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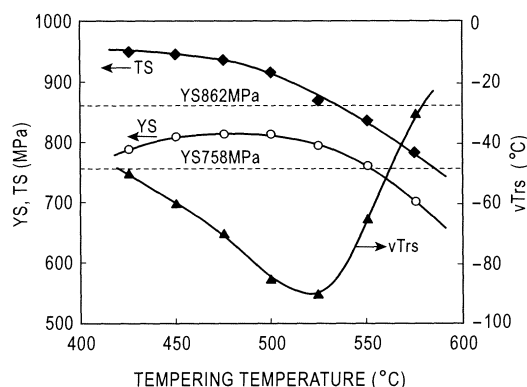
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(54) **MARTENSITIC STAINLESS-STEEL SEAMLESS PIPE FOR OIL WELL PIPE AND PROCESS FOR PRODUCING THE SAME**

(57) A seamless steel pipe for oil country tubular goods which simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness and a method for manufacturing the same are provided. A quenching treatment is performed on a stainless steel seamless pipe having a composition which contains on a mass percent basis, less than 0.010% of C, 1.0% or less of Si, 0.1% to 2.0% of Mn, 0.020% or less of P, 0.010% or less of S, 0.10% or less of Al, 10% to 14% of Cr, 0.1% to 4.0% of Ni, 0.05% or less of N, and the balance being Fe and inevitable impurities in which after heating is performed to a heating temperature for quenching equivalent to or more than the A_{c3} transformation point, cooling is performed to a temperature range of 100°C or less at a cooling rate equivalent to or more than that of air cooling; and following the quenching treatment, a tempering treatment is performed in which heating is performed to a tempering temperature in the range of more than 450°C to 550°C, and cooling is then performed. As a result, a martensitic stainless steel seamless pipe for oil country tubular goods is obtained which simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness

having a $vTrs$ of -60°C or less. In addition to the above composition, at least one selected from the group consisting of Cu, Mo, V, Nb, and Ti may also be contained.

FIG. 1



Description

Technical Field

5 **[0001]** The present invention relates to a martensitic stainless steel seamless pipe for oil country tubular goods, and in more particular relates to a seamless steel pipe for oil country tubular goods which has a high strength, such as a yield strength of 110 ksi (758 MPa) or more, and a superior low temperature toughness and to a method for manufacturing the martensitic stainless steel seamless pipe.

10 Background Art

[0002] In consideration of a steep rise in crude oil prices and depletion of petroleum resources to be expected in near future, in recent years, for example, deep oil wells; oil wells and gas wells with a severe corrosive environment containing carbon dioxide, chlorine ions, and the like; and oil wells with a severe drilling environment, such as in a cold district or on a sea bed, to which attention has not been paid in the past, have been aggressively developed. Oil country tubular goods used in the environments as described above are required to include a material which simultaneously has a high strength, a superior corrosion resistance, and also a superior toughness.

15 **[0003]** Heretofore, in oil wells and gas wells with an environment containing carbon dioxide CO₂, chlorine ions Cl⁻, and the like, as oil country tubular goods used for drilling operation, a 13% Cr martensitic stainless steel pipe has been frequently used.

20 **[0004]** For example, in Patent Document 1, martensitic stainless steel suitably used for oil country tubular goods has been proposed which contains 0.01% to 0.1% of C, 9% to 15% of Cr, and 0.1% or less of N, and which has a high toughness even though having a relatively high C content and a high strength. According to a technique disclosed in Patent Document 1, when the amount of carbides present in prior-austenite grain boundaries is decreased to 0.5 volume percent or less, the maximum minor axis of the carbides is set to 10 and 200 nm, the ratio between an average Cr concentration and an average Fe concentration in the carbides is set to 0.4 or less, a M₂₃C₆ type carbide is suppressed from being precipitated, and a M₃C type carbide is positively precipitated, the toughness can be significantly improved. In order to control the structure and the composition of the carbides described above in a desired range, according to the technique disclosed in Patent Document 1, air cooling (spontaneous cooling) is performed after hot working, air cooling (spontaneous cooling) is performed after a solution treatment, or following air cooling (spontaneous cooling) performed after a solution treatment, tempering is performed at a low temperature of 450°C or less.

Patent Document 1: Japanese Unexamined Patent Application Publication No. 2002-363708

35 Disclosure of Invention

[0005] However, according to the technique disclosed in Patent Document 1, when only air cooling (spontaneous cooling) is performed after hot rolling, or when only air cooling (spontaneous cooling) is performed after a solution treatment, there has been a problem in that a desired strength of a 110 ksi grade of yield strength (758–862 MPa), and a superior low temperature toughness cannot be simultaneously obtained. In addition, in order to ensure a strength of a 110 ksi grade of yield strength by the technique disclosed in Patent Document 1, the C content must be set to 0.01 mass percent or more. However, when the C content is set to 0.01 mass percent or more, the low temperature toughness is degraded, and a superior low temperature toughness having a fracture transition temperature of -60°C or less cannot be disadvantageously ensured. In addition, when the technique disclosed in Patent Document 1 is applied to a steel pipe so as to perform low temperature tempering at 450°C or less, a working stress is generated by correction performed immediately after the finish of heating of the tempering treatment, and there has been a problem in that variation of steel pipe characteristics is increased. The present invention is made to solve the related technical problems described above, and an object of the present invention is to propose a seamless steel pipe for oil country tubular goods which simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness and a stable method for manufacturing the seamless steel pipe. In addition, the "superior low temperature toughness" of the present invention indicates the case in which the fracture transition temperature vTrs in a Charpy impact test is -60°C or less.

