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(54) Method for making high-strength high-toughness martensitic stainless steel seamless pipe

Verfahren zum Herstellen von nahtlosen Rohren aus hochfester, hochzäher, martensitischer Rostfreistahl

Procédé de fabrication de tubes sans soudure en acier inoxydable martensitique à résistance et tenacité élévéés

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Description

BACKGROUND

1. Field of the Invention

[0001] This invention relates to a method for making a martensitic stainless steel seamless pipe. The seamless pipe has high corrosion resistance and is suitable for oil country tubular goods (OCTGs). In particular, the invention relates to improvements in toughness and a decrease in anisotropy of toughness.

2. Description of the Related Art

[0002] In consideration of the advance in crude oil prices and anticipated depletion of oil resources in the near future, deep stratum oil fields and highly corrosive sour gas fields are being developed all over the world.

[0003] These oil and gas fields generally spread out at very deep layers and in severely corrosive environments at high temperatures containing CO_2, Cl ions and the like. Thus, OCTGs used in these fields must have high toughness and high corrosion resistance. In general, under severe corrosive environments containing such CO_2, Cl^- ions and the like, martensitic stainless steel seamless pipes with high CO_2 corrosion resistance containing 13% chromium are primarily used.

[0004] Martensitic stainless steel seamless pipes are generally produced by the following process: A raw steel material is heated to a temperature capable of piercing, and subjected to piercing using a piercing mill and elongating using a mandrel mill or plug mill to form an original pipe. The original pipe is reheated to an austenitic temperature range and subjected to finishing rolling using a hot stretch reducing mill or a sizing mill. After air-cooling, the composition of the seamless pipe comprises martensite. The seamless pipe is subjected to quenching from the austenitic temperature range and tempering at a temperature below the A_{C1} transformation point if higher strength and higher toughness are required.

[0005] Oil well pipes used in deteriorating well environments must have higher mechanical properties, such as higher toughness at low temperatures and higher resistance to sulfide stress cracking.

[0006] In order to satisfy such requirements, for example, Japanese Unexamined Patent Application Publication No. 1-123025 discloses a method for making a martensitic stainless steel seamless pipe. This method includes the steps of piercing and rolling a martensitic stainless steel slab at a temperature of 1,050°C to 1,250°C; cooling the rolled pipe at a cooling rate of 30°C/min to at least 500°C and further cooling the pipe to a temperature below the martensite transformation temperature to form a steel structure containing at least 80% of martensite; reheating the pipe to a temperature between (A_{c1} transformation point - 200°C) and A_{c1} transformation point and finishing-rolling the pipe at a reduction in area of at least 5%; maintaining the pipe at the final finishing-rolling temperature or reheating the pipe to a temperature below the A_{c1} transformation point immediately after the finishing rolling step, and then cooling the pipe by spontaneous or forced air cooling. Alternatively, (JP-A-01-123028) after the step of forming the martensitic structure, this method may include the steps of reheating the pipe to a temperature between the (A_{c1} transformation point - 200 °C) and the A_{c1} transformation point, finishing-rolling the pipe at a reduction in area of at least 5%, and then cooling the pipe by spontaneous or forced air cooling; reheating the pipe to a temperature below the A_{c1} transformation point immediately after the finishing rolling step, and then cooling the pipe by spontaneous or forced air cooling.

[0007] However, the seamless pipe produced by this method has the following problem: Since the pipe is rolled at a non-recrystallization temperature range, the structure is elongated in the rolling direction. As a result, the toughness and corrosion resistance of the seamless pipe are high in the rolling direction, but low in the circumferential direction perpendicular to the rolling direction. In other words, the seamless pipe exhibits noticeable anisotropy in mechanical properties.

SUMMARY OF THE INVENTION

[0008] It would, therefore, be advantageous to provide a method for making a martensitic stainless steel seamless pipe having high strength, high toughness, and low anisotropy of mechanical properties, at low cost. In the invention, "high strength" means a yield strength YS of the pipe of about 551 MPa or more, and "high toughness" means an absorbed energy per unit area at -40°C by the Charpy impact test (hereinafter referred to as "E_{-40}") is about 90 J/cm^2 or more.

[0009] We intensively investigated the effects of finishing rolling conditions on toughness, and discovered that a seamless pipe having a fine martensitic structure with low anisotropy was obtained by reheating an original pipe that had been preliminarily treated so as to have a martensitic structure to a dual-phase temperature range at which both a ferritic (α) phase and an austenitic (γ) phase; finishing-rolling the pipe at a specific initial rolling temperature and a specific reduction in area; cooling the pipe; and tempering the pipe.

[0010] Hence, this invention is directed to a method as defined in claim 1, for making a high-strength high-toughness martensitic stainless steel seamless pipe including an original pipe production step of heating a martensitic stainless steel raw material to an austenitic range, piercing and elongating the raw material to form an original pipe, cooling the original pipe to form a structure substantially composed of martensite in the original pipe; a finishing rolling step of reheating the original pipe to a temperature in the dual-phase range between the A_{c1} transformation point and the A_{c3} transformation point, finishing-rolling the original pipe at an initial rolling temperature T (°C) between the A_{c1} transformation point and the A_{c3} transformation point, cooling the original pipe to form a processed pipe having a predetermined size; and tempering the processed pipe at a temperature below the A_{c1} transformation point.

