



(11)

EP 3 421 630 A1

(12)

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

(43) Date of publication:

02.01.2019 Bulletin 2019/01

(21) Application number: **17756207.1**

(22) Date of filing: **08.02.2017**

(51) Int Cl.:

C22C 38/00 (2006.01)	C21D 6/00 (2006.01)
C22C 38/58 (2006.01)	C22C 38/02 (2006.01)
C22C 38/04 (2006.01)	C22C 38/06 (2006.01)
C22C 38/42 (2006.01)	C22C 38/44 (2006.01)
C22C 38/48 (2006.01)	C21D 8/02 (2006.01)
C21D 9/46 (2006.01)	

(86) International application number:

PCT/JP2017/004617

(87) International publication number:

WO 2017/145766 (31.08.2017 Gazette 2017/35)

(84) Designated Contracting States:

**AL 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 RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

MA MD

(30) Priority: **25.02.2016 JP 2016034390**

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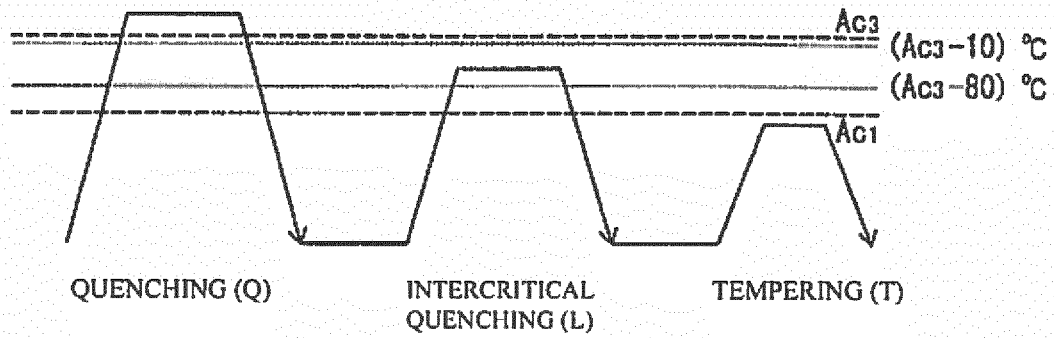
(54) **CU-CONTAINING LOW ALLOY COPPER HAVING EXCELLENT BALANCE BETWEEN
STRENGTH AND LOW-TEMPERATURE TOUGHNESS AND METHOD FOR PRODUCING SAME**

(57) Provided is a Cu-containing low alloy steel having excellent balance between strength and low-temperature toughness. The Cu-containing low alloy steel has a chemical composition comprising, by mass%, C: 0.01 to 0.08%, Si: 0.10 to 0.40%, Mn: 0.80 to 1.80%, Ni: 0.80 to 2.50%, Cr: 0.50 to 1.00%, Cu: 0.80 to 1.50%, Mo: 0.20 to 0.60%, Al: 0.010 to 0.050%, Nb: 0.030 to 0.080%, and N: 0.005 to 0.020%, and further comprising Ca: 0.010%

or less as needed, and consisting of Fe and inevitable impurities as the balance; has a 0.2% yield strength of 525 MPa or higher. The Cu-containing low alloy steel has a ductile-brittle fracture appearance transition temperature (FATT) as measured by the 2 mm V-notch Charpy impact test of -70°C or less.

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Fig. 1



Description

TECHNICAL FIELD

[0001] The present invention relates to a Cu-containing low-alloy steel which has an excellent balance between strength and low-temperature toughness and is for use in applications where low-temperature toughness is required, and relates to a process for producing the Cu-containing low-alloy steel.

BACKGROUND ART

[0002] Petroleum and natural gas are extensively used as main energy sources. In recent years, exploitation of these resources is shifting from the land to the sea. Especially in the exploitation of marine resources, digging at depths of water deeper than continental shelves is coming to be mainly performed. Steels for marine structures for use in this very-large-depth exploitation are required to have not only excellent low-temperature toughness but also high yield strength from the standpoint of ensuring safety.