45 **[0006]** In order to achieve the object described above, the inventors of the present invention carried out an intensive research on the influences of component compositions and heat treatment conditions upon the change in toughness with an increase in strength of a 13 Cr martensitic stainless steel pipe. As a result, it was found that in a component system in which the C content is controlled to be less than 0.010 mass percent, the Cr content is set to a relatively low content, such as approximately 11% of Cr, and the Ni content is also set to a relatively low content, such as 4.0% or less, after a quenching treatment is performed, when an appropriate tempering treatment is performed in which heating is performed to a tempering temperature in the range of more than 450°C to 550°C, and cooling is then performed, even

if Mo is not added, a high strength of a 110 ksi grade of yield strength can be ensured, and a high toughness having a $vTrs$ of $-60^{\circ}C$ or less can also be obtained. First, the results of fundamental experiments performed by the inventors of the present invention will be described.

[0007] After a quenching treatment ($810^{\circ}C \times 15$ minutes) was performed on a seamless steel pipe having a composition containing on a mass percent basis, 0.008% of C, 0.12% of Si, 1.14% of Mn, 0.019% of P, 0.001% of S, 0.04% of Al, 10.9% of Cr, 2.3% of Ni, 0.5% of Cu, 0.01% of N, and the balance being Fe, a tempering treatment was then performed in such a way that heating was performed to a temperature in the range of $425^{\circ}C$ to $575^{\circ}C$, and spontaneous cooling was then performed. In addition, in the cooling of the tempering treatment, a correctional treatment was performed. A tensile test and a Charpy impact test were performed on the obtained seamless steel pipe, so that tensile characteristics (yield strength YS, and tensile strength TS) and the low temperature toughness (fracture transition temperature $vTrs$) were measured. The obtained results are shown in Fig. 1. From Fig. 1, according to this component system, it is found that when tempering is performed at a temperature in the range of more than $450^{\circ}C$ to $550^{\circ}C$ after a quenching treatment, a high toughness and a high strength can be simultaneously obtained. That is, it is found that even if a 11% Cr-2% Ni composition is used, when tempering is performed at a temperature in the range of more than $450^{\circ}C$ to $550^{\circ}C$ after a quenching treatment, a high toughness having a $vTrs$ of $-60^{\circ}C$ or less and a high strength of a YS 110 ksi grade can be stably ensured. Based on the above findings, intensive researches were further carried out, and as a result, the present invention was made. That is, the summary of the present invention are as follows.

(1) A martensitic stainless steel seamless pipe for oil country tubular goods comprises: a composition which contains on a mass percent basis, less than 0.010% of C, 1.0% or less of Si, 0.1% to 2.0% of Mn, 0.020% or less of P, 0.010% or less of S, 0.10% or less of Al, 10% to 14% of Cr, 0.1% to 4.0% of Ni, 0.05% or less of N, and the balance being Fe and inevitable impurities. The martensitic stainless steel seamless pipe simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness having a fracture transition temperature $vTrs$ of $-60^{\circ}C$ or less in a Charpy impact test.

(2) In the martensitic stainless steel seamless pipe for oil country tubular goods according to the above (1), the composition further contains on a mass percent basis, at least one selected from the group consisting of 2.0% or less of Cu and 2.0% or less of Mo.

(3) In the martensitic stainless steel seamless pipe for oil country tubular goods according to the above (1) or (2), the composition further contains on a mass percent basis, at least one selected from the group consisting of 0.10% or less of V, 0.10% or less of Nb, and 0.10% or less of Ti.

(4) A method for manufacturing a martensitic stainless steel seamless pipe for oil country tubular goods which simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness, comprises: performing a quenching treatment on a stainless steel seamless pipe having a composition which contains on a mass percent basis, less than 0.010% of C, 1.0% or less of Si, 0.1% to 2.0% of Mn, 0.020% or less of P, 0.010% or less of S, 0.10% or less of Al, 10% to 14% of Cr, 0.1% to 4.0% of Ni, 0.05% or less of N, and the balance being Fe and inevitable impurities in which after heating is performed to a heating temperature for quenching equivalent to or more than the Ac_3 transformation point, cooling is performed from the heating temperature for quenching to a temperature range of $100^{\circ}C$ or less at a cooling rate equivalent to or more than that of air cooling; and performing a tempering treatment in which following the quenching treatment, heating is performed to a tempering temperature in the range of more than $450^{\circ}C$ to $550^{\circ}C$, and cooling is then performed.