[0011] Preferably, the reduction in area R in the finishing rolling step is in the range of about 10% to about 90%, and the initial rolling temperature T and the reduction in area R satisfies the relationship: $800 \leq T - 0.625R \leq 850$.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

Fig. 1 is a graph showing the effects of the reduction in area R and the initial rolling temperature T in finishing rolling on the toughness of a martensitic stainless steel seamless pipe; and

Fig. 2 is a schematic diagram showing a process for making the martensitic stainless steel seamless pipe in accordance with aspects of the invention.

DETAILED DESCRIPTION

[0013] Any known martensitic stainless steel can be used in the invention as a raw material for a martensitic stainless steel seamless pipe. A composition of the martensitic stainless steel is as follows: 0.005% by weight (hereinafter merely %) to 0.30% C, 0.10% to 1.00% Si, 0.05% to 2.00% Mn, 0.03% or less of P, about 0.005% or less of S, 10.0% to 15.0% Cr, 0.001% to 0.05% Al; and the balance Fe and incidental impurities. The composition may further contain at least one element of about 7.0% or less of Ni, about 3.0% or less of Mo, and about 3.0% or less of Cu; at least one element of about 0.2% or less of Nb, about 0.2% or less of V, about 0.3% or less of Ti, about 0.2% or less of Zr, 0.0005% to 0.01% B, and about 0.07% or less of N; and/or at least one element of 0.0005% to 0.01% Ca and 0.0005% to 0.01% REM (rare earth metals).

[0014] The reasons for the limitation of the composition will now be described.

C: 0.005% to 0.30%

[0015] Carbon (C) is an essential element for ensuring desired strength of the martensitic stainless steel seamless pipe. The desired strength is achieved at a C content of at least about 0.005%. However, a C content exceeding about 0.30% causes an increase in formation of course carbide grains that decrease toughness and corrosion resistance. Thus, the upper limit of the C content is preferably about 0.30% in the invention and more preferably about 0.22% to achieve higher corrosion resistance.

Si: 0.10% to 1.00%

[0016] Silicon (Si) is an essential element that functions as a deoxidizing agent in the steel making process. The deoxidizing effect is noticeable at a Si content of at least about 0.10%. However, a Si content exceeding about 1.00% decreases toughness and hot workability. Thus, the upper limit of the Si content is preferably about 1.00%. More preferably, the Si content is in the range of about 0.10% to about 0.50%.

Mn: 0.05% to 2.00%

[0017] Manganese (Mn) is an essential element that ensures strength of the martensitic stainless steel seamless pipe. The desired strength is achieved at an Mn content of at least about 0.05%. However, an Mn content exceeding about 2.00% decreases toughness. Thus, the C content is preferably in the range of about 0.05% to about 2.00% and more preferably about 0.30% to about 1.60%.

P: 0.03% or less

[0018] Phosphorus (P) is an element that causes a decrease in corrosion resistance, sulfide stress cracking resistance, and hot workability; the P content is preferably as low as possible. However, an extreme reduction in P content leads to a significant increase in process costs. Thus, the P content is about 0.03% or less in the invention in view of the balance between production costs and mechanical properties, i.e., corrosion resistance and sulfide stress cracking resistance.

S: 0.005% or less

[0019] Sulfur (S) is an element that causes a noticeable decrease in hot workability. The P content is preferably as low as possible for improving pipe productivity and improving toughness and stress corrosion cracking resistance. However, an extreme reduction in S content leads to a significant increase in process costs. Thus, the S content is about 0.010% or less and more preferably about 0.005% or less in the invention in view of pipe production by a general process.

Cr: 10.0% to 15.0%

[0020] Chromium (Cr) is a primary element that ensures high corrosion resistance and stress corrosion cracking resistance of the martensitic stainless steel seamless pipe. The desired corrosion resistance is achieved at a Cr content of at least about 10.0%. However, a Cr content exceeding about 15.0% causes deterioration of hot workability. Thus, the Cr content is preferably in the range of about 10.0% to about 15.0%.

Al: 0.001% to 0.05%

[0021] Aluminum (Al) is an element that functions as a strong deoxidizing agent in the steel making process. The deoxidizing effect is noticeable at an Al content of at least about 0.001%. However, an Al content exceeding about 0.05% leads to an increase in oxide inclusions, which decrease toughness. Thus, the upper limit of the Al content is about 0.05%.

[0022] The composition may further contain at least one element of Ni, Mo, and Cu; at least one element of Nb, V, Ti, Zr, B, and N; and/or at least one element of Ca and REM (rare earth metals).

At least one element of 7.0% or less of Ni, 3.0% or less of Mo, and 3.0% or less of Cu

[0023] Ni, Mo, and Cu improve corrosion resistance of the pipe and may be added if necessary.

[0024] Ni significantly improves strength and toughness of the pipe, in addition to the corrosion resistance. These effects are noticeable at a Ni content of 1.0% or more. However, these effects are not comparable with the Ni content if the Ni content exceeds about 7.0%.

[0025] Mo increases corrosion resistance and particularly pitting corrosion resistance. This effect is noticeable at a Mo content of 0.1% or less. However, if the Mo content exceeds about 3.0% leads to a decrease in corrosion resistance, stress corrosion cracking resistance, and hot workability due to the formation of γ-ferrite.

[0026] Cu contributes to the formation of a stiff protective film, which increases corrosion resistance. This effect is noticeable at a Cu content of 0.1% or more. However, a Cu content exceeding 3.0% causes a decrease in hot workability.

