(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 407 570 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
18.01.2012 Bulletin 2012/03

(21) Application number: **10750916.8**

(22) Date of filing: **12.03.2010**

(51) Int Cl.:
C22C 38/00 ^(2006.01)^ ***B21B 1/38*** ^(2006.01)^
B21B 3/00 ^(2006.01)^ ***B21C 37/08*** ^(2006.01)^
C21D 8/02 ^(2006.01)^ ***C22C 38/58*** ^(2006.01)^

(86) International application number:
PCT/JP2010/054173

(87) International publication number:
WO 2010/104165 (16.09.2010 Gazette 2010/37)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR

(30) Priority: **12.03.2009 JP 2009059639**

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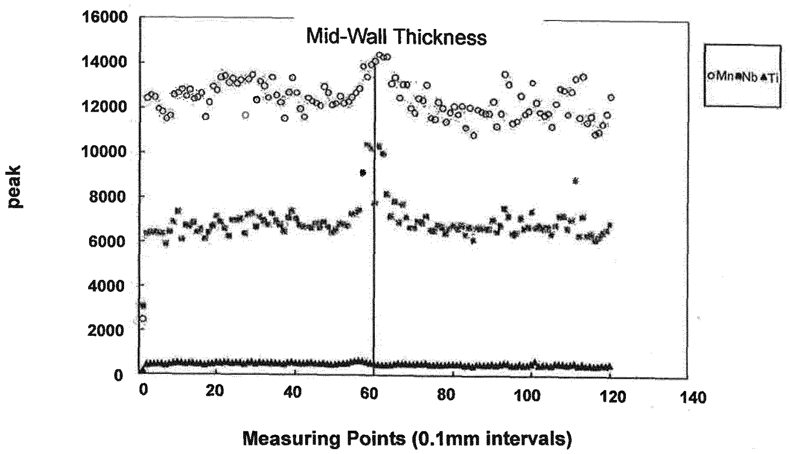
(54) HIC-RESISTANT THICK STEEL SHEET AND UOE STEEL PIPE

(57) A thick steel plate and a UOE steel pipe having a high strength of at least X60 grade and improved resistance to HIC have a chemical composition consisting essentially of, in mass percent, C: 0.02 - 0.07%, Si: 0.05 - 0.50%, Mn: 1.1 - 1.6%, P: at most 0.015%, S: at most 0.002%, Nb: 0.005 - 0.060%, Ti: 0.005 - 0.030%, Al: 0.005 - 0.06%, Ca: 0.0005 - 0.0060%, N: 0.0015 - 0.007%, at least one of Cu, Ni, Cr, and Mo in a total amount of greater than 0.1% and less than 1.5%, and a remainder of Fe and impurities, wherein the degrees of segregation of Nb and Ti are both at most 2.0, and the ratio of (the degree of Nb segregation) / (the degree of Mn segregation) and the ratio of (the degree of Ti segregation) / (the degree of Mn segregation) are both at least 1.0 and at most 1.5.

Fig. 1



Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] This invention relates to a thick steel plate and a UOE steel pipe. More specifically, it relates to a high strength thick steel plate of at least X60 grade which is improved in resistance to hydrogen induced cracking (HIC resistance) and which is suitable for use in applications such as line pipe, offshore structures, and pressure vessels. It also relates to a UOE steel pipe made from this thick steel plate. In this description, a thick steel plate means a steel plate with a thickness of at least 6.0 mm.

Background Art

[0002] Line pipe used for transporting crude oil and natural gas requires not only ordinary properties such as strength, toughness, and weldability, but it is also important for it to have resistance to hydrogen induced cracking (abbreviated below as HIC) because it is sometimes used in corrosive environments containing hydrogen sulfide.

[0003] In the past, oil leaks, breakage, and explosions have actually taken place in connection with line pipes and oil country tubular goods due to HIC. Therefore, intensive research has been performed concerning HIC. As a result, it has been found that HIC occurs by the following mechanism. Hydrogen ions which are formed by a corrosion reaction are adsorbed by the surface of steel and diffuse into the steel in the form of atomic hydrogen, which accumulates around MnS or oxide inclusions in the steel and becomes molecular hydrogen thereby forming a gas. Cracks develop due to the internal pressure of the gas. Accordingly, countermeasures for preventing HIC which have been disclosed are generally classified into the following categories.

(1) If MnS is present in steel, cracks develop with the MnS as the starting point and that cracking sensitivity increases as MnS is elongated at the time of rolling. Based on these finding, Patent Document 1 discloses that S is contained in steel in the form of fine spheroidized CaS or REM sulfides by decreasing the S content of steel and adding Ca or REM to steel.

(2) Hard phases such as martensite or bainite are formed at a location corresponding to the region of center segregation in a cast slab due to segregation of C, Mn, P, and the like and become pathways for propagation of cracks. Taking this into consideration, Patent Document 2 discloses that the formation of such hard phases is prevented by decreasing the concentration of C, Mn, P, and the like in steel, by carrying out soaking treatment in order to decrease segregation by diffusion, and by increasing the cooling rate after rolling.

Patent Documents 3 and 4 disclose that center segregation itself can be eliminated by causing bulging of a cast slab in a stage of continuous casting in which unsolidified molten steel remains and then subjecting the slab to reduction in thickness.

(3) As the strength specifications which are recently being demanded of steel have become more stringent, individual countermeasures against the above-described center segregation or formation of MnS are often inadequate. Patent Documents 5-7 disclose that the formation of a protective coating on the steel surface by adding Cu or Ni to the steel in order to suppress the infiltration of hydrogen into the steel is combined with the addition of Cr, Mo or similar elements or application of a thermo-mechanical control process (TMCP) to rolling.

Prior Art Documents

Patent Documents

[0004]

Patent Document 1: JP 54-110119 A1
Patent Document 2: JP 61-60866 A1
Patent Document 3: JP 09-57410 A1
Patent Document 4: JP 2002-105604 A1
Patent Document 5: JP 06-220577 A1
Patent Document 6: JP 09-209037 A1
Patent Document 7: JP 2003-226922 A1

Summary of the Invention

[0005] The present inventors discovered that a mechanism of the occurrence of HIC which cannot be prevented by the conventional countermeasures explained above in (1) - (3) exists in a high strength thick steel plate of at least X60 grade (having a YS on the order of 60 ksi and YP on the order of 70 ksi) which is primarily used for line pipe and the like.