(5) In the method for manufacturing a martensitic stainless steel seamless pipe for oil country tubular goods according to the above (4), the composition further contains on a mass percent basis, at least one selected from the group consisting of 2.0% or less of Cu and 2.0% or less of Mo.

(6) In the method for manufacturing a martensitic stainless steel seamless pipe for oil country tubular goods according to the above (4) or (5), the composition further contains on a mass percent basis, at least one selected from the group consisting of 0.10% or less of V, 0.10% or less of Nb, and 0.10% or less of Ti.

(7) In the method for manufacturing a martensitic stainless steel seamless pipe for oil country tubular goods according to one of the above (4) to (6), in the cooling of the tempering treatment, a correctional treatment is performed in a temperature range of $400^{\circ}C$ or more.

[0008] According to the present invention, a seamless steel pipe for oil country tubular goods which simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness having a fracture transition temperature $vTrs$ of $-60^{\circ}C$ or less can be easily and also stably manufactured, and significant industrial advantages can be obtained.

Brief Description of Drawings

[0009]

[Fig. 1]

Fig. 1 is a graph showing the relationship of the tempering temperature with the yield strength YS, tensile strength TS, and fracture transition temperature $vTrs$.

Best Modes for Carrying Out the Invention

[0010] First, a method for manufacturing a seamless steel pipe for oil country tubular goods will be described. In the present invention, as a starting material, a stainless steel seamless pipe is used which has a composition containing less than 0.010% of C, 1.0% or less of Si, 0.1% to 2.0% of Mn, 0.020% or less of P, 0.010% or less of S, 0.10% or less of Al, 10% to 14% of Cr, 0.1% to 4.0% of Ni, 0.05% or less of N, and the balance being Fe and inevitable impurities.

[0011] In addition, hereinafter, "mass percent" is simply represented by "%". First, the reasons for limiting the composition of the starting material will be described.

C: less than 0.010%

[0012] C is an important element relating to the strength of martensitic stainless steel, and in order to ensure a desired strength, the content is preferably 0.003% or more; however, when the content is 0.010% or more, the toughness and also the corrosion resistance are liable to be degraded. Hence, in the present invention, the C content is limited to less than 0.010%. In addition, in order to stably ensure the strength and the toughness, the content is preferably in the range of 0.003% to 0.008%.

Si: 1.0% or less

[0013] Si is an element functioning as a deoxidizing agent in a normal steelmaking process, and in the present invention, the content is preferably 0.1% or more; however, when the content is more than 1.0%, the toughness is degraded, and hot workability is also degraded. Hence, the Si content is limited to 1.0% or less. In addition, the content is preferably in the range of 0.1% to 0.3%.

Mn: 0.1% to 2.0%

[0014] Mn is an element to increase the strength, and in order to ensure a strength necessary as a steel pipe for oil country tubular goods, the content must be 0.1% or more in the present invention; however, when the content is more than 2.0%, the toughness is adversely influenced. Hence, the Mn content is limited in the range of 0.1% to 2.0%. In addition, the content is preferably in the range of 0.5% to 1.5%.

P: 0.020% or less

[0015] P is an element to degrade the corrosion resistance, such as CO₂ corrosion resistance, and is preferably decreased as small as possible in the present invention; however, an excessive decrease may cause an increase in cost. As the range in which the corrosion resistance, such as CO₂ corrosion resistance, is not degraded and in which the decrease can be industrially performed at a relatively low cost, the P content is limited to 0.020% or less. In addition, the content is preferably 0.015% or less.

S: 0.010% or less

[0016] S is an element to considerably degrade the hot workability in a pipe manufacturing process and is preferably decreased as small as possible; however, when the content is decreased to 0.010% or less, pipe manufacturing can be performed by a normal process, and hence the S content is limited to 0.010% or less. In addition, the content is preferably 0.003% or less.

Al: 0.10% or less

[0017] Al is an element having a strong deoxidizing function, and in order to obtain this effect, the content is preferably 0.001% or more; however, when the content is more than 0.10%, the toughness is adversely influenced. Hence the Al content is limited to 0.10% or less. In addition, the content is preferably 0.05% or less.

Cr: 10% to 14%

[0018] Cr is an element to improve the corrosion resistance by forming a passivation film and is also an element to particularly contribute to an effective improvement in CO₂ corrosion resistance and resistance to CO₂ stress corrosion cracking. When the content is 10% or more, corrosion resistance required for oil country tubular goods can be ensured, and hence the lower limit is set to 10% in the present invention. On the other hand, when the content is large, such as more than 14%, since ferrite is easily generated, a large amount of an expensive austenite generation element must be added in order to stably ensure a martensitic phase or to prevent degradation of the hot workability, so that economical problems may arise. Hence, the Cr content is limited in the range of 10% to 14%. In addition, in order to ensure more stable microstructure and hot workability, the content is preferably in the range of 10.5% to 11.5%.