At least one element of 0.2% or less of Nb, 0.2% or less of V, 0.3% or less of Ti, 0.2% or less of Zr, 0.0005% to 0.01% B, and 0.07% or less of N

[0027] Nb, V, Ti, Zr, B, and N improve mechanical strength such as toughness and may be added to the raw material, if necessary. However, if the raw material contains not less than 0.2% Nb, not less than 0.2% V, not less than 0.3% Ti, not less than 0.2% Zr, not less than 0.01% B, or not less than 0.07% N, the toughness and corrosion resistance decrease.

At least one element of 0.0005% to 0.01% Ca and 0.0005% to 0.01% REM (rare earth metals)

[0028] Ca and REM contribute to spheroidization of inclusions. Preferably, the Ca content is at least about 0.0005% or the REM content is at least about 0.0005% for the spheroidization. However, a Ca content exceeding 0.01% or an REM content exceeding 0.01% decreases toughness and corrosion resistance

[0029] The balance of the composition is composed of Fe and incidental impurities

[0030] A martensitic stainless steel molten metal having the above composition is prepared in the invention by a known process using a converter or the like. Preferably, the molten metal is cast into slabs by a continuous casting process, and the slabs are rolled to form billets (raw materials for making original pipes). Alternatively, the molten metal is preferably cast into billets directly by a continuous casting process.

[0031] Fig. 2 shows outline of the production process according to selected aspects of the invention. A billet of the martensitic stainless steel having the above composition is heated to an austenitic temperature range and subjected to piercing and elongation to form an original pipe (original pipe production step).

[0032] Preferably, the austenitic temperature range is between 1,100°C and 1,300°C. A temperature below 1,100°C causes unsuccessful piercing and elongation due to high deformation resistance. A temperature above 1,300°C causes a significant decrease in hot workability and toughness due to the formation of γ-ferrite, and a decrease in yield and an unsatisfactory surface state due to significant scaling.

[0033] Piercing may be performed by any known piercing mills of a skew rolling type (Mannesmann type) or press piercing type, without limitation. The pierced raw material is subjected to elongation to form an original pipe. The elongation may be performed with any known mill, such as, for example, a mandrel mill and a plug mill without limitation. Preferably, the elongation is completed at a temperature above 800°C.

[0034] After elongation, the original pipe is cooled to the martensitic transforming temperature (Ms temperature) to form a structure substantially composed of martensite in the original pipe. The term "structure substantially composed of martensite" means that the structure of the cooled original pipe is composed of at least about 90% by area of martensitic phase. The balance is composed of 10% or less of austenitic phase and 2% or less of ferritic phase. This martensitic structure facilitates formation of a recrystallized microstructure during the subsequent reheating step. If the main phase is a phase other than the martensitic phase, the recrystallized microstructure is not formed during the reheating step. As a result, toughness is not so significantly improved or the toughness exhibits noticeable anisotropy.

[0035] In the finishing rolling step, the initial rolling temperature T (°C) is between about the A_{c1} transformation point and about the A_{c3} transformation point. A low initial rolling temperature T below the A_{c1} transformation point results in insufficient recrystallization. Mechanical properties exhibit significant anisotropy due to remaining rolling texture. A high initial rolling temperature T above the A_{c3} transformation point accelerates recrystallization after the rolling step. As a consequence, toughness is not improved due to the inhibited formation of a microstructure. Accordingly, the initial rolling temperature T (°C) is set to the range of about the A_{c1} transformation point to about the A_{c3} transformation point.

[0036] Preferably, in the finishing rolling step, the reduction in area R is in the range of 10% to 90%, and the initial rolling temperature T and the reduction in area R satisfies relationship (1):

$$800 \le T - 0.625R \le 850 \qquad (1)$$

wherein the reduction in area R (%) is the ratio of a decrement by rolling to the sectional area before rolling:

$$\text{Reduction in area } R = [\{(\text{sectional area before rolling}) - (\text{sectional area after rolling})\}/(\text{sectional area before rolling})] \text{ H } 100$$

[0037] At a reduction in area R of less than about 10%, strain generated during the rolling is small. The formation of a microstructure during the rolling is inhibited. Thus, the resulting pipe does not exhibit desired strength and toughness. At a reduction rate in area R exceeding about 90%, anisotropy is noticeable because of elongation of the structure. Accordingly, the reduction in area R during the finishing rolling step is in the range of 10% to 90% and more preferably 30% to 70%.

[0038] In addition, the initial rolling temperature T is preferably controlled according to the reduction in area R so that these two parameters satisfy relationship (1) in the finishing rolling step of the invention.

[0039] Fig. 1 is a graph showing the effects of the reduction in area R and the initial rolling temperature T in finishing rolling on the toughness of a martensitic stainless steel seamless pipe.