[0006] The object of the present invention is to provide a thick steel plate having excellent HIC resistance (referred to below as a HIC-resistant thick steel plate) and a UOE steel pipe which can prevent HIC, which could not be prevented by previously known countermeasures against HIC, in a thick steel plate having a strength level of at least X60 grade and particularly in a thick steel plate with a thickness of at least 10 mm in which marked segregation easily occurs.

[0007] The present invention is based on the important finding that in addition to MnS, C, Mn, and P which were conventionally thought to be the main impediments to HIC resistance, carbonitrides of Nb become starting points of HIC.

[0008] The present invention is a thick steel plate having improved HIC resistance characterized by having a chemical composition consisting essentially of, in mass percent, C: 0.02 - 0.07%, Si: 0.05 - 0.50%, Mn: 1.1 - 1.6%, P: at most 0.015%, S: at most 0.002%, Nb: 0.005 - 0.060%, Ti: 0.005 - 0.030%, Al: 0.005 - 0.06%, Ca: 0.0005 - 0.0060%, N: 0.0015 - 0.007%, at least one of Cu, Ni, Cr, and Mo in an amount satisfying Equation (1), V: 0 - 0.10%, and a remainder of Fe and impurities, wherein the degree ofNb segregation is at most 2.0, the ratio α of the degree of Nb segregation to the degree of Mn segregation (α = the degree of Nb segregation/the degree of Mn segregation) is at least 1.0 and at most 1.5, the degree of Ti segregation is at most 2.0, and the ratio β of the degree of Ti segregation to the degree of Mn segregation (β = the degree of Ti segregation/the degree of Mn segregation) is at least 1.0 and at most 1.5.

$$\text{Equation (1):}\quad 0.1\% < (Cu + Ni + Cr + Mo) < 1.5\%$$

[0009] In the above equation, the symbols for elements indicate the content (mass percent) of each element.

[0010] In the present invention, the degree of Nb segregation, the degree of Mn segregation, and the degree of Ti segregation mean the values determined by measuring the concentration of Nb, Mn, and Ti at 50 or more points and preferably at 100 or more points above and below the center (midpoint) of the plate thickness in a cross section cut parallel to the rolling direction of a steel plate (a cross section perpendicular to the plate surface), and for each of Nb, Mn, and Ti, dividing the maximum concentration which is the maximum measured value among all the measurement points by the average concentration which is the arithmetic mean of all the measured values. Namely, the degree of Nb segregation is (the maximum Nb concentration) / (the average Nb concentration). Similarly, the degree of Mn segregation is (the maximum Mn concentration) / (the average Mn concentration), and the degree of Ti segregation is (the maximum Ti concentration) / (the average Ti concentration).

[0011] The 50 or more and preferably 100 or more measurement points are preferably positioned so that in a region having a length of at least 20% of the overall thickness in the plate thickness direction (namely, in a region having a length of at least 10% of the overall plate thickness above and below the center of the plate thickness), the points have a distance which increases by approximately the same rate above and below the center of the plate thickness. For example, at 25 or more points and preferably at 50 or more points at intervals of 100 μm (0.1 mm) each of above and below the center of the plate thickness, the concentrations of Nb, Mn, and Ti are measured. In all the cases, the degree of segregation of each element can be calculated by finding the average concentration and the maximum concentration of Nb, Mn, and Ti from the measured values obtained at 50 or more points. As described below, in the examples of the present invention, the degree of segregation is determined by measurement at 60 points at intervals of 0.1 mm above and below the center of the plate thickness (along the total measured length of 12 mm).

[0012] As stated above, a thick steel plate means a steel plate having a plate thickness of at least 6.0 mm. A preferred plate thickness is at least 10 mm in which segregation occurs particularly easily. There is no particular upper limit on the plate thickness, but the present invention can achieve a HIC-resistant thick steel plate having a thickness up to 40 mm.

[0013] From another standpoint, the present invention is a UOE steel pipe characterized by being formed from the above-described HIC-resistant thick steel plate.

[0014] A UOE steel pipe is manufactured by press forming a thick steel plate into the shape of a U and then into the shape of an O, joining the abutting ends of the plate by submerged arc welding, and then expanding the pipe from the inner side with an expander to finish the pipe to predetermined dimensions.

[0015] A HIC-resistant thick steel plate and UOE steel pipe according to the present invention can achieve a high strength of at least X60 grade (YP on the order of 70 ksi). In addition, elements such as Mn, C, P, and S which have been proposed in the past as causes of HIC are controlled, and HIC caused by carbonitrides of Nb or Ti can be prevented. Therefore, the occurrence of HIC in a high strength thick steel plate can be prevented with certainty.

[0016] A thick steel plate according to the present invention having improved HIC resistance can be used in structures such as offshore structures or pressure vessels, or it can be used for the manufacture of UOE steel pipes. A UOE steel pipe according to the present invention having improved HIC resistance is particularly suitable for line pipe, but it can also be used for offshore structures. Because the occurrence of HIC can be prevented with certainty, the reliability of products is markedly increased.

Brief Explanation of the Drawings

[0017]

Figure 1 is a graph showing the results of investigation of the degree of segregation of Mn, P, S, Nb, and C by the laser ICP method.

Figure 2(a) is a graph showing the relationship between the Mn concentration and the Nb concentration, and Figure 2(b) is a graph showing the relationship between the Mn concentration and the Ti concentration.

Modes for Carrying Out the Invention

[0018] The chemical composition of a thick steel plate according to the present invention is as explained below. In the following explanation, percent with respect to the chemical composition of steel always means mass percent.

[C: at least 0.02% and at most 0.07%]

[0019] C is generally known as an element which has a great effect on the strength of steel. If the C content is less than 0.02%, it is difficult to obtain a sufficient strength required in applications such as line pipe. On the other hand, if the C content exceeds 0.07%, as stated above, macroscopic segregation takes place at the center of the thickness of a cast slab during continuous casting and causes HIC. Therefore, the C content is at least 0.02% and at most 0.07%. From the above standpoints, the lower limit on the C content is preferably 0.03%, and the upper limit is preferably 0.06%.