Ni: 0.1% to 4.0%

[0019] Ni has a function to strengthen a passivation film and is an element to improve the corrosion resistance, such as CO₂ corrosion resistance. In order to obtain the effect as described above, the content must be 0.1% or more. On the other hand, when the content is more than 4.0%, the improvement effect is saturated, and as a result, a manufacturing cost is inevitably increased. Hence, the Ni content is limited in the range of 0.1% to 4.0%. In addition, the content is preferably in the range of 1.5% to 3.0%.

N: 0.05% or less

[0020] N is an element to significantly improve pitting resistance, and when the content is 0.003% or more, the effect described above becomes significant. On the other hand, when the content is more than 0.05%, various nitrides are formed, and as a result, the toughness is degraded. Hence, the N content is limited to 0.05% or less. In addition, the content is preferably in the range of 0.01% to 0.02%.

[0021] Although the components described above are basic components of the starting material, according to the present invention, besides those basic components described above, at least one selected from the group consisting of 2.0% or less of Cu and 2.0% or less of Mo and/or at least one selected from the group consisting of 0.10% or less of V, 0.10% or less of Nb, and 0.10% or less of Ti may also be contained.

[0022] At least one selected from the group consisting of 2.0% or less of Cu and 2.0% or less of Mo

[0023] Cu and Mo are elements each having a function to improve the corrosion resistance and, whenever necessary, at least one of them may be selected and contained.

[0024] Cu is an element having a function to improve the pitting resistance by strengthening a passivation film, and in order to obtain the effect as described above, the content is preferably 0.2% or more. On the other hand, when the content is more than 2.0%, Cu is partly precipitated, and as a result, the toughness is degraded. Hence, when Cu is contained, the content thereof is preferably limited to 2.0% or less. In addition, more preferably, the content is in the range of 0.2% to 1.0%.

[0025] In addition, Mo is an element having a function to increase the resistance against pitting caused by Cl⁻, and in order to obtain the above effect, the content is preferably 0.2% or more. On the other hand, when the content is more than 2.0%, the strength is not only decreased, but a material cost is also increased. Hence, the Mo content is preferably limited to 2.0% or less. In addition, more preferably, the content is in the range of 0.2% to 1.0%.

[0026] At least one selected from the group consisting of V: 0.10% or less, Nb: 0.10% or less, and Ti: 0.10% or less. V, Nb, and Ti are components to increase the strength, and whenever necessary, at least one of them may be selected and contained.

[0027] In order to obtain the effect as described above, at least one of 0.02% or more of V, 0.01% or more of Nb, and 0.02% or more of Ti is preferably contained. On the other hand, when at least one of more than 0.10% of V, more than 0.10% of Nb, and more than 0.10% of Ti is contained, the toughness is degraded. Hence, when being contained, the contents of V, Nb, and Ti are each preferably limited to 0.10% or less. In addition, more preferably, the V content is 0.02% to 0.05%, the Nb content is 0.01% to 0.05%, and the Ti content is 0.02% to 0.05%.

[0028] The balance other than those components described above contains Fe and inevitable impurities. In addition, as the inevitable impurities, 0.010% or less of O may be contained.

[0029] In the present invention, although a method for manufacturing a starting material having the above composition is not particularly limited, it is preferable that after molten steel having the above composition is formed by a commonly known steelmaking method, for example, using a converter, an electrical furnace, a vacuum melting furnace, and the like, a steel pipe material, such as a billet, be formed by a common method, such as a continuous casting method, or an ingot-making and blooming method. Subsequently, the steel pipe material is heated and is processed by hot working using a common Mannesmann-plug mill type or Mannesmann-mandrel mill type manufacturing process to form a seamless steel pipe having a desired dimension, and this seamless steel pipe is preferably used as the starting material. In

addition, a seamless steel pipe may also be manufactured by press type hot extrusion. In addition, after the pipe is formed, the seamless steel pipe is preferably cooled to room temperature at a cooling rate equivalent to or more than that of air cooling.

[0030] The starting material (seamless steel pipe) is first processed by a quenching treatment.

[0031] The quenching treatment of the present invention is a treatment in which after re-heating is performed to a heating temperature for quenching equivalent to or more than the Ac_3 transformation point, cooling is performed from the heating temperature for quenching to a temperature range of 100°C or less at a cooling rate equivalent to or more than that of air cooling. As a result, a fine martensitic microstructure can be obtained. When a heating temperature for quenching is less than the Ac_3 transformation point, since heating cannot be performed to the austenite single phase region, and a sufficient martensitic microstructure cannot be obtained by subsequent cooling, a desired strength cannot be ensured. Hence, the heating temperature for quenching of the quenching treatment is limited to be equivalent to or more than the Ac_3 transformation point. In addition, the heating temperature is preferably 950°C or less. The cooling from the quenching heating temperature is performed to a temperature range of 100°C or less at a cooling rate equivalent to or more than that of air cooling. Since the starting material of the present invention has high hardenability, when the cooling is performed to a temperature range of 100°C or less at a cooling rate approximately equivalent to that of air cooling, a sufficiently quenched microstructure (martensitic microstructure) can be obtained. In addition, a holding time at the heating temperature for quenching is preferably set to 10 minutes or more in view of uniform heating.