[0040] In region C, the initial rolling temperature T and the reduction in area R satisfy relationship (1) and the initial rolling temperature T lies between the A_{c1} transformation point and the Ac3 transformation point. In region C, both the absorbed energy $(E_{-40})_L$ per unit area of the longitudinal direction (L direction) and the absorbed energy $(E_{40})_C$ per unit area of the circumferential direction (C direction) are about 180 J/cm^2 or more, and the ratio $(E_{-40})_C(E_{-40})_L$ is about 0.80 or more. Accordingly, the pipe exhibits high absorbed energy per unit area indicating high toughness and reduced anisotropy in toughness. In regions A and B wherein $T - 0.625R < 800$, the absorbed energy per unit area in the C direction decreases to less than about 180 J/cm^2 and the ratio $(E_{-40})_C/(E_{-40})_L$. decreases to less than about 0.80. This indicates large anisotropy. In region B in which the initial rolling temperature T is higher than the A_{c1} transformation point, however, the absorbed energy per unit area in the C direction is about 90 J/cm^2 or more, which is a sufficiently satisfactory level in practice. In regions D and E wherein $850 < T- 0.625R$, the absorbed energy per unit area in the L direction and the absorbed energy per unit area in the C direction decrease to less than about 180 J/cm^2. However, in region D in which the initial rolling temperature T is lower than the A_{c3} transformation point, the absorbed energy per unit area in the L direction and the absorbed energy per unit area in the D direction are about 90 J/cm^2 or more, which is a sufficiently satisfactory level in practice. In conclusion, in ranges in which the initial rolling temperature T lies between the A_{c1} transformation point and the A_{c3} transformation point, the absorbed energy per unit area in the L direction and the absorbed energy per unit area in the D direction are about 90 J/cm^2 or more, which indicates sufficiently high toughness in practice.

[0041] Preferably, after the finishing rolling satisfying relationship (1), the pipe is cooled in air or cooled at a cooling rate that is larger than that of air cooling. During the subsequent tempering, a martensitic microstructure having low anisotropy is formed. As a result, the processed pipe (final pipe product) has high mechanical strength and small anisotropy.

[0042] Preferably, the finishing rolling step is performed using a tandem mill, for example, a hot stretching reducing mill or a sizing mill.

EXAMPLES

[0043] Each of martensitic stainless steel molten metals having a composition shown in Table 1 was prepared in a converter and cast into a slab by a continuous casting process. The slab was rolled to form a billet (material for an original pipe). The billet was subjected to piercing using a Mannesmann-type piercing mill and elongation using a mandrel mill to form an original pipe as shown in Table 2. After elongation, the original pipe was cooled to a temperature below the Ms point so that the composition of the pipe was substantially composed of a martensitic structure. A test piece was prepared from a part of the original pipe and the structure was observed with an optical microscope. In comparative examples, original pipes were reheated immediately after elongation, without cooling to the temperature below the Ms point.

[0044] Each original pipe was reheated to a temperature shown in Table 2 and subjected to finishing rolling under conditions shown in Table 2 using a hot stretching reducing mill to form a pipe product having a size shown in Table 2. Next, the pipe was cooled in air and tempered at a temperature shown in Table 2.

[0045] Test pieces were prepared along the longitudinal direction (L direction) of each pipe product, and the yield strength YS and tensile strength TS in the L direction were measured according to ASTM A370. The absorbed energy E_{-40} per unit area at -40°C was measured by a Charpy impact test in the circumferential direction (C direction) and the L direction according to ASTM A370. Each test piece had a thickness of 5 mm (sub size), and both ends along the C direction of the test piece for the C direction test were corrected. The ratio $(E_{-40})_C(E_{-40})_L$ of the absorbed energy in the C direction to the L direction was calculated. These results are shown in Table 3.

[0046] Each pipe according to the invention had a high yield strength of 550 MPa or more and a high absorbed energy per unit area in the L direction $(E_{-40})_L$ of 180 J/cm^2 or more. The ratio $(E_{-40})_C/(E_{-40})_L$ of the absorbed energy in the C direction to the L direction was at least 0.80. Accordingly, each pipe according to invention exhibits high toughness and low anisotropy of toughness compared with a conventional example (Pipe 8) and comparative examples. Each pipe in the comparative examples exhibited low toughness in the L direction or in the C direction and high anisotropy indicated by a low ratio $(E_{-40})_C/(E_{-40})_L$ of less than 0.80.

Table 1

Steel	Composition (mass percent)										A_{c1} °C	A_{c3} °C	Ms °C
	C	Si	Mn	P	S	Al	Cr	Ni, Mo, Cu	N, Nb, Ti, V	REM, Ca			
A	0.20	0.26	0.44	0.017	0.002	0.001	13.0	Ni: 0.14	N: 0.03	-	810	920	380
B	0.19	0.35	0.65	0.019	0.001	0.023	12.8	Ni: 0.01	N: 0.02, V: 0.05	-	810	940	370
C	0.20	0.24	0.76	0.013	0.001	0.002	13.0	Ni: 0.05	N: 0.02, Nb: 0.03, V: 0.03	-	820	940	370

(continued)

Steel	Composition (mass percent)										A_{c1} °C	A_{c3} °C	Ms °C
	C	Si	Mn	P	S	Al	Cr	Ni, Mo, Cu	N, Nb, Ti, V	REM, Ca			
D	0.03	0.15	0.50	0.014	0.001	0.002	13.1	Ni: 4.0, Mo: 1.0	N: 0.05, Nb: 0.02	Ca: 0.0012	650	855	220