[Si: at least 0.05% and at most 0.50%]

[0020] When present with a content of at least 0.05%, Si generally acts as a deoxidizing element in the manufacture of steel and is effective at decreasing the oxygen concentration in steel. Si also has an effect of increasing the strength of steel. However, an Si content exceeding 0.50% leads to the formation of martensite-austenite constituent, which deteriorates the toughness of HAZs (heat affected zones) in welding. In addition, due to the strong interaction of Si with Ti, Si affects the formation of TiN notwithstanding it is not a constituent element of TiN. Nb carbonitrides which have been identified as starting points for HIC in the present invention have a high probability of precipitating with TiN as nuclei. Therefore, if the Si concentration becomes too high, a deterioration in HIC resistance may occur. Accordingly, the Si content is at least 0.05% and at most 0.50%. A preferred Si content is at least 0.05% and less than 0.3%.

[Mn: at least 1.1 % and at most 1.6%]

[0021] Mn is an element which generally has a large effect on the strength of steel. It is difficult to obtain sufficient strength if the Mn content is less than 1.1%. If the Mn content exceeds 1.6%, as discussed previously, Mn concentrates in the region of center segregation, and HIC resistance deteriorates. Therefore, the Mn content is at least 1.1 % and at most 1.6%. In order to guarantee HIC resistance in the region of center segregation with certainty, the Mn content is preferably at least 1.1% and less than 1.5%.

[P: at most 0.015%]

[0022] The content of P, which is an impurity unavoidably contained in steel, is preferably as low as possible. Due to its low distribution coefficient at a solid-liquid interface at the time of solidification, P has a marked tendency to segregate, so as discussed previously, it concentrates in the region of center segregation and causes HIC resistance to deteriorate. Therefore, the upper limit on the P content is 0.015%. In order to prevent a deterioration in HIC resistance due to segregation of P in the region of center segregation with certainty, the P content is preferably less than 0.008%. There is no lower limit on the P content. However, in view of the fact that reducing the P content to an extremely low level is accompanied by a corresponding increase in costs, the P content is preferably at least 0.004%.

[S: at most 0.002%]

[0023] The content of S, which is an impurity which is unavoidably contained in steel, is preferably as low as possible. In the same manner as P, S has a low distribution coefficient at a solid-liquid interface at the time of solidification and hence a marked tendency to segregate. Furthermore, as discussed previously, in the region of segregation, it forms MnS which becomes a starting point for HIC. Therefore, the upper limit on the S content is 0.002%. In order to obtain stable HIC resistance under more severe conditions such as are required with high strength steel, the upper limit on the

S content is preferably 0.001 %. There is no lower limit on the S content, but lowering the S content to an extremely low level is accompanied by a corresponding increase in costs. Therefore, the S content is preferably at least 0.0003%.

[Nb: at least 0.005% and at most 0.060%]

[0024] Nb is an element which forms carbonitrides in steel, thereby increasing the strength of steel and which is also effective at improving the toughness of steel. For this purpose, the Nb content is at least 0.005%. Particularly in TMCP, Nb is used in order to control the microsttucture of a thick steel plate by controlling the formation of solid solution and precipitation. Also in order to obtain this effect, the Nb content is made at least 0.005%. However, if the Nb content exceeds 0.060%, Nb does not completely dissolve to form a solid solution at the heating stage and the structure can no longer be controlled. At the same time, an increase in the Nb content means an increase in the amount of Nb carbonitrides, and this may cause a decrease in resistance to HIC. Therefore, the Nb content is at least 0.005% and at most 0.060%. In order to stably guarantee resistance to HIC under more severe conditions which are demanded of high strength steel, for example, the Nb content is preferably at least 0.010% and at most 0.040%.

[Ti: at least 0.005% and at most 0.030%]

[0025] Ti is effective at increasing the strength of steel, and it fixes N in steel as TiN leading to a decrease in the amount of precipitation of NbN or AlN. Therefore, it has the effect of preventing surface cracking in a cast slab caused by dynamic precipitation of NbN or AlN at austenite grain boundaries at the time of bending or straightening of a continuously cast slab. In order to achieve these effects, the Ti content is at least 0.005%. However, with a Ti content exceeding 0.030%, a large number of Ti carbide is formed, resulting in a decrease in the toughness of HAZs and causing the formation of coarse TiN. In addition, as described above, there is a high possibility of the precipitation of Nb carbonitrides occurring with TiN as nuclei, and the presence of coarse TiN causes a decrease in resistance to HIC. Therefore, the Ti content is at least 0.005% and at most 0.030%. A preferred Ti content is at least 0.010% and at most 0.025%.

[Al: at least 0.005% and at most 0.06%]

[0026] Al is an element which is effective as a deoxidizing element which decreases the oxygen concentration in steel. The Al content necessary for deoxidation is at least 0.005%. If the Al content is below this level, desulfurization becomes inadequate, and the yield of added Ca worsens so that the effect thereof can no longer be adequately obtained. As a result, HIC caused by segregation of sulfides or S in steel takes place. However, alumina which is formed by deoxidation with Al sometimes becomes the cause of HIC. Therefore, the Al content is at most 0.06%. For the same reason, the Al content is preferably at most 0.04%.

[Ca: at least 0.0005% and at most 0.0060%]

[0027] In HIC-resistant steel, Ca is a kind of essential element for preventing the formation of MnS by decreasing the concentration of S as well as for controlling the shape of sulfides. Therefore, at least 0.0005% of Ca is added. However, with a Ca content exceeding 0.0060%, its effects saturate and an increase in manufacturing costs results. Therefore, the Ca content is at least 0.0005% and at most 0.0060%.