[0032] The seamless steel pipe processed by the quenching treatment is subsequently processed by a tempering treatment. In the present invention, the tempering treatment is an important treatment to ensure a superior low temperature toughness. The tempering treatment of the present invention is defined as a treatment in which after heating is performed to a tempering temperature in the range of more than 450°C to 550°C and is maintained preferably for 30 minutes or more, cooling is performed preferably to room temperature preferably at a cooling rate equivalent to or more than that of air cooling. As a result, a seamless steel pipe which simultaneously has a high strength of YS 110 ksi or more and a superior low temperature toughness having a $vTrs$ of -60°C or less can be obtained. When the tempering temperature is 450°C or less, since the tempering is insufficient, the toughness is degraded, and as a result, a high strength and a high toughness cannot be simultaneously obtained. On the other hand, when the tempering temperature is more than 550°C, besides a decrease in strength, since the grain boundaries become brittle, the intergranular fracture is liable to occur, and the toughness is also degraded; hence, a high strength and a high toughness cannot be simultaneously obtained. The tempering temperature is preferably in the range of 500°C to 550°C. In addition, in order to stably maintain the properties, the holding time at the tempering temperature is preferably set to 30 minutes or more. In addition, the cooling from the tempering temperature is preferably performed at a cooling rate equivalent to or more than that of air cooling.

[0033] In addition, in the present invention, whenever necessary, a correction treatment for correcting defect in pipe shape may be performed in the cooling of the tempering treatment. The correction treatment is preferably performed in a temperature range of 400°C or more. When the temperature of the correction treatment is less than 400°C, a working strain is locally applied to the steel pipe when the correction treatment is performed, and hence variation in mechanical characteristics is liable to be generated. Hence, it is decided that the correction treatment is performed in a temperature range of 400°C or more.

[0034] A seamless steel pipe manufactured by the above-described manufacturing method is a martensitic stainless steel seamless pipe which has the composition described above and which simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness having a fracture transition temperature $vTrs$ of -60°C or less in a Charpy impact test. In addition, this martensitic stainless steel seamless pipe has a microstructure including a tempered martensitic phase as a primary phase. Hence, a steel pipe can be obtained which simultaneously has a desired high strength and a desired high toughness and which also has a sufficient corrosion resistance as oil country tubular goods.

Examples

[0035] After various types of molten steel having the compositions shown in Table 1 were degassed, slabs were formed by a continuous casting method, and billets (size: 207 mm in diameter) were obtained by billet rolling of the slabs processed by re-heating, so that steel-pipe materials were prepared. After the steel pipe materials were heated and formed into pipes by hot working using a Mannesmann-type manufacturing process, cooling was performed, so that seamless steel pipes (outside diameter: 177.8 mm, and wall thickness: 12.7 mm) were obtained.

[0036] The seamless steel pipes thus obtained were subjected to a quenching treatment and a tempering treatment, and were further subjected to a correction treatment whenever necessary.

[0037] After API strip tensile specimens were obtained from the seamless steel pipes which were subjected to the quenching treatment and the tempering treatment and were further subjected to the correction treatment whenever necessary, a tensile test was performed, so that the tensile characteristics (yield strength YS, and tensile strength TS)

were obtained.

[0038] In addition, V-notch test pieces (10 mm thick) in accordance with JIS Z 2242 standard were obtained from the seamless steel pipes which were subjected to the quenching treatment and the tempering treatment and were further subjected to the correction treatment whenever necessary, a Charpy impact test was carried out to obtain the fracture transition temperature $vTrs$ and absorption energy vE_{-60} at a temperature of $-60^{\circ}C$, so that the toughness was evaluated. In addition, after test pieces were obtained from 12 points along the circumference of each steel pipe subjected to the correction treatment, a Charpy impact test was performed at a temperature of $-60^{\circ}C$, and the variation was evaluated from the average value (ave) and the minimum value (min) of the absorption energy vE_{-60} .

[0039] In addition, corrosion test pieces having a thickness of 3 mm, a width of 25 mm, and a length of 50 mm were formed from the steel pipes by machining, and a corrosion test was performed.

[0040] The corrosion test was performed in such a way that the corrosion test pieces were immersed for one week (168 hours) in a test solution, a 20%-NaCl aqueous solution (solution temperature: $80^{\circ}C$, and a CO_2 gas environment at 30 bar pressure), which was placed in an autoclave. The weights of the test pieces subjected to the corrosion test were measured, and corrosion rates were obtained by calculating the weight loss before and after the corrosion test. In addition, the surfaces of the test pieces subjected to the corrosion test were observed with a loupe having a magnification of 10 to confirm the pitting generation. As for the pitting, in the case in which at least one pit was observed, it was regarded that pitting occurred, and in the other cases, it was regarded that no pitting occurred. The obtained results are shown in Table 3.