[0003] Steels for marine structure use which are for ensuring an excellent balance between strength and toughness are known. These steels include steel plates containing 1.0-1.3% by mass Cu, as provided for in, for example, ASTM A710, and forged steel materials containing up to 0.43% by mass Cu, as provided for in, for example, ASTM A707.

[0004] These steels are based on a low-carbon low-carbon-equivalent composition system in which strength is ensured by causing Cu precipitation by aging, and thus combine strength and low-temperature toughness.

[0005] Non-Patent Document 1 describes an improvement of a composition system on the basis of ASTM A707 Grade L5, and indicates that the improved material was quenched and tempered and evaluated for mechanical property. The results of the evaluation are explained therein. The steel of Non-Patent Document 1 has an FATT of -60°C, and a further improvement in low-temperature toughness is necessary from the standpoint of insuring safety.

[0006] Conventional techniques used for ensuring low-temperature toughness in steel plates include direct quenching after rolling and controlled rolling. For example, Patent Document 1 proposes a production process in which an M* value determined by C, Si, Al, N, and B is specified and direct quenching is conducted after rolling, in order to produce a high-strength steel plate having excellent CTOD (crack tip opening displacement) characteristics.

[0007] Patent Document 1 indicates the following M* value.

$$M^* = 5C (\%) + 2Si (\%) + 20Al (\%) + 70N (\%) + 1400B (\%)$$

[0008] Patent Document 2 proposes a process for producing a low-C high-tension steel of the Cu precipitation hardening type excellent in terms of low-temperature toughness and weldability, the process including rolling a steel plate containing 0.7-1.5% by mass Cu at a temperature of 900-700°C and at a rolling reduction of 30% or more and then subjecting the steel plate to a Cu precipitation treatment at a temperature in the range of 500-650°C to thereby produce the high-tension steel.

[0009] Results of researches concerning an improvement in material property by intercritical quenching have also been reported. For example, Patent Document 3 proposes a method for the intercritical quenching of a B-containing steel, wherein the contents of B, N, and Ti are specified and the temperature for the intercritical quenching is specified, thereby stably producing a high-tension steel having a low yield ratio.

[0010] Patent Document 4 proposes that a Ni-containing steel plate excellent in terms of low-temperature toughness and balance between strength and toughness is produced by intercritical quenching.

BACKGROUND ART DOCUMENTS

PATENT DOCUMENTS

[0011]

Patent Document 1: JP-A-2001-81529

Patent Document 2: JP-A-61-149430

Patent Document 3: JP-A-5-171263

Patent Document 4: JP-A-2008-81776

NON-PATENT DOCUMENT

[0012] Non-Patent Document 1: Steel Forgings: Second Volume, ASTM STP 1259, p.196

5 SUMMARY OF THE INVENTION

PROBLEMS THAT THE INVENTION IS TO SOLVE

[0013] Steels having not only excellent low-temperature toughness but also high yield strength are becoming necessary also in large structures employing a Cu-containing low-alloy steel which is extensively used as a steel for marine structures, from the standpoint of ensuring safety. This Cu-containing low-alloy steel considerably changes in material strength upon aging as stated above, and it is hence difficult to attain an excellent balance between strength and low-temperature toughness by merely improving the tempering conditions.

[0014] The processes proposed in Patent Documents 1 and 2 each necessitate a step for refining rolling and cannot hence be applied to the case where no rolling is performed or where the plate is too thick to roll. In Patent Document 1, the plate thickness is 120 mm at the most. Consequently, the proposed production processes cannot be applied to processes in which no rolling is performed or to large structures including, for example, a flange part having a thickness of 150 mm or larger.

[0015] Furthermore, Patent documents 3 and 4 do not define Cu content, and do not clearly show a production process for obtaining a Cu-containing low-alloy steel which, although changing in strength upon aging, has an excellent balance between strength and toughness.

[0016] An object of the present invention, which has been achieved under the circumstances described above, is to provide a Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness. First, a proper composition range in the present invention is clarified. Secondly, proper conditions for thermal refining including intercritical quenching for producing a Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness are shown.