[N: at least 0.0015% and at most 0.007%]

[0028] N is an element which is unavoidably incorporated in steel when steel undergoes melting in air such as in a convertor. N is a constituent element of coarse Nb carbonitrides on which the present invention is focused. Nb carbonitrides is not directly preferentially linked to N, but it is known that Nb carbonitrides precipitate with crystallized TiN as nuclei. N is an element which forms nitrides with Al, Ti, or the like in steel, and these nitrides have the effect of refining crystal grains as pinning particles during hot working. Therefore, N has an effect on the mechanical properties of steel and also on the formation of the microstructure. For this reason, it is necessary for the N concentration to be at least 0.0015%. On the other hand, as stated above, in view of the fact that surface cracking of a cast slab is caused due to dynamic precipitation of these nitrides at the austenite grain boundaries during continuous casting, the upper limit on N is 0.007%.

$$[0.1\% < (\mathrm{Cu} + \mathrm{Ni} + \mathrm{Cr} + \mathrm{Mo}) < 1.5\%]$$

[0029] As stated with respect to Equation (1), the symbols for elements in the above equation means the contents of those elements (in mass %).

[0030] In a HIC-resistant steel, the upper limits on the contents of C and Mn are determined with the object of decreasing the formation of MnS and the segregation of C. Therefore, at least one alloying element selected from Cu, Ni, Cr, and Mo is added for ensuring strength. In order to achieve an effect on improvement in strength with certainty, it is effective for the overall content of these alloying elements to be larger than 0.1 %. However, a too high content of these alloying elements is accompanied by an increased hardenability, which increases the strength and causes the structure to locally harden, resulting in a deterioration in HIC resistance. Therefore, the overall content of these alloying elements in the present invention is less than 1.5%.

[0031] The individual contents of these alloying elements will be explained. As can be seen from these explanations, it is preferable to add all four of these elements, but depending upon the desired strength level, it is also possible to add one to three of these. In any case, the total content of these elements is greater than 0.1 % and less than 1.5%.

[0032] Cu with a content of at least 0.1 % increases the hardenability of the steel. On the other hand, if the Cu content exceeds 0.5%, the hot workability and machinability of the steel decrease, and at the time of continuous casting, surface cracking referred to as copper checking is induced. Accordingly, the Cu content is preferably at least 0.1% and at most 0.5%. When at least 0.2% of Cu is added, Ni in an amount of at least one-third of the Cu content is preferably also added in order to prevent copper checking.

[0033] Ni has the effects of increasing the strength of steel by solid solution strengthening and improving its toughness. These effects are obtained with a Ni content of at least 0.1%. However, these effects reach a limit and weldability worsens when the Ni content exceeds 1.0%. Therefore, the Ni content is preferably at least 0.1 % and at most 1.0%.

[0034] Cr increases the strength and toughness of steel. Therefore, the addition of Cr is effective particularly for steel which requires high strength. The fact that adding even a small amount of Cr greatly contributes to increasing strength can be seen from the equation for carbon equivalent $Ceq = C + Mn/6 + (Cr + Mo)/5 + (Cu + Ni)/15$. This effect is obtained with a Cr content of at least 0.05%. On the other hand, addition of Cr in an amount exceeding 0.5% causes weld cracking to occur. Therefore, the Cr content is preferably at least 0.05% and at most 0.5%.

[0035] Mo increases the hardenability of steel, thereby contributing to an increase in strength. In addition, since Mo is an element which does not readily undergo microscopic segregation, it has the effect of suppressing the occurrence of HIC caused by center segregation. These effects of Mo are obtained with a Mo content of at least 0.02%. However, Mo is not only an expensive element which leads to an increase in costs, but if greater than 0.5% of Mo is added, a hard phase such as a bainite phase or a martensite phase is formed, and HIC resistance ends up worsening. Therefore, the Mo content is preferably at least 0.02% and at most 0.5%. In view of its effect on HIC resistance which is large compared to that of the other three above-described elements, the Mo content is more preferably at most 0.3%.

[0036] Next, optional elements will be explained.

[V: at most 0.10%]

[0037] V is effective at increasing the strength of steel by forming a solid solution in ferrite and carbonitrides in steel. Therefore, V may be added when a particularly high strength is demanded. However, if the V content exceeds 0.1 %, it has an adverse effect on toughening of HAZs. Accordingly, when V is added, its content is at most 0.10%. In order to obtain the above-described effect of V with certainty, the V content is preferably at least 0.01%.

[0038] A remainder of the composition other than the above-described elements is Fe and impurities.

[Degree of Nb segregation: at most 2.0, (degree of Nb segregation) / (degree of Mn segregation) (α): at least 1.0 and at most 1.5]

[Degree of Ti segregation: at most 2.0; (degree of Ti segregation) / (degree of Mn segregation) (β): at least 1.0 and at most 1.5]

[0039] The degree of Mn segregation, the degree of Nb segregation, and the degree of Ti segregation are the degrees of segregation in the central portion of the plate thickness and are determined as described above.

[0040] The present inventors found that in a thick steel plate used in line pipe or the like of at least X60 grade (YP on the order of 70 ksi), HIC sometimes occurs even when the contents of MnS and C, Mn, and P, which were conventionally thought to be the main causes of impairment of HIC resistance, are decreased. This was thought to be because even if conventional countermeasures against HIC due to MnS or macroscopic segregation were carried out, carbonitrides of Nb or Ti remaining in the steel became starting points which cause cracks to develop.

[0041] By carrying out HIC tests on thick steel plates with varying degree of segregation to investigate the effect of segregation, it was found that the causes of HIC in a thick steel plate include not only segregation of C, Mn, P, and S but also segregation of Nb and Ti. Namely, in addition to relying on conventional knowledge, by additionally controlling segregation of Nb and Ti, the HIC resistance of a thick steel plate of at least X60 grade which is used in line pipe or the like can be improved.

[0042] The present inventors carried out HIC tests on test pieces taken from thick steel plate products. Cracks all developed in central portions in the thickness direction of the plates. This fact shows that HIC occurs in the region of center segregation. The regions where cracks developed in the test pieces which showed cracking were investigated in detail. Upon analysis by SEM/EDS of inclusions which became the starting points of cracks, it was found that although the concentration may varied, the inclusions were primarily carbonitrides containing Nb and indicated as Nb(C,N) (containing at most 10 volume % of Ti and referred to in this description as Nb carbonitrides).