[0041] According to the invention examples, a martensitic stainless steel seamless pipe could be obtained which had a sufficient corrosion resistance as oil country tubular goods and which simultaneously had a high strength of a 110 ksi grade of YS and a superior low temperature toughness having a $vTrs$ of $-60^{\circ}C$ or less. On the other hand, according to the comparative examples out of the range of the present invention, since the strength was not sufficient, or the low temperature toughness was degraded, desired high strength and high toughness could not be ensured.

TABLE 1

STEEL No.	CHEMICAL COMPOSITION (mass%)											REMARKS
	C	Si	Mn	P	S	Al	Cr	Ni	N	Cu, Mo	V, Ti, Nb	
A	0.008	0.16	1.25	0.015	0.001	0.02	11.0	2.8	0.01	-	-	INVENTION EXAMPLE
B	0.008	0.12	1.14	0.019	0.001	0.04	10.9	2.3	0.01	Cu:0.5	-	INVENTION EXAMPLE
C	0.008	0.15	1.31	0.018	0.001	0.03	11.1	2.8	0.03	Mo:0.6	-	INVENTION EXAMPLE
D	0.007	0.13	1.28	0.016	0.001	0.02	11.1	2.4	0.01	-	V: 0.03	INVENTION EXAMPLE
E	0.008	0.24	0.87	0.016	0.001	0.02	11.0	1.3	0.01	-	Nb:0.03	INVENTION EXAMPLE
F	0.008	0.15	1.72	0.015	0.001	0.03	13.2	3.5	0.01	-	Ti:0.03	INVENTION EXAMPLE
G	0.008	0.19	1.55	0.015	0.001	0.02	11.1	2.3	0.01	Cu:0.4	V:0.02, Nb: 0.02	INVENTION EXAMPLE
H	<u>0.012</u>	0.16	1.33	0.014	0.001	0.03	11.4	2.0	0.01	-	-	COMPARATIVE EXAMPLE
I	<u>0.012</u>	0.24	1.05	0.014	0.001	0.03	11.4	2.6	0.01	-	V: 0.03	COMPARATIVE EXAMPLE
J	0.008	0.21	0.84	0.015	0.001	0.02	<u>9.4</u>	2.3	0.01	-	-	COMPARATIVE EXAMPLE
K	0.008	0.18	1.21	0.015	0.001	0.03	<u>14.5</u>	3.5	0.01	Cu:0.5	-	COMPARATIVE EXAMPLE

TABLE 2

STEEL PIPE No.	STEEL No.	QUENCHING TREATMENT			TEMPERING TREATMENT			CORRECTION TREATMENT	REMARKS
		HEATING TEMPERATURE (°C)	COOLING	COOLING STOP TEMPERATURE (°C)	TEMPERING TEMPERATURE (°C)	COOLING	COOLING STOP TEMPERATURE (°C)		
1	A	850	AIR COOLING	25	510	AIR COOLING	25	-	INVENTION EXAMPLE
2	B	810	AIR COOLING	25	425	AIR COOLING	25	385	COMPARATIVE EXAMPLE
3	B	810	AIR COOLING	25	450	AIR COOLING	25	410	INVENTION EXAMPLE
4	B	810	AIR COOLING	25	475	AIR COOLING	25	435	INVENTION EXAMPLE
5	B	810	AIR COOLING	25	500	AIR COOLING	25	460	INVENTION EXAMPLE
6	B	810	AIR COOLING	25	525	AIR COOLING	25	485	INVENTION EXAMPLE
7	B	810	AIR COOLING	25	550	AIR COOLING	25	510	INVENTION EXAMPLE
8	B	810	AIR COOLING	25	575	AIR COOLING	25	535	COMPARATIVE EXAMPLE
9	C	840	AIR COOLING	25	500	AIR COOLING	25	-	INVENTION EXAMPLE
10	D	820	AIR COOLING	25	500	AIR COOLING	25	-	INVENTION EXAMPLE
11	E	820	AIR COOLING	25	500	AIR COOLING	25	-	INVENTION EXAMPLE
12	F	810	AIR COOLING	25	500	AIR COOLING	25	-	INVENTION EXAMPLE

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(continued)