Table 2

Pipe	Steel	Original pipe production step					Finishing rolling step							Tempering Temp.	Remarks *5
		Heating temp. of billet	Pipe Cooling final temp.	Structure *1	Pipe size		Reheating temp.	Initial Finishing Rolling temp.	Reduction Rate (%)	P *4	Pipe size		Cooling		
					OD *2 (mm)	T *3 (mm)					OD *2 (mm)	T *3 (mm)			
1	A	1,250°C	50°C	M+A	172	7.2	850°C	830°C	61.1	792	73.0	7.0	Air	720°C	PI
2	A	1,250°C	50°C	M+A	172	7.2	870°C	850°C	61.1	812	73.0	7.0	Air	700°C	PI
3	A	1,250°C	50°C	M+A	172	7.2	890°C	870°C	61.1	832	73.0	7.0	Air	700°C	PI
4	A	1,250°C	50°C	M+A	172	7.2	920°C	900°C	61.1	862	73.0	7.0	Air	700°C	PI
5	A	1,250°C	50°C	M+A	172	7.2	970°C	950°C	61.1	912	73.0	7.0	Air	700°C	CE
6	A	1,250°C	50°C	M+A+F *6	172	7.2	870°C	850°C	61.1	812	73.0	7.0	Air	720°C	CE
7	A	1,250°C	400°C	A	172	7.2	870°C	850°C	61.1	812	73.0	7.0	Air	720°C	CE
8	A	1,250°C	750°C	A	172	7.2	970°C	950°C	61.1	912	73.0	7.0	Air	720°C	TE
9	A	1,250°C	50°C	M+A	110	10.0	850°C	830°C	80.5	780	33.2	7.6	Air	720°C	PI
10	A	1,250°C	50°C	M+A	110	10.0	890°C	870°C	80.5	820	33.2	7.6	Air	700°C	PI
11	B	1,250°C	50°C	M+A	172	7.0	820°C	800°C	35.8	778	114.3	6.9	Air	700°C	CE
12	B	1,250°C	50°C	M+A	172	7.0	870°C	850°C	35.8	828	114.3	6.9	Air	700°C	PI
13	B	1,250°C	50°C	M+A	172	7.0	910°C	890°C	35.8	868	114.3	6.9	Air	700°C	PI
14	B	1,250°C	50°C	M+A	192	8.9	800°C	780°C	13.0	772	168.2	8.9	Air	720°C	CE
15	B	1,250°C	50°C	M+A	192	8.9	840°C	820°C	13.0	812	168.2	8.9	Air	720°C	PI
16	B	1,250°C	50°C	M+A	192	8.9	870°C	850°C	13.0	842	168.2	8.9	Air	720°C	PI
17	B	1,250°C	50°C	M+A	192	8.9	890°C	870°C	13.0	862	168.2	8.9	Air	700°C	PI
18	D	1,250°C	50°C	M+A	192	8.9	840°C	820°C	13.0	812	168.2	8.9	Air	720°C	PI
19	D	1,250°C	50°C	M+A	192	8.9	650°C	630°C	13.0	622	168.2	8.9	Air	640°C	CE
20	A	1,250°C	50°C	M+A	110	10.0	970°C	950°C	80.5	900	33.2	7.6	Air	700°C	CE
21	A	1,250°C	50°C	M+A	172	7.2	770°C	750°C	61.1	712	73.0	7.0	Air	720°C	CE

(continued)

Pipe	Steel	Original pipe production step					Finishing rolling step							Tempering Temp.	Remarks *5
		Heating temp. of billet	Pipe Cooling final temp.	Structure *1	Pipe size		Reheating temp.	Initial Finishing Rolling temp.	Reduction Rate (%)	P *4	Pipe size		Cooling		
					OD *2 (mm)	T *3 (mm)					OD *2 (mm)	T *3 (mm)			
22	B	1,250°C	50°C	M+A	172	7.0	770°C	750°C	35.8	728	114.3	6.9	Air	720°C	CE
23	B	1,250°C	50°C	M+A	172	7.0	970°C	950°C	35.8	928	114.3	6.9	Air	700°C	CE
24	B	1,250°C	50°C	M+A	192	8.9	770°C	750°C	13.0	742	168.2	8.9	Air	720°C	CE
25	C	1,250°C	50°C	M+A	172	7.2	890°C	870°C	61.1	832	73.0	7.0	Air	700°C	PI

*1: Crystal structure of the composition of original pipe, M = martensite, A = austenite, F = ferrite
*2: OD = outer diameter, 3: T = thickness
*4: parameter (center in relationship (1) = T - 0.625R)
*5: PI = present invention, CE = comparative example, TE = conventional example
*6: F content = 4%

Table 3

Pipe	Tensile Properties		Toughness			Remarks
	YS (MPa)	TS (MPa)	Absorbes energy (J/mm^2)		Ratio C/L	
			L direction	C direction		
1	601	769	241	116	0.48	Present Invention
2	593	763	230	205	0.89	Present Invention
3	623	783	208	195	0.94	Present Invention
4	599	769	128	106	0.83	Present Invention
5	587	760	96	89	0.93	Comparative example
6	573	764	73	65	0.89	Comparative example
7	600	774	221	96	0.43	Comparative example
8	572	760	78	72	0.92	Conventional Example
9	621	790	249	108	0.43	Present Invention
10	618	792	219	198	0.90	Present Invention
11	605	773	229	85	0.37	Comparative example
12	598	767	208	185	0.89	Present Invention
13	620	798	121	109	0.90	Present Invention
14	612	779	227	90	0.40	Comparative example
15	589	762	210	183	0.87	Present Invention
16	608	785	196	186	0.95	Present Invention
17	592	763	108	93	0.86	Present Invention
18	639	795	251	221	0.88	Present Invention
19	702	873	248	85	0.34	Comparative example
20	584	775	79	75	0.95	Comparative example
21	612	793	203	76	0.37	Comparative example
22	599	753	189	82	0.43	Comparative example
23	604	755	86	82	0.95	Comparative example
24	586	754	221	75	0.34	Comparative example
25	723	901	219	196	0.89	Present Invention