[0043] The extent of concentration of each element (degree of segregation) can be known by investigating the region of center segregation over a wider range of steel compositions. Investigation of the degree of segregation can be carried out by the EPMA (electron probe microanalyzer) method, by the laser ICP (laser ablation inductively coupled plasma) method, or by chemical analysis.

[0044] The present inventors investigated the degree of segregation of each element in the central portion of the plate thickness using a thick steel plate produced by rolling and investigated the relationship of the degree of segregation to the occurrence of HIC.

[0045] The degree of segregation of each element was determined by the laser ICP method. The apparatus which was used was a laser ICP analyzer manufactured by Shimadzu Corp. In the laser ICP method which is a kind of emission spectroscopy, a cut cross section of a sample is irradiated with a laser beam to generate vapor, the vapor is transported by a carrier gas into an induction plasma to cause emission, and the wavelength and intensity of the emission spectrum are analyzed for quantitative analysis of each element. By repeating the analysis while moving the sample in one direction and irradiating it with a laser beam, the variation in the concentration of each element over a certain length can be investigated.

[0046] In a laser ICP apparatus, it is possible to perform measurement every 100 μm (0.1 mm; measurement is carried out by moving the sample by 100 μm at a time), so measurement can be obtained at 100 points over a length of 10 mm. In the present invention, measured values of the concentration of each element are obtained at 120 points over a total length of 12 mm having a distance of 6 mm above and below the center of the plate thickness in a cut cross section using a sample of a cross section cut perpendicular to the plate surface and parallel to the rolling direction of a steel plate. In this manner, macroscopic segregation can be adequately evaluated. The degree of segregation of each element is determined by taking the arithmetic mean of the measured values obtained at the 120 points as the average concentration of the element in the thick plate and dividing the maximum of the measured values (the maximum concentration) by the average concentration.

[0047] The degree of segregation of each element can be obtained by actually determining the concentration (mass %) of each element from the measured values (emission peak strength) at the 120 points obtained by the laser ICP method and calculating the ratio of the maximum concentration to the average concentration. However, due to the fact that the concentration and the emission peak strength assigned to each element obtained by measurement are proportional to each other, the degree of segregation can be easily found as the ratio of the maximum peak strength to the average peak strength for each element.

[0048] The diameter of a laser beam is approximately 1 mm, so all inclusions of 1 mm or less are reflected in the measured data. The size of inclusions is usually on the order of several micrometers and even large inclusions measure around several tens of micrometer. Therefore this measurement technique makes it possible to adequately investigate the degree of segregation which is accompanied by the formation of inclusions.

[0049] Figure 1 is a graph showing the degree of segregation for Mn, P, S, Nb, and C obtained by the laser ICP method for a thick steel plate having 8.8% occurrence of HIC. In the graph of Figure 1, the abscissa shows the locations of the measurement points in the plate thickness direction (the center of the plate thickness was at 60 in units of 0.1 mm, the measurement was performed over a length of 6 mm above and below the center of the plate thickness, and the total number of measurement points was 120), and the ordinate shows the measured results for each element (emission peak strength in arbitrary unit). The level on the ordinate is different from element to element, but the average composition and the degree of segregation can be calculated by this measurement method.

[0050] As stated above, it is possible to use methods other than the laser ICP method. For example, it is possible to determine the degree of segregation by measuring the concentration of elements in a location of interest using chemical analysis or the like and comparing the results of analysis with the results for portions where there is no segregation. It is also possible to determine the degree of segregation by the EPMA method or by the laser ablation inductive coupled plasma mass spectroscopy (LA-ICP-MS) method in which quantitative determination in the laser ICP method is carried out by mass spectrometry instead of by emission spectroscopy.

[0051] In the example shown in the graph of Figure 1, it can be seen from the graph that the degree of Nb segregation is 2.1, the degree of Ti segregation is 1.8, and the degree of Mn segregation is 1.3. Thus, the ratio of the degree of Nb segregation to the degree of Mn segregation (α) is calculated at 1.7 and the ratio of the degree of Ti segregation to the degree of Mn segregation (β) is calculated at 1.4.

[0052] Figure 2(a) is a graph using the data of Figure 1 in which the abscissa is the Mn concentration and the ordinate is the Nb concentration, and Figure 2(b) is a graph in which the abscissa is the Mn concentration and the ordinate is the Ti concentration. The concentration of each element is actually indicated by the emission peak intensity. These graphs make it possible to compare the degree of Nb segregation or the degree of Ti segregation with the degree of Mn segregation.

[0053] From the graphs shown in Figures 2(a) and 2(b), it can be seen that the degree of Mn segregation is representative of the segregation of each element in a cast slab, and if the degree of segregation of a cast slab (degree of Mn segregation) worsens, the degree of Nb segregation and the degree of Ti segregation similarly worsen. Furthermore, it can be seen that if the degree of Mn segregation exceeds a certain critical point, as shown by the regions surrounded by circles in these graphs, Nb and Ti show a tendency to abruptly precipitate as inclusions.

[0054] The present inventors thought that inclusions which develop in large quantities could become the cause of HIC, and they investigated the relationship between the occurrence of HIC and the ratio of the degree of Nb segregation to the degree of Mn segregation (α) and the ratio of the degree of Ti segregation to the degree of Mn segregation (β). As a result, they found that the occurrence of HIC can be markedly suppressed if the degree of Nb segregation is at most 2.0 and α, which is the ratio of (the degree of Nb segregation) / (the degree of Mn segregation), is at least 1.0 and at most 1.5, and if the degree of Ti segregation is at most 2.0 and β, which is the ratio of (the degree of Ti segregation) / (the degree of Mn segregation9, is at least 1.0 and at most 1.5.

[0055] The criterion for the occurrence of HIC according to the present invention is particularly effective with respect to the resistance to HIC of high strength steels of at least X60 grade for which the conventional criterion was ineffective. If the criterion based on the degree of segregation of Nb and Ti according to the present invention is employed together with a decrease in C, Mn, P, and S which has been employed in the past, the occurrence of HIC can of course be effectively prevented.