STEEL PIPE No.	STEEL No.	COOLING AFTER PIPE FORMATION	QUENCHING TREATMENT			TEMPERING TREATMENT			CORRECTION TREATMENT	REMARKS
			HEATING TEMPERATURE (°C)	COOLING	COOLING STOP TEMPERATURE (°C)	TEMPERING TEMPERATURE (°C)	COOLING	COOLING STOP TEMPERATURE (°C)		
13	G	AIR COOLING	810	AIR COOLING	25	500	AIR COOLING	25	-	INVENTION EXAMPLE
14	H	AIR COOLING	830	AIR COOLING	25	450	AIR COOLING	25	-	COMPARATIVE EXAMPLE
15	H	AIR COOLING	830	AIR COOLING	25	550	AIR COOLING	25	-	COMPARATIVE EXAMPLE
16	I	AIR COOLING	830	AIR COOLING	25	450	AIR COOLING	25	-	COMPARATIVE EXAMPLE
17	I	AIR COOLING	830	AIR COOLING	25	550	AIR COOLING	25	-	COMPARATIVE EXAMPLE
18	J	AIR COOLING	850	AIR COOLING	25	500	AIR COOLING	25	-	COMPARATIVE EXAMPLE
19	K	AIR COOLING	850	AIR COOLING	25	500	AIR COOLING	25	-	COMPARATIVE EXAMPLE

55 50 45 40 35 30 25 20 15 10 5

TABLE 3

STEEL PIPE No.	STEEL No.	TENSILE CHARACTERISTICS		TOUGHNESS			CORROSION RESISTANCE		REMARKS
		YS (MPa)	TS (MPa)	vTrs (°C)	vE ₋₆₀ (J)		CORROSION RATE (mm/y)	GENERATION OF PITTING	
					ave	min			
1	A	768	921	-70	210	205	0.06	NO	INVENTION EXAMPLE
2	B	789	950	<u>-50</u>	185	52	0.03	NO	COMPARATIVE EXAMPLE
3	B	810	945	-60	215	200	0.03	NO	INVENTION EXAMPLE
4	B	814	939	-70	223	216	0.04	NO	INVENTION EXAMPLE
5	B	815	919	-85	302	281	0.04	NO	INVENTION EXAMPLE
6	B	796	870	-90	305	294	0.04	NO	INVENTION EXAMPLE
7	B	763	839	-65	211	203	0.04	NO	INVENTION EXAMPLE
8	B	<u>703</u>	785	<u>-30</u>	28	25	0.05	NO	COMPARATIVE EXAMPLE
9	C	810	942	-65	217	205	0.02	NO	INVENTION EXAMPLE
10	D	822	938	-70	261	255	0.04	NO	INVENTION EXAMPLE
11	E	843	978	-70	273	267	0.04	NO	INVENTION EXAMPLE
12	F	805	934	-65	261	254	0.04	NO	INVENTION EXAMPLE
13	G	842	963	-70	282	278	0.03	NO	INVENTION EXAMPLE
14	<u>H</u>	<u>889</u>	1050	<u>-55</u>	201	184	0.05	NO	COMPARATIVE EXAMPLE
15	<u>H</u>	784	934	<u>-40</u>	31	28	0.05	NO	COMPARATIVE EXAMPLE
16	<u>I</u>	<u>902</u>	1079	<u>-50</u>	181	176	0.05	NO	COMPARATIVE EXAMPLE
17	<u>I</u>	776	974	<u>-35</u>	24	22	0.05	NO	COMPARATIVE EXAMPLE
18	<u>J</u>	<u>687</u>	821	<u>-30</u>	28	25	0.26	YES	COMPARATIVE EXAMPLE

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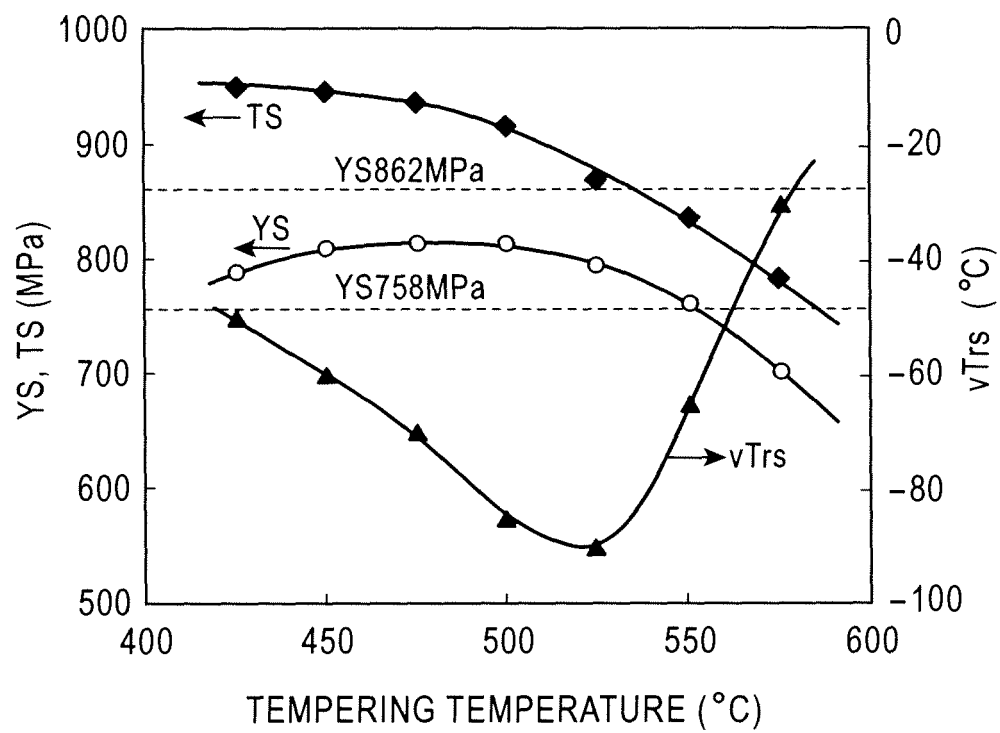
(continued)