Claims

1. A method for making a high-strength high-toughness martensitic stainless steel seamless pipe comprising:

heating a martensitic stainless steel raw material to an austenitic range, wherein the raw material contains:

0.005% by weight to 0.30% C,
0.10% to 1.00% Si,
0.05% to 2.00% Mn,
0.03% or less of P,
0.005% or less of S,
10.0% to 15.0% Cr,
0.001 % to 0.05% Al;

optionally further:
7.0% or less of Ni,
3.0% or less of Mo,
3.0% or less of Cu;
at least one element of 0.2% or less of Nb, 0.2% or less of V, 0.3% or less of Ti, 0.2% or less of Zr, 0.0005% to 0.01% B, and 0.07% or less of N;
0.0005% to 0.01 % Ca and/or
0.0005% to 0.01 % REM (rare earth metals)

the balance Fe and incidental impurities;
piercing and elongating the raw material to form an original pipe;
cooling the original pipe to form a structure substantially composed of martensite in the original pipe;
reheating the original pipe to a temperature in a dual-phase range between the A_{c1} transformation point and the A_{c3} transformation point;
finishing-rolling the original pipe at an initial rolling temperature T (°C) between the A_{c1} transformation point and the A_{c3} transformation point;
cooling the original pipe to form a processed pipe having a predetermined size; and
tempering the processed pipe at a temperature below the A_{c1} transformation point such that the steel has an absorbed energy $(E_{-40})_L$ per unit area of a longitudinal direction (L direction) and an absorbed energy $(E_{-40})_C$ per unit area of a circumferential direction (C direction) of 90 J/cm^2 or more.

2. The method according to claim 1, wherein a reduction in area R during finishing rolling is in the range of 10% to 90%, and the initial rolling temperature T and the reduction in area R satisfy the relationship: $800 \leq T - 0.625R \leq 850$.

3. The method of claim 1, wherein the austenitic temperature is between 1100 °C and 1300 °C.

4. The method of claim 1, wherein elongating the raw material is performed at a temperature of above 800 °C.

5. The method of claim 1, wherein the A_{c1} transformation point is at about 815 °C.

6. The method of claim 1, wherein the A_{c3} transformation point is at about 920 °C.

7. The method of claim 1, wherein a reduction in area R during finish rolling is between 30% and 70%.

8. The method of claim 1, wherein the steel has an absorbed energy $(E_{-40})_L$ per unit area of a longitudinal direction (L direction) and an absorbed energy $(E_{-40})_C$ per unit area of a circumferential direction (C direction) of 180 J/cm^2 or more.

9. The method of claim 8, wherein a ratio $(E_{-40})_C/(E_{-40})_L$ is 0.80 or more.

Patentansprüche

1. Verfahren zum Herstellen eines nahtlosen Rohrs aus hochfestem, hochzähem martensitischem Edelstahl, das umfasst:

Erhitzen eines Rohmaterials aus martensitischem Edelstahl auf einen austenitischen Bereich, wobei das Rohmaterial enthält:

0,005 bis 0,30 Gew.% C,
0,10% bis 1,00 % Si,
0,05 % bis 2,00 % Mn,
0,03 % oder weniger P,
0,005 % oder weniger S,
10,0 % bis 15,0 % Cr,
0,001 % bis 0,05 % Al;
wahlweise des Weiteren:
7,0 % oder weniger Ni,

3,0 % oder weniger Mo,
3,0 % oder weniger Cu;
wenigstens ein Element von
0,2 % oder weniger Nb,
0,2 % oder weniger V;
0,3 % oder weniger Ti,
0,2 % oder weniger Zr,
0,0005 % bis 0,01 % B und
0,07 % oder weniger N;
0,0005 % bis 0,01 % Ca und/oder
0,0005 % bis 0,01 % Seltenerdmetalle,

wobei der Rest Eisen und zufällige Verunreinigungen sind;
Lochen und Strecken des Rohmaterials, um ein Ausgangsrohr auszubilden;
Kühlen des Ausgangsrohrs, um eine Struktur, die im Wesentlichen aus Martensit besteht, in dem Ausgangsrohr auszubilden;
Wiedererwärmen des Ausgangsrohrs auf eine Temperatur in einem Zweiphasenbereich zwischen dem A_{c1}-Umwandlungspunkt und dem A_{c3}-Umwandlungspunkt;
Fertigwalzen des Ausgangsrohrs bei einer Anfangs-Walztemperatur T (°C) zwischen dem A_{c1}-Umwandlungspunkt und dem A_{c3}-Umwandlungspunkt;
Kühlen des Ausgangsrohrs, um ein bearbeitetes Rohr mit einer vorgegebenen Größe auszubilden; und
Anlassen des bearbeiteten Rohrs bei einer Temperatur unterhalb des A_{c1}-Ausgangspunktes, so dass der Stahl eine absorbierte Energie $(E\text{-}_{40})_L$ pro Flächeneinheit einer Längsrichtung (L-Richtung) und eine absorbierte Energie $(E_{-40})_C$ pro Flächeneinheit einer Umfangsrichtung (C-Richtung) von 90 J/cm^2 oder mehr hat.