[0056] Even when thick steel plates have the same chemical composition, if the manufacturing conditions are different, their state of segregation differs from each other. As a result, there are cases in which the above-described requirements concerning the degree of segregation (the degree of segregation of Nb and Ti and the values of α and β) may not be satisfied. Accordingly, a thick steel plate according to the present invention can be manufactured by selecting not only the chemical composition but also the steel making conditions and the rolling conditions so that segregation does not readily take place. Operating conditions which are effective for decreasing segregation will be briefly explained below.

[0057] In the steel making stage, application of IR (injection refining) and shape control of oxides by addition of Ca are effective at reducing segregation.

[0058] In the next continuous casting (CC) stage, segregation in the thickness direction of a plate can be decreased by providing the cast slab with a slope approximately corresponding to the amount of contraction due to solidification of the slab when the central portion of the slab solidifies or with a slightly greater slope. Employing suitable water cooling conditions or selecting the casting speed so that marked non-uniformity of solidification does not develop in the widthwise direction of casting and the lengthwise direction of casting is also effective at decreasing segregation.

[0059] In hot rolling of the cast slab into a thick plate (this may be direct rolling carried out in succession with CC), it is effective to first perform heating to at least 1100° C and at most 1200° C. This heating causes Nb which crystallized out in the cast slab to go into solid solution, thereby preventing Nb from forming Nb carbonitrides. In order to cause Nb to form a solid solution, it is effective to adjust the heating temperature or the duration of heating in accordance with the Nb content. When the Nb content is high, the heating temperature and/or the duration of heating is increased.

[0060] After rolling, water cooling is started at a temperature equal to or higher than the Ar_3 point. The reason why the temperature at the start of water cooling is controlled in this manner is because if water cooling is started at a temperature below the Ar_3 point, the formation of ferrite which is accompanied by discharge of carbon begins before water cooling. As a result, water cooling causes a hard structure containing an increased amount of carbon to form, thereby deteriorating resistance to HIC.

[0061] Water cooling is effective because diffusion of elements such as C and P is decreased as much as possible and C can be prevented from combining with Nb. As the temperature decreases, the speed of diffusion of each element decreases. If the steel is let cool after rolling without water cooling, the length of time for which the steel is exposed to a higher temperature increases and diffusion of elements may be promoted. The diffused elements segregate at grain boundaries and in inclusions.

[0062] The rate of water cooling is preferably at least 5° C per second and at most 30° C per second. At a rate of water cooling which is less than 5° C per second, diffusion of elements is promoted, while if it is greater than 30° C per second, hardening is excessively introduced to the steel and a hard structure is formed.

[0063] A UOE steel pipe manufactured from a thick steel plate according to the present invention has increased reliability when used in a corrosive environment because it does not develop HIC due to coarse carbonitrides of Ti and Nb. Methods of manufacturing a UOE steel pipe are known to those skilled in the art. In the present invention as well, a UOE steel pipe can be manufactured by the same methods as in the prior art.

Example 1

[0064] The present invention will be explained more specifically while referring to examples.

[0065] Steels Nos. 1-14 having the chemical compositions and Ar_3 points shown in Table 1 was subjected to continuous casting using a continuous casting machine of a vertical bending type with a thickness of 300 mm and a width of 2300 mm at a casting rate of at least 0.7 meters per minute and at most 0.8 meters per minute to obtain a cast slab.

[0066] The resulting cast slab was heated to at least approximately 1100° C and at most approximately 1200° C, and then it was subjected to hot rolling to give a plate thickness of around 25.4 mm under conditions such that the finish rolling temperature was at least approximately 750° C and at most approximately 850° C. Immediately after hot rolling, the plate was water cooled. Water cooling was stopped at a temperature of at least approximately 450° C and at most approximately 550° C and followed by air cooling. The cooling rate during water cooling was 10 - 30° C per second.

[0067] The resulting thick steel plate was subjected to investigation of the degree of segregation using the above-described laser ICP method (120 measurement points) and to a tensile test and a HIC test. The test results and the chemical compositions of the steels are also shown in Table 1.

[0068] The HIC test was carried out by a NACE test prescribed by NACE TM-02-84, and the crack area ratio (CAR) was measured as the rate of occurrence of HIC. A value of CAR of at most 3% was considered satisfactory, while a value exceeding 3% indicated that substantial HIC occurred and was determined to be unsatisfactory.

Table 1

Steel No.	Category	Chemical composition of steel (mass %) (reminder: Fe and Impurities)											Ar_3 point (°C)	Degree of segregation					% Occurrence of HIC	Strength (MPa)
		C	Si	Mn	P	S	Nb	Ti	Al	Ca	Cu+Ni +Cr +Mo	N		Nb	Ti	Mn	Nb/ Mn (α)	Ti/ Mn (β)		
1	Invent.	0.04	0.15	1.35	0.008	0.0004	0.03	0.012	0.015	0.003	0.4	0.0033	776	1.35	1.32	1.2	1.1	1.1	0	568
2	Invent.	0.07	0.05	1.15	0.008	0.0008	0.015	0.008	0.044	0.0045	0.45	0.0042	783	1.44	1.57	1.15	1.3	1.4	0	525
3	Invent.	0.05	0.4	1.4	0.012	0.001	0.045	0.025	0.03	0.0007	0.12	0.0045	777	1.51	1.44	1.2	1.3	1.2	2.9	541
4	Compar.	0.04	0.15	1.35	0.008	0.0004	0.03	0.012	0.015	0.003	0.4	0.0052	771	2.12	1.78	1.22	1.5	1.2	11.1	588
5	Invent.	0.05	0.15	1.5	0.006	0.0005	0.03	0.03	0.02	0.0026	1	0.0058	739	1.32	1.43	1.25	1.1	1.1	2.2	641
6	Compar.	0.05	0.07	1.12	0.006	0.0004	0.03	0.01	0.023	0.0027	0.02	0.0039	793	1.23	1.22	1.19	1	1	0	489
7	Compar.	0.05	0.15	1.33	0.01	0.0005	0.065	0.012	0.015	0.0033	0.44	0.0042	777	1.35	.1.45	1.22	1.1	1.2	7.8	579
8	Compar.	0.05	0.15	1.32	0.01	0.0009	0.025	0.035	0.025	0.0037	0.42	0.0044	774	1.35	1.78	1.18	1.1	1.5	12.7	551
9	Compar.	0.06	0.19	1.4	0.01	0.0005	0.03	0.015	0.029	0.0003	0.1	0.0050	781	1.25	1.44	1.22	1	1.2	25.7	578
10	Invent.	0.04	0.15	1.35	0.006	0.0004	0.03	0.012	0.015	0.003	0.89	0.0048	760	1.35	1.44	1.2	1.1	1.2	0	568
11	Compar.	0.07	0.05	1.15	0.008	0.0008	0.015	0.008	0.044	0.0045	0.45	0.0042	777	1.76	1.54	1.1	1.6	1.4	9.3	525
12	Compar.	0.05	0.22	1.4	0.012	0.001	0.035	0.025	0.03	0.0025	0.55	0.0043	763	1.32	2.04	1.2	1.1	1.7	13.3	541
13	Compar.	0.06	0.15	1.03	0.008	0.0004	0.026	0.012	0.024	0.003	0.05	0.0044	804	1.32	1.44	1.29	1	1.1	0	472
14	Compar.	0.04	0.15	1.65	0.007	0.0006	0.031	0.03	0.022	0.0026	0.38	0.0038	753	1.52	1.53	1.47	1	1	8.5	641

