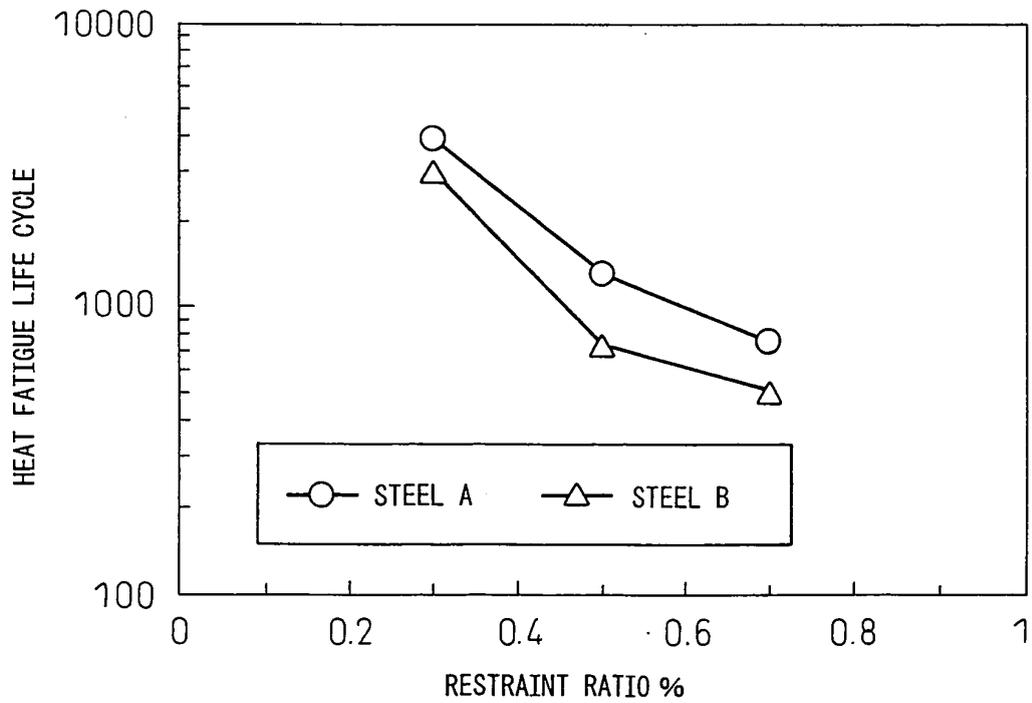


Fig.3

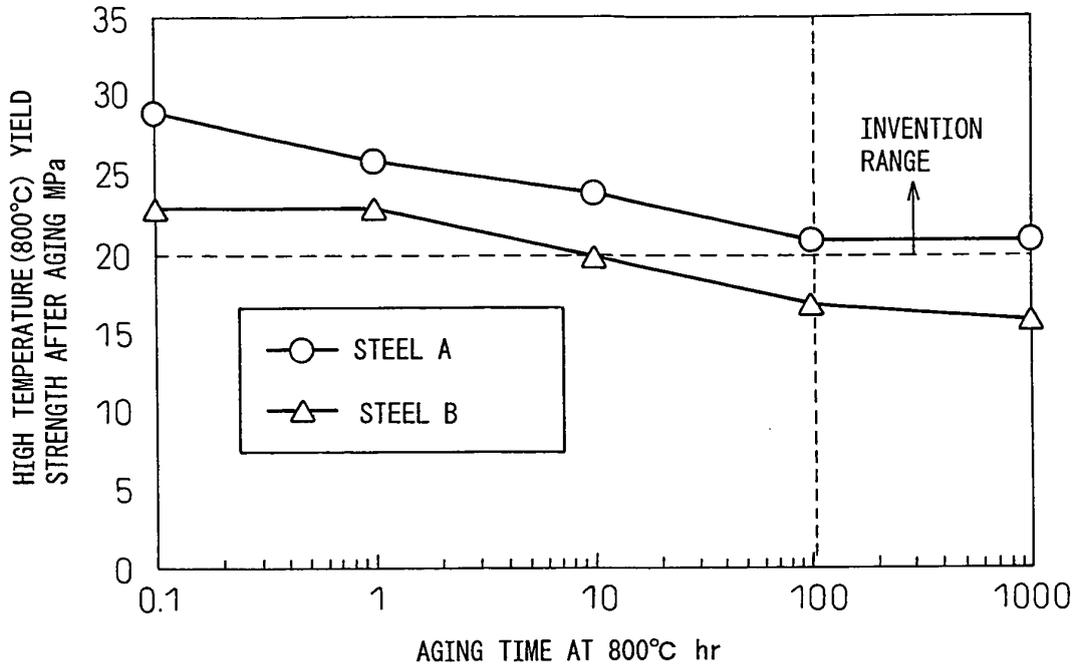


Fig.4

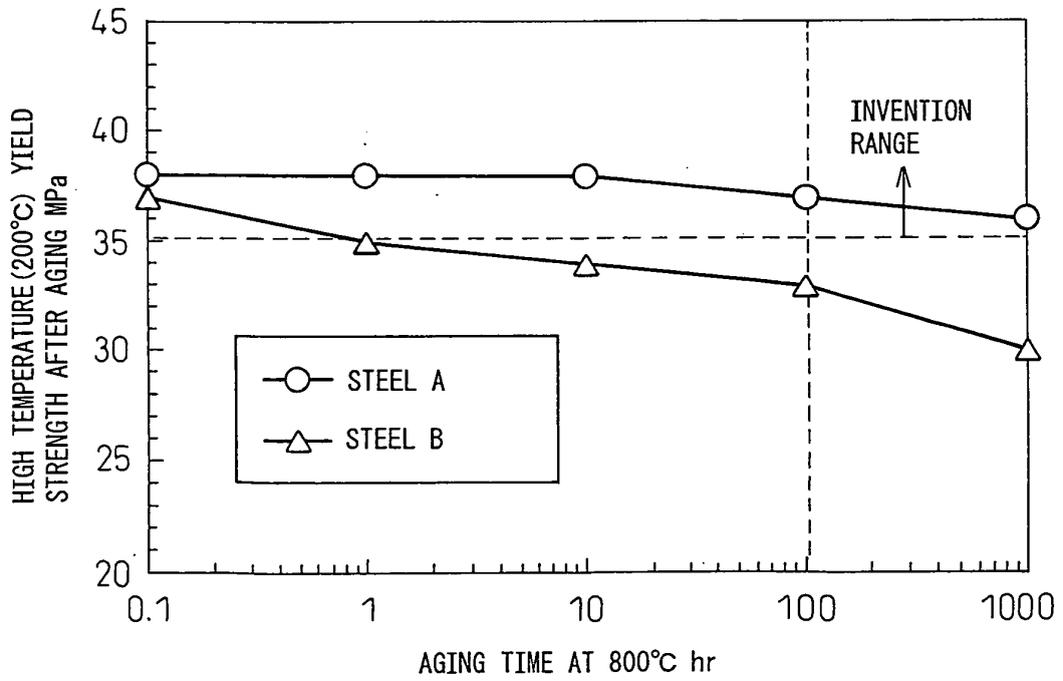


Fig.5

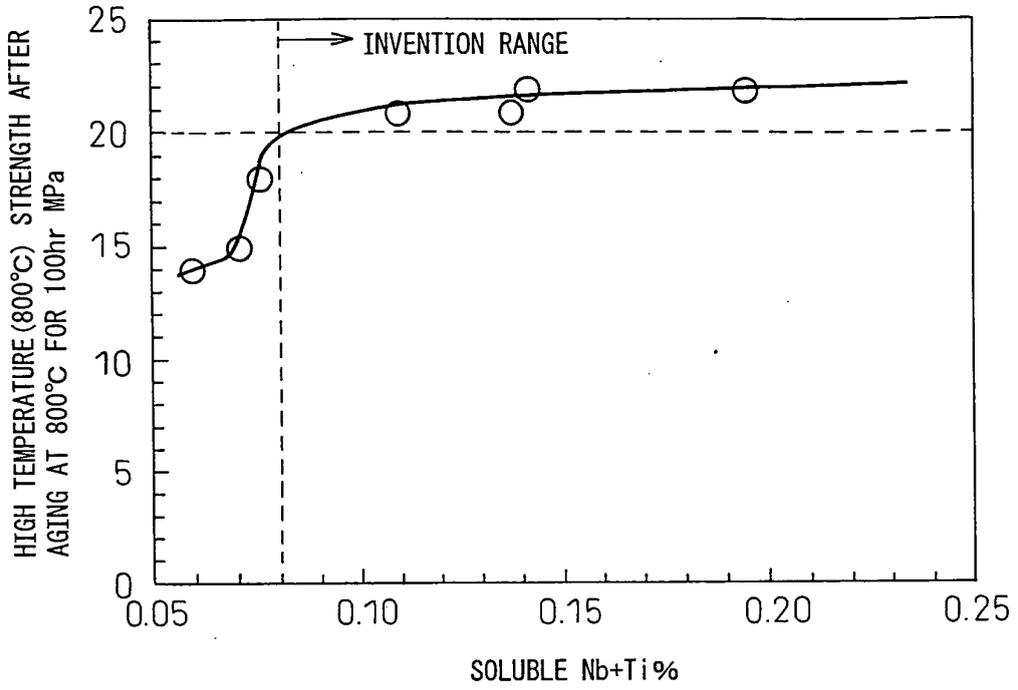
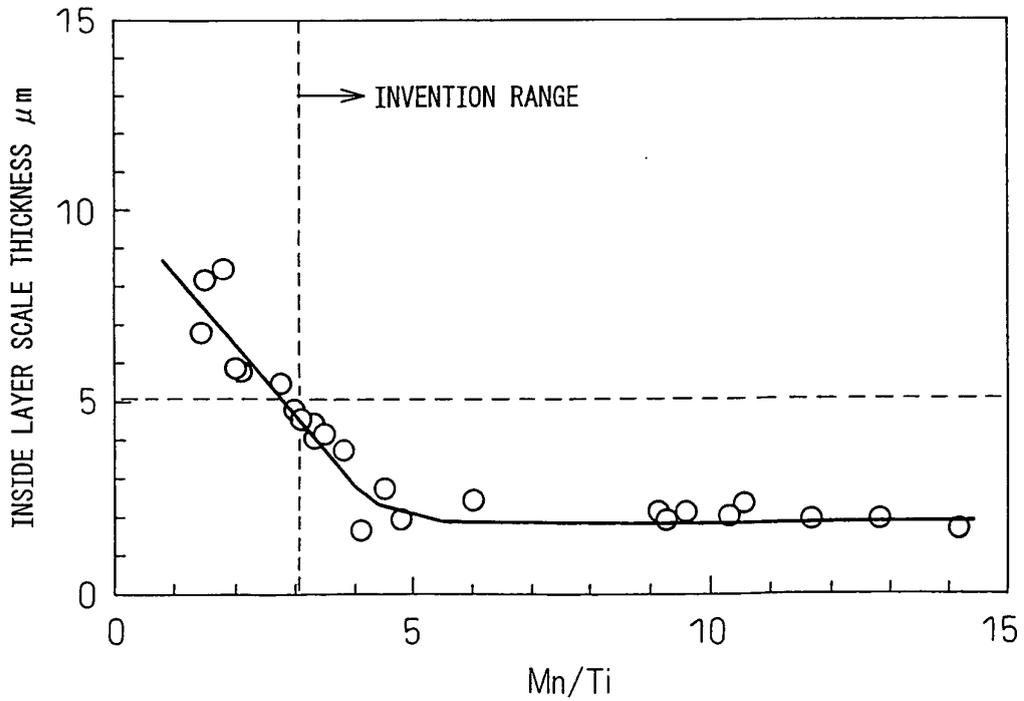


Fig.6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/063185

A. CLASSIFICATION OF SUBJECT MATTER C22C38/00(2006.01) i, C22C38/54(2006.01) i, C21D9/46(2006.01) n		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C22C38/00-38/60, C21D9/46		
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 1996-2007 Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2005-240112 A (JFE Steel Corp.), 08 September, 2005 (08.09.05), Table 1 (steel 10, 11); Claims 2, 3 (Family: none)	1-4
A	JP 2005-264269 A (Nisshin Steel Co., Ltd.), 29 September, 2005 (29.09.05), Par. No. [0036] (Family: none)	1-4
A	JP 2002-194507 A (Nisshin Steel Co., Ltd.), 10 July, 2002 (10.07.02), Par. No. [0036] & EP 1219719 A1 & US 2002/117239 A1	1-4
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* 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 "&" document member of the same patent family		
Date of the actual completion of the international search 13 September, 2007 (13.09.07)		Date of mailing of the international search report 25 September, 2007 (25.09.07)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/063185

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 10-204590 A (Kawasaki Steel Corp.), 04 August, 1998 (04.08.98), Par. No. [0068] (Family: none)	1-4
A	JP 9-3606 A (Kawasaki Steel Corp.), 07 January, 1997 (07.01.97), Par. No. [0027] & EP 750052 A1 & US 5653825 A	1-4
A	JP 2000-336462 A (Nippon Steel Corp.), 05 December, 2000 (05.12.00), Par. No. [0032] (Family: none)	1-4

REFERENCES CITED IN THE DESCRIPTION

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