MEANS FOR SOLVING THE PROBLEM

[0017] Namely, among Cu-containing low-alloy steels having an excellent balance between strength and low-temperature toughness of the present invention, first embodiment is a Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness, having a chemical composition including, in terms of % by mass, 0.01-0.08% C, 0.10-0.40% Si, 0.80-1.80% Mn, 0.80-2.50% Ni, 0.50-1.00% Cr, 0.80-1.50% Cu, 0.20-0.60% Mo, 0.010-0.050% Al, 0.030-0.080% Nb, and 0.005-0.020% N, with the balance being Fe and unavoidable impurities, in which a 0.2% proof stress is 525 MPa or higher and a ductile/brittle fracture appearance transition temperature (FATT), as measured through a 2-mm V-notched Charpy impact test, is -70°C or lower.

[0018] In another embodiment of the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness, the chemical composition further includes up to 0.010% by mass Ca.

[0019] In another embodiment of the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness, the Cu-containing low-alloy steel has an absorbed energy of 130 J or higher in a 2-mm V-notched Charpy impact test at -80°C.

[0020] In another embodiment of the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness, after thermal refining, an average EBSD grain diameter is 10 μ m or less and a maximum EBSD grain diameter is 120 μ m or less in cases when boundaries having a misorientation of 15° or larger are taken as grain boundaries.

[0021] Among processes for producing the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness of the present invention, first embodiment is a process for producing the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature, including thermal refining which includes:

heating a steel to a temperature in a range of 850-950°C to conduct quenching, thereafter heating the steel to a temperature in a range of [(A_{C3} transformation point)-80°C] to [(A_{C3} transformation point)-10°C] to conduct intercritical quenching, and further conducting tempering at 560-660°C.

[0022] In another embodiment of the process for producing the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness, the thermal refining is applied to a steel for a large structure, the steel having a thick portion with a thickness of 150-500 mm.

[0023] In another embodiment of the process for producing the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness, the steel is produced by hot forging and then subjected to the thermal refining.

[0024] The features specified in the present invention are explained below. The contents in the chemical composition are given in % by mass.

C: 0.01-0.08%

[0025] C is a necessary additive element from the standpoint of ensuring strength, and a lower limit is hence 0.01%. However, inclusion thereof in an amount exceeding 0.08% results not only in a decrease in toughness due to strength enhancement but also in precipitation of a hard phase during intercritical quenching and a decrease in weldability. Consequently, an upper limit is 0.08%. For the same reasons, the lower limit is desirably 0.02% and the upper limit is desirably 0.05%.

Si: 0.10-0.40%

[0026] Si is used as a deoxidizing element in performing melting/smelting for alloy production. Si is an element necessary for ensuring strength. A lower limit is hence 0.10%. However, excessive inclusion thereof results in a decrease in toughness or a decrease in weldability. An upper limit is hence 0.40%. For the same reasons, the lower limit is desirably 0.20% and the upper limit is desirably 0.35%.

Mn: 0.80-1.80%

[0027] Mn is a useful deoxidizing element like Si, and contributes to an improvement in quench hardenability. For exerting the effect, the content thereof must be 0.80% or higher. However, excessive inclusion thereof results in a decrease in toughness. An upper limit is hence 1.80%. For the same reasons, the lower limit is desirably 1.00% and the upper limit is desirably 1.50%. More preferably, the lower limit is 1.20% and the upper limit is 1.45%.

Ni: 0.80-2.50%

[0028] Ni is an element necessary for improving quench hardenability and for thereby ensuring strength and low-temperature toughness. A lower limit is hence 0.80%. However, excessive inclusion thereof stabilizes the retained γ , resulting in a decrease in toughness. An upper limit is hence 2.50%. For the same reasons, the lower limit is desirably 1.50% and the upper limit is desirably 2.30%. Preferably, the lower limit is 2.00% and the upper limit is 2.20%. More preferably, the lower limit is 2.10% and the upper limit is 2.15%.