[0069] As can be seen from Table 1, with thick steel plates made from the inventive steels in which the ratios α and β of the degree of segregation of Nb and Ti, respectively were small values of at most 1.5, the strength was of at least X60 grade with a tensile strength of at least 520 MPa and the rate of occurrence of IHC (CAR) was at most 3%. Accordingly, it is obvious to those skilled in the art that UOE steel pipes of high reliability can be manufactured from these thick steel plates.

[0070] In contrast, thick steel plates made from the comparative steels were unsatisfactory with respect to either strength or the rate of occurrence of HIC. In particular, Steels Nos. 4, 11, and 12 had a chemical composition which satisfied the requirements of the present invention, but the value of the degree of Nb segregation, the ratio (α) of (the degree of Nb segregation) / (the degree of Mn segregation), or the ratio (β) of (the degree of Ti segregation) / (the degree of Mn segregation) did not satisfy the ranges for the present invention, and for each of these examples, the strength was inadequate or the rate of occurrence of HIC was high.

Claims

1. A thick steel plate having improved resistance to HIC **characterized by** having a chemical composition consisting essentially of, in mass percent, C: 0.02 - 0.07%, Si: 0.05 - 0.50%, Mn: 1.1 - 1.6%, P: at most 0.015%, S: at most 0.002%, Nb: 0.005 - 0.060%, Ti: 0.005 - 0.030%, Al: 0.005 - 0.06%, Ca: 0.0005 - 0.0060%, N: 0.0015 - 0.007%, at least one of Cu, Ni, Cr, and Mo in amounts which satisfy Equation (1), V: 0 - 0.10%, and a remainder of Fe and impurities, wherein the degree of Nb segregation is at most 2.0, the ratio α of the degree of Nb segregation to the degree of Mn segregation (α = the degree of Nb segregation/the degree of Mn segregation) is at least 1.0 and at most 1.5, the degree of Ti segregation is at most 2.0, and the ratio β of the degree of Ti segregation to the degree of Mn segregation (β = the degree of Ti segregation/the degree of Mn segregation) is at least 1.0 and at most 1.5:

$$\text{Equation (1): } 0.1\% < (\mathrm{Cu} + \mathrm{Ni} + \mathrm{Cr} + \mathrm{Mo}) < 1.5\%$$

   wherein the symbols for elements in the equation indicate the content (mass percent) of each element.