STEEL PIPE No.	STEEL No.	TENSILE CHARACTERISTICS		TOUGHNESS			CORROSION RESISTANCE		REMARKS
		YS (MPa)	TS (MPa)	vTrs (°C)	vE ₋₆₀ (J)		CORROSION RATE (mm/y)	GENERATION OF PITTING	
					ave	min			
19	<u>K</u>	<u>706</u>	852	<u>-25</u>	25	22	0.02	NO	COMPARATIVE EXAMPLE

Claims

1. A martensitic stainless steel seamless pipe for oil country tubular goods comprising: a composition which contains on a mass percent basis,
 5 less than 0.010% of C, 1.0% or less of Si,
 0.1% to 2.0% of Mn, 0.020% or less of P,
 0.010% or less of S, 0.10% or less of Al,
 10% to 14% of Cr, 0.1% to 4.0% of Ni,
 0.05% or less of N, and
 10 the balance being Fe and inevitable impurities, wherein the martensitic stainless steel seamless pipe simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness having a fracture transition temperature $vTrs$ of -60°C or less in a Charpy impact test.
2. The martensitic stainless steel seamless pipe for oil country tubular goods according to Claim 1, wherein the composition further contains on a mass percent basis, at least one selected from the group consisting of 2.0% or less of Cu and 2.0% or less of Mo.
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3. The martensitic stainless steel seamless pipe for oil country tubular goods according to Claim 1 or 2, wherein the composition further contains on a mass percent basis, at least one selected from the group consisting of 0.10% or less of V, 0.10% or less of Nb, and 0.10% or less of Ti.
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4. A method for manufacturing a martensitic stainless steel seamless pipe for oil country tubular goods which simultaneously has a high strength of a 110 ksi grade of yield strength and a superior low temperature toughness, the method comprising: performing a quenching treatment on a stainless steel seamless pipe having a composition
 25 which contains on a mass percent basis,
 less than 0.010% of C, 1.0% or less of Si,
 0.1% to 2.0% of Mn, 0.020% or less of P,
 0.010% or less of S, 0.10% or less of Al,
 10% to 14% of Cr, 0.1% to 4.0% of Ni,
 30 0.05% or less of N, and
 the balance being Fe and inevitable impurities in which after heating is performed to a heating temperature for quenching equivalent to or more than the Ac_3 transformation point, cooling is performed from the heating temperature for quenching to a temperature range of 100°C or less at a cooling rate equivalent to or more than that of air cooling; and performing a tempering treatment in which following the quenching treatment, heating is performed to a tempering temperature in the range of more than 450°C to 550°C , and cooling is then performed.
 35
5. The method for manufacturing a martensitic stainless steel seamless pipe for oil country tubular goods according to Claim 4, wherein the composition further contains on a mass percent basis, at least one selected from the group consisting of 2.0% or less of Cu and 2.0% or less of Mo.
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6. The method for manufacturing a martensitic stainless steel seamless pipe for oil country tubular goods according to Claim 4 or 5, wherein the composition further contains on a mass percent basis, at least one selected from the group consisting of 0.10% or less of V, 0.10% or less of Nb, and 0.10% or less of Ti.
7. The method for manufacturing a martensitic stainless steel seamless pipe for oil country tubular goods according to one of Claims 4 to 6, wherein in the cooling of the tempering treatment, a correctional treatment is performed in a temperature range of 400°C or more.
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FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/070209

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, B21D3/00(2006.01)i, C21D9/08(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)

C22C38/00-38/60, B21D3/00, C21D9/08

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

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 Y	JP 2002-309349 A (Sumitomo Metal Industries, Ltd.), 23 October, 2002 (23.10.02), Examples (Family: none)	1, 4 2, 3, 5-7
Y	JP 6-41638 A (Nippon Steel Corp.), 15 February, 1994 (15.02.94), Examples (Family: none)	2, 3, 5-7
Y	JP 2001-98348 A (Kawasaki Steel Corp.), 10 April, 2001 (10.04.01), Examples (Family: none)	3, 6, 7

☒ 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
04 January, 2008 (04.01.08)Date of mailing of the international search report
15 January, 2008 (15.01.08)Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/070209

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 9-287028 A (Sumitomo Metal Industries, Ltd.), 04 November, 1997 (04.11.97), Par. No. [0050] & US 6024808 A & EP 842715 A1 & WO 97/39843 A1	7

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2002363708 A [0004]