Cr: 0.50-1.00%

[0029] Cr is an important element for ensuring quench hardenability and ensuring strength and toughness. A lower limit is hence 0.50%. However, excessive inclusion thereof enhances quench hardenability, resulting in a decrease in toughness and enhanced susceptibility to weld cracking. An upper limit is hence 1.00%. For the same reasons, the lower limit is desirably 0.60% and the upper limit is desirably 0.80%. Preferably, the lower limit is 0.70% and the upper limit is 0.75%.

Cu: 0.80-1.50%

[0030] Cu precipitates during aging to improve the strength of the steel. In low-carbon steels, it is crucially important to ensure strength by Cu precipitation. Cu is an important element also for improving the corrosion resistance. A lower limit is hence 0.80%. However, excessive inclusion thereof results in a decrease in toughness or a decrease in hot workability. An upper limit is hence 1.50%. For the same reasons, the lower limit is desirably 1.10% and the upper limit is desirably 1.30%. Preferably, the lower limit is 1.20% and the upper limit is 1.25%.

Mo: 0.20-0.60%

[0031] Mo contributes to an improvement in quench hardenability and is an important element for ensuring strength and toughness. A lower limit is hence 0.20%. However, excessive inclusion thereof results in a decrease in toughness or a decrease in weldability. An upper limit is hence 0.60%. Preferably, the lower limit is 0.30% and the upper limit is 0.50%. More preferably, the lower limit is 0.40% and the upper limit is 0.45%.

Al: 0.010-0.050%

[0032] Al combines with N to form AlN, thereby inhibiting the growth of crystal grains. Formation of finer crystal grains is essential for improving the toughness. A lower limit of Al content is hence 0.010%. However, excessive inclusion thereof results in a decrease in toughness due to coarse AlN grains. An upper limit is hence 0.050%. For the same reasons, the lower limit is desirably 0.010% and the upper limit is 0.030%. Preferably, the lower limit is 0.020% and the upper limit is 0.030%.

Nb: 0.030-0.080%

[0033] Nb forms carbonitrides to inhibit the growth of crystal grains, and is an important element for forming finer crystal grains. A lower limit is hence 0.030%. However, excessive addition thereof accelerates the aggregation or enlargement of the carbonitride grains, resulting in a decrease in toughness. An upper limit is hence 0.080%. For the same reasons, the lower limit is desirably 0.04% and the upper limit is desirably 0.060%. Preferably, the lower limit is 0.040% and the upper limit is 0.050%.

N: 0.005-0.020%

[0034] N forms AlN and carbonitrides to inhibit the growth of crystal grains, and is contained because N is an important element for forming finer crystal grains. A lower limit is set at 0.005% in order to sufficiently obtain the effect. However, excessive addition thereof accelerates the precipitation of a large amount of AlN and carbonitrides and the aggregation or enlargement thereof, resulting in a decrease in toughness. An upper limit is hence 0.020%. Preferably, the lower limit is 0.005% and the upper limit is 0.011%.

Ca: up to 0.010%

[0035] Ca forms oxides and sulfides and is hence used as a deoxidizing or desulfurizing element according to need. However, excessive addition thereof results in a decrease in toughness. The content thereof is hence 0.010% or less. For the same reason, the upper limit is desirably 0.005%. For obtaining the effect, it is desirable that the chemical composition should contain Ca in an amount of 0.0005% or larger. In the case where Ca is not added positively, the chemical composition may contain Ca as an unavoidable impurity in an amount less than 0.0005%.

EBSD Grain Diameters: 10 μm or less on average; 120 μm or less at maximum

[0036] EBSD (electron backscatter diffractometry) is a technique for determining the orientation of each crystal grain. It has been reported that in the case of steels, the diameters of crystal grains each surrounded by high-angle grain boundaries having a misorientation of 15° or larger (EBSD grain diameters) generally correlate with the toughness. The smaller the EBSD grain diameters, the better the low-temperature toughness of the steel. In cases when the average EBSD grain diameter is 10 μm or less and the maximum EBSD grain diameter is 120 μm or less, a Cu-containing low-alloy steel having an even better balance between strength and low-temperature toughness is obtained. Meanwhile, in case where the average EBSD grain diameter exceeds 10 μm or the maximum EBSD grain diameter exceeds 120 μm , the low-temperature toughness decreases. More preferably, the average EBSD grain diameter is 10 μm or less and the maximum EBSD grain diameter is 110 μm or less.