2. Verfahren nach Anspruch 1, wobei eine Querschnittsreduktion R während des Fertigwalzens im Bereich von 10 % bis 90 % liegt und die Anfangs-Walztemperatur T sowie die Querschnittsreduktion R die Beziehung $800 \leq T - 0.625R \leq 850$ erfüllen.

3. Verfahren nach Anspruch 1, wobei die austenitische Temperatur zwischen 1100 °C und 1300 °C liegt.

4. Verfahren nach Anspruch 1, wobei Strecken des Rohmaterials bei einer Temperatur über 800 °C durchgeführt wird.

5. Verfahren nach Anspruch 1, wobei der A_{c1}-Umwandlungspunkt bei ungefähr 815 °C liegt.

6. Verfahren nach Anspruch 1, wobei der A_{c3}-Umwandtungspunkt bei ungefähr 920 °C liegt.

7. Verfahren nach Anspruch 1, wobei eine Querschnittsreduktion R während des Fertigwalzens zwischen 30 % und 70 % beträgt.

8. Verfahren nach Anspruch 1, wobei der Stahl eine absorbierte Energie $(E\text{-}_{40})_L$ pro Flächeneinheit einer Längsrichtung (L-Richtung) und eine absorbierte Energie $(E_{-40})_C$ pro Flächeneinheit einer Umfangsrichtung (C-Richtung) von 180 J/cm^2 oder mehr hat.

9. Verfahren nach Anspruch 8, wobei ein Verhältnis $(E_{-40})_C$ / $(E_{-40})_L$ 0,80 oder mehr beträgt.

Revendications

1. Procédé de fabrication d'un tube sans soudure en acier inoxydable martensitique à résistance et ténacité élevées comprenant :

le chauffage d'une matière première constituée par un acier inoxydable martensitique jusqu'à une plage austénitique, laquelle matière première contient :

0,005 % en poids à 0,30 % de C,
0,10 % à 1,00 % de Si,
0,05 % 2,00 % de Mn,

0,03 % ou moins de P,
0,005 % ou moins de S,
10,0 % à 15,0 % de Cr,
0,001 % à 0,05 % d'Al;
éventuellement en outre :
7,0 % ou moins de Ni,
3,0 % ou moins de Mo,
3,0 % ou moins de Cu ;
au moins un élément parmi 0,2 % ou moins de Nb, 0,2 % ou moins de V, 0,3 % ou moins de Ti, 0,2 % ou moins de Zr, 0,0005 % à 0,01 % de B et 0,07 % ou moins de N ;
0,0005 % à 0,01% de Ca et/ou
0,0005 % à 0,01% de REM (métaux de terres rares)

le complément étant Fe et des impuretés insignifiantes ;
le perçage et l'allongement de la matière première pour former un tube d'origine ;
le refroidissement du tube d'origine pour former une structure essentiellement constituée de martensite dans le tube d'origine ;
le réchauffage du tube d'origine jusqu'à une température dans une plage à double phase entre le point de transformation A_{c1} et le point de transformation A_{c3} ;
le finissage-laminage du tube d'origine à une température de laminage initiale T (°C) située entre le point de transformation A_{c1} et le point de transformation A_{c3} ;
le refroidissement du tube d'origine pour former un tube traité ayant une dimension prédéterminée ; et
le traitement de revenu du tube traité à une température inférieure au point de transformation A_{c1} de telle sorte que l'acier possède une énergie absorbée $(E_{-40})_L$ par unité de surface dans une direction longitudinale (direction L) et une énergie absorbée $(E_{-40})_C$ par unité de surface dans une direction circonférentielle (direction C) de 90 J/cm^2 ou plus.

2. Procédé selon la revendication 1, dans lequel une réduction de surface R pendant le finissage-laminage se situe dans la plage de 10 % à 90 %, et la température de laminage initiale T et la réduction de surface R satisfont à la relation :

$$800 \leq T - 0,625R \leq 850.$$

3. Procédé selon la revendication 1, dans lequel la température austénitique est comprise entre 1100 °C et 1300°C.

4. Procédé selon la revendication 1, dans lequel l'allongement de la matière première est effectué à une température supérieure à 800 °C.

5. Procédé selon la revendication 1, dans lequel le point de transformation A_{c1} est d'environ 815 °C.

6. Procédé selon la revendication 1, dans lequel le point de transformation A_{c3} est d'environ 920 °C.

7. Procédé selon la revendication 1, dans lequel une réduction de surface R au cours du laminage de finition est comprise entre 30 % et 70 %.

8. Procédé selon la revendication 1, dans lequel l'acier possède une énergie absorbée $(E\text{-}_{40})_L$ par unité de surface dans une direction longitudinale (direction L) et une énergie absorbée $(E\text{-}_{40})_C$ par unité de surface dans une direction circonférentielle (direction C) de 180 J/cm^2 ou plus.