2. A thick steel plate as set forth in claim 1 wherein the chemical composition contains 0.01 - 0.10% of V.

3. A UOE steel pipe **characterized by** being formed from a thick steel plate as set forth in claim 1 or claim 2.

Fig. 1

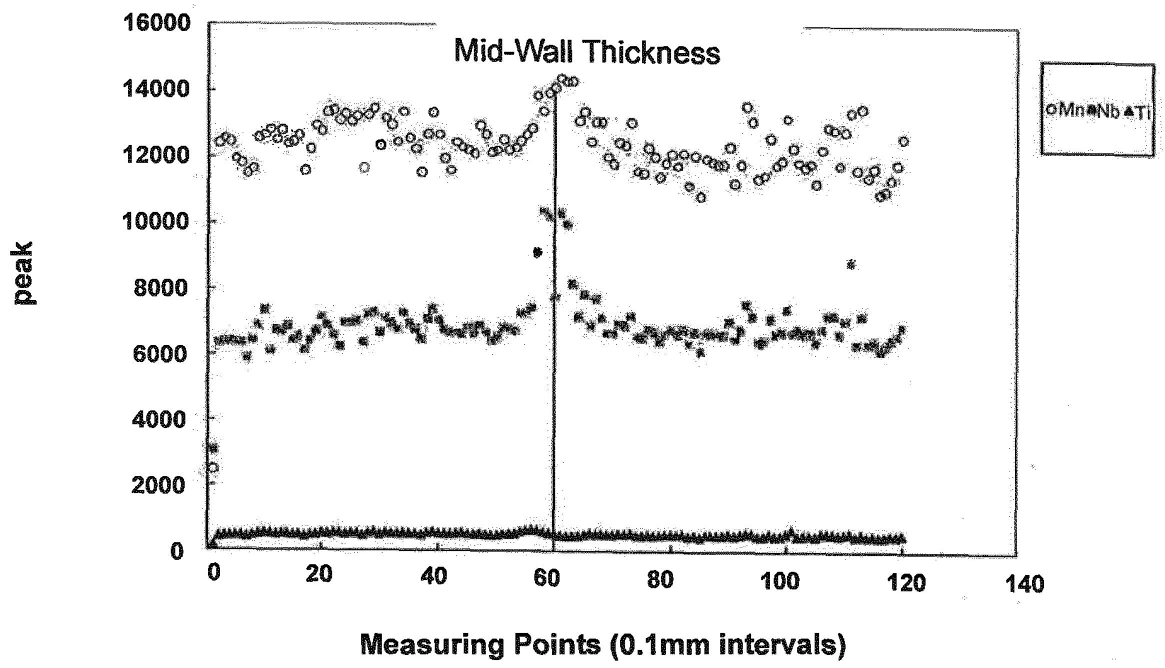
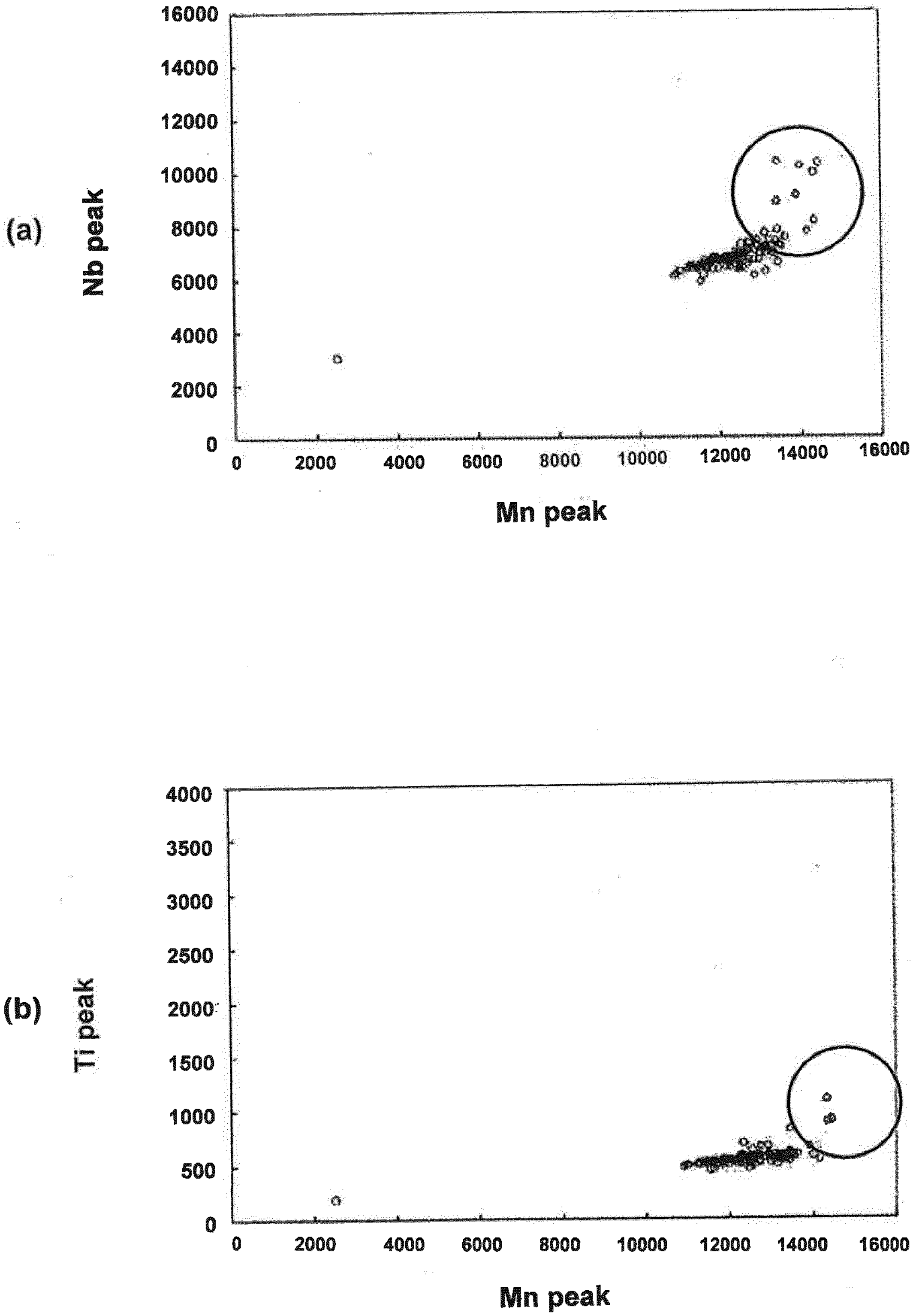

Mid-Wall Thickness
16000
14000
12000
10000
8000
6000
4000
2000
0
peak
0
20
40
60
80
100
120
140
Measuring Points (0.1mm intervals)
○Mn ■Nb ▲Ti

Fig. 2


(a)
Nb peak
16000
14000
12000
10000
8000
6000
4000
2000
0
0
2000
4000
6000
8000
10000
12000
14000
16000
Mn peak
(b)
Ti peak
4000
3500
3000
2500
2000
1500
1000
500
0
0
2000
4000
6000
8000
10000
12000
14000
16000
Mn peak

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/054173

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *B21B1/38*(2006.01)i, *B21B3/00*(2006.01)i, *B21C37/08*(2006.01)i, *C21D8/02*(2006.01)i, *C22C38/58*(2006.01)i

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, B21B1/38, B21B3/00, B21C37/08, C21D8/02, C22C38/58

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2008-7841 A (Sumitomo Metal Industries, Ltd.), 17 January 2008 (17.01.2008), claims 4 to 6; paragraphs [0001], [0149] to [0155] (Family: none)	1,2
X	JP 2006-63351 A (Sumitomo Metal Industries, Ltd.), 09 March 2006 (09.03.2006), claims 1 to 5; paragraphs [0001], [0071] to [0075] (Family: none)	1,2

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

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"&" document member of the same patent family

Date of the actual completion of the international search 10 June, 2010 (10.06.10)	Date of mailing of the international search report 22 June, 2010 (22.06.10)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/054173

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2005-264217 A (JFE Steel Corp.), 29 September 2005 (29.09.2005), claims 1 to 4; paragraphs [0001], [0062] to [0066] (Family: none)	1,2
X	JP 9-209037 A (NKK Corp.), 12 August 1997 (12.08.1997), claims 1, 2; paragraphs [0001], [0040], [0041] (Family: none)	1-3
A	JP 2002-363689 A (Sumitomo Metal Industries, Ltd.), 18 December 2002 (18.12.2002), claims 1 to 4 (Family: none)	1-3
A	JP 2000-160245 A (NKK Corp.), 13 June 2000 (13.06.2000), claims 1, 2; paragraph [0001] (Family: none)	1-3

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