Thermal Refining Conditions

[0037] In the case of quenching, it is necessary to heat the steel at least to a temperature not lower than the A_{C3} transformation point (temperature at which austenite transformation occurs). Even in cases when the heating temperature for quenching is not lower than the A_{C3} transformation point, quench hardenability is not ensured if the temperature is still low. A lower-limit temperature is hence 850°C. However, too high temperatures for quenching cause the enlargement of γ grains during the heating, resulting later in a decreased toughness. An upper limit is hence 950°C.

[0038] This quenching can be repeatedly conducted multiple times according to need. The present invention is not particularly limited in means for heating or cooling to be used in this quenching, and means having desired heating or cooling ability can be suitably selected.

[0039] The steel which has undergone the quenching is subsequently subjected to intercritical quenching, in which the steel is heated to a temperature in the range of $[(A_{C3} \text{ transformation point}) - 80^\circ\text{C}]$ to $[(A_{C3} \text{ transformation point}) - 10^\circ\text{C}]$ and then cooled. The intercritical quenching is a heat treatment method in which a steel is heated to a temperature (intercritical temperature) which lies between the A_{C1} point and the A_{C3} point and at which the α phase and the γ phase

are both present, and is then cooled. The present invention is not particularly limited in means for heating or cooling to be used in this intercritical quenching, and means having desired heating or cooling ability can be suitably selected. This heat treatment is the most important in the invention.

[0040] The heating temperature in this intercritical quenching is limited to a temperature in the range of $[(A_{C3} \text{ transformation point}) - 80^{\circ}\text{C}]$ to $[(A_{C3} \text{ transformation point}) - 10^{\circ}\text{C}]$, as stated above. In case where the heating temperature is lower than $[(A_{C3} \text{ transformation point}) - 80^{\circ}\text{C}]$, transformation to the γ phase occurs in an insufficient amount and a large amount of the α phase suffers isothermal tempering, resulting in an enlarged Cu precipitate. Consequently, a 0.2% proof stress cannot be ensured. In addition, the later size reduction of crystal grains does not proceed, making it difficult to ensure low-temperature toughness. Meanwhile, in case where the steel is heated to a high temperature exceeding $[(A_{C3} \text{ transformation point}) - 10^{\circ}\text{C}]$, transformation to the γ phase occurs in an excessive amount and crystal grain enlargement occurs, making it impossible to ensure sufficient low-temperature toughness. For these reasons, the temperature for this intercritical quenching is limited to a temperature in the range of $[(A_{C3} \text{ transformation point}) - 80^{\circ}\text{C}]$ to $[(A_{C3} \text{ transformation point}) - 10^{\circ}\text{C}]$.

[0041] Subsequent to the intercritical quenching, tempering is given to the steel at a temperature in the range of $560\text{--}660^{\circ}\text{C}$. In case where the heating temperature is lower than 560°C , an increase in 0.2% proof stress occurs due to the aging effect of the Cu precipitate, resulting in a decrease in toughness. In addition, at tempering temperatures lower than 560°C , the internal stress generated during the thermal refining cannot be relaxed, and this is causative of damages during use. Meanwhile, in case where the tempering temperature exceeds 660°C , overaging occurs, making it impossible to ensure a 0.2% proof stress. Consequently, the temperature for the tempering is in the range of $560\text{--}660^{\circ}\text{C}$.

Thick Portion

[0042] The present invention is applicable to production of a material having a thick portion. Examples of the material include ones having a thick portion with a maximum thickness of 150-500 mm.