9. Procédé selon la revendication 8, dans lequel un rapport $(E_{-40})_C/(E_{-40})_L$ est de 0, 80 ou plus.

FIG. 1

REGION	SYMBOL	ABSORPTION ENERGY PER UNIT AREA IN C DIRECTION (J/cm^2)	ABSORPTION ENERGY PER UNIT AREA IN L DIRECTION (J/cm^2)	C/L
A	◆	<90	≧180	<0.80
B	▲	90 – 180	≧180	<0.80
C	○	≧180	≧180	≧0.80
D	△	90 – 180	90 – 180	≧0.80
E	◇	<90	<90	≧0.80

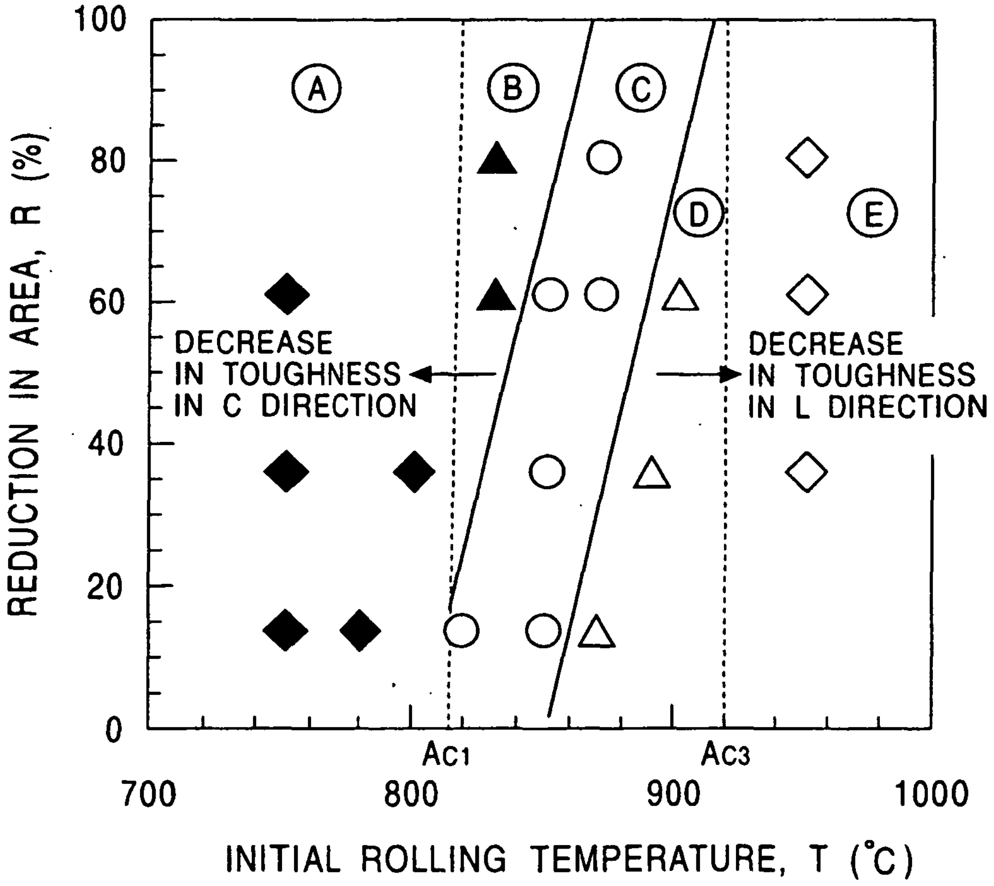
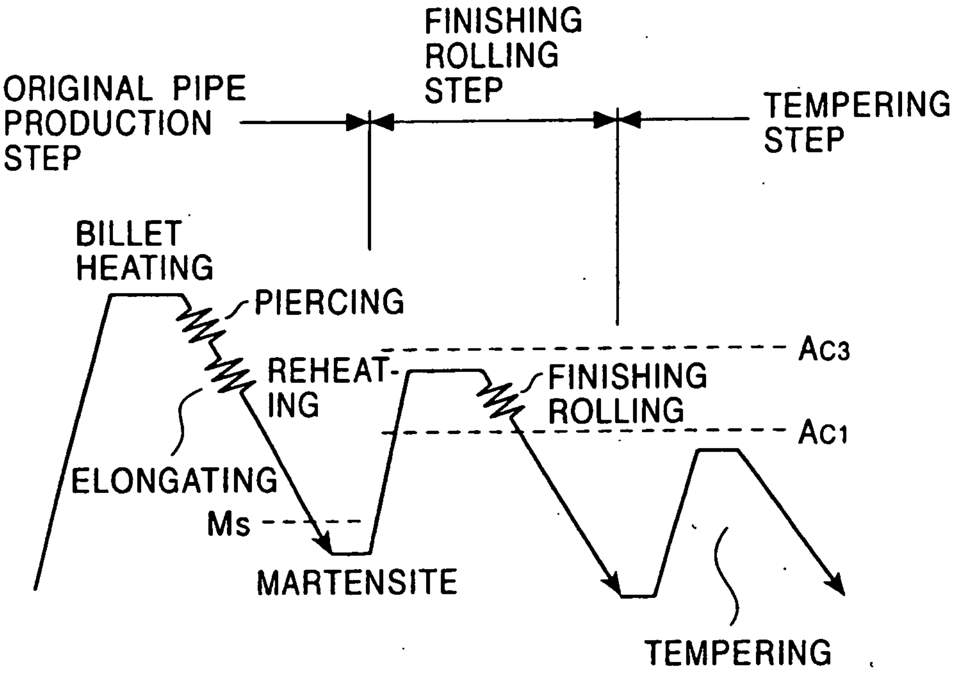


FIG. 2


FINISHING ROLLING STEP
ORIGINAL PIPE PRODUCTION STEP
TEMPERING STEP
BILLET HEATING
PIERCING
REHEAT-ING
ELONGATING
FINISHING ROLLING
Ac3
Ac1
Ms
MARTENSITE
TEMPERING

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 1123025 A **[0006]**
- JP 1123028 A **[0006]**