[0043] Materials having a thickness of 150 mm or larger are difficult to work by refining rolling, and the effects of the present invention can be remarkably enjoyed. Meanwhile, in case where the thickness exceeds 500 mm, a decrease in cooling rate occurs during the cooling in the quenching and intercritical quenching, resulting in a decrease in strength.

ADVANTAGES OF THE INVENTION

[0044] As explained above, the present invention can produce the following effects.

- (1) A 0.2% proof stress of 525 MPa or higher is ensured; and
- (2) the low-alloy steel has satisfactory low-temperature toughness with a ductile/brittle fracture appearance transition temperature (FATT), as measured through a V-notched Charpy impact test, of -70°C or lower. The ductile/brittle fracture appearance transition temperature is the temperature at which the mode of fracture changes from ductile fracture to brittle fracture with declining temperature. The lower the ductile/brittle fracture appearance transition temperature, the lower the temperature down to which the steel has toughness. The ductile/brittle fracture appearance transition temperature is more preferably -80°C or lower.

[0045] Consequently, a Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046]

[Fig. 1] Fig. 1 is a diagram showing a heat pattern for thermal refining in one embodiment of the invention.

Fig. 2s are drawing-substitute photomicrographs of specimens of an Example according to the invention.

Fig. 3s are drawings showing high-angle boundary maps of the specimens, the boundary maps indicating grain boundaries having a misorientation of 15° or larger and obtained from the results of an examination by EBSD.

MODE FOR CARRYING OUT THE INVENTION

[0047] A steel having the chemical composition specified in the invention can be produced as an ingot through melting in an ordinary way so that the composition is attained. The present invention is not particularly limited in methods for producing the ingot.

[0048] The steel ingot produced through melting is hot-forged into any desired shape and then subjected to the thermal

refining, which includes quenching (Q), intercritical quenching (L), and tempering (T).

[0049] There are no particular limitations on the details of and methods for the hot forging, or on forging ratio, etc. The hot-forged material can be a thick one. For example, the hot-forged material can have a thick portion having a thickness of 150-500 mm.

[0050] In the thermal refining, the Cu-containing low-alloy steel is heated to a temperature in a range of 850-950°C to conduct quenching. Thereafter, the steel is subjected to intercritical quenching at a temperature in a range of [(Ac₃ transformation point)-80°C] to [(A_{C3} transformation point)-10°C] and then to tempering at 560-660°C.

[0051] A heat treatment such as, for example, normalizing (N) may be conducted between the hot forging and the thermal refining. Conditions for the normalizing can include heating conditions of, for example, 950-1,000°C.

[0052] The specified composition ranges and the production process described above make it possible to produce a thick Cu-containing low-alloy forged steel which has excellent low-temperature toughness and, in particular, has an excellent balance between strength and low-temperature toughness and which is suitable for use as a steel for marine structures such as mooring equipment, risers, flowlines, etc.

[0053] The Cu-containing low-alloy steel thus obtained has a 0.2% proof stress of 525 MPa or higher and a ductile/brittle fracture appearance transition temperature (FATT), as measured through a 2-mm V-notched Charpy impact test, of -70°C or lower.

[0054] Furthermore, this low-alloy steel has an absorbed energy of 130 J or higher in a 2-mm V-notched Charpy impact test at -80°C. The absorbed energy is preferably 140 J or higher.

[0055] The low-alloy steel, after the thermal refining, has an average EBSD grain diameter of 10 μm or less and a maximum EBSD grain diameter of 120 μm or less in cases when boundaries having a misorientation of 15° or larger are taken as grain boundaries. It is preferable that the average EBSD grain diameter be 10 μm or less and the maximum EBSD grain diameter be 110 μm or less.

[0056] With respect to strength, the low-alloy steel preferably has a 0.2% proof stress of 525 MPa or higher and a tensile strength of 600 MPa or higher. With respect to low-temperature toughness, the low-alloy steel preferably has a ductile/brittle fracture appearance transition temperature (FATT), as measured through a 2-mm V-notched Charpy impact test, of -80°C or lower.

EXAMPLE 1

[0057] Examples according to the present invention are explained below while comparing the Working Examples with Comparative Examples.

[0058] Specimens respectively having the compositions shown in Table 1 were each produced as a 50-kg steel ingot through melting with a vacuum induction melting furnace. Each steel ingot produced was hot-forged at 1,250°C into a plate having a thickness of 45 mm and a width of 130 mm (forging ratio: 3.1s or higher), subsequently normalized (960°C), and then subjected to thermal refining under the refining conditions (Q treatment, L treatment, T treatment) shown in Table 2. In all the Examples, the Q treatment (quenching) was conducted at 900°C. However, the quenching temperature is not particularly limited so long as the temperature is in the range of 850-950°C, for the reasons shown above. The cooling in the Q treatment and L treatment (intercritical quenching) was conducted at a cooling rate of 10 °C/min, as a simulation of the water cooling of a plate having a thickness of 450 mm. The T treatment (tempering) conditions for each specimen are shown in Table 2.

[Table 1]

Kind of steel	Chemical composition (mass%)										A _{C3} transformation point (°C)	Remarks
	C	Si	Mn	Ni	Cr	Cu	Mo	Al	Nb	Ca	N (ppm)	
A	0.01	0.24	1.41	2.15	0.71	1.23	0.45	0.023	0.046	0.002	81	steels of the invention
B	0.02	0.33	1.31	2.14	0.72	1.24	0.42	0.020	0.044	<0.001	101	
C	0.03	0.25	1.40	2.15	0.72	1.24	0.45	0.025	0.046	0.005	82	
D	0.05	0.25	1.42	2.14	0.72	1.24	0.45	0.026	0.047	0.003	65	comparative steels
E	0.03	0.25	1.40	2.15	0.71	0.60	0.44	0.023	0.045	<0.001	86	
F	0.10	0.25	1.35	2.15	0.70	1.23	0.45	0.250	0.045	<0.001	92	

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[Table 2]

Steel No.	Steel Kind (Table 1)	Heat treatments	(A _{C3} -80)° C	(A _{C3} -10)° C	Heat treatment conditions		Remarks
					L temperature (°C)	T temperature (°C)	
1	C	QT	735	805	-	600	Comparative Examples
2	C	QT	735	805	-	640	
3	C	QLT	735	805	780	600	Working Examples
4	C	QLT	735	805	800	600	
5	A	QLT	750	820	780	600	
6	A	QLT	750	820	800	600	
7	A	QLT	750	820	815	600	
8	B	QL	730	800	795	-	Comparative Examples
9	B	QLT	730	800	680	600	
10	B	QLT	730	800	730	600	Working Examples
11	B	QLT	730	800	765	600	
12	B	QLT	730	800	780	600	
13	B	QLT	730	800	795	600	
14	B	QLT	730	800	810	600	Comparative Example
15	B	QLT	730	800	780	580	Working Example
16	B	QLT	730	800	795	550	Comparative Example
17	B	QLT	730	800	795	570	Working Examples
18	B	QLT	730	800	795	625	
19	B	QLT	730	800	795	670	Comparative Example
20	D	QLT	720	790	770	600	Working Examples
21	D	QLT	720	790	780	600	
22	E	QLT	740	810	795	600	Comparative Examples
23	F	QLT	700	770	760	600	

[0059] Test pieces were taken out of each test material obtained, and were subjected to a tensile test and a Charpy impact test to evaluate the strength and low-temperature toughness. The test methods are as follows.

[0060] Tensile Test: Round-bar tensile test pieces (parallel-portion diameter, 12.5 mm; G. L., 50 mm) were taken out of the obtained test material and subjected to a tensile test at room temperature in accordance with JIS Z 2241:2005 to determine the 0.2% proof stress (Y. S.) and tensile strength (T. S.).

[0061] Impact Test: Two-millimeter V-notched Charpy impact test pieces were taken out of the obtained test material and subjected to a Charpy impact test in accordance with JIS Z 2242:2005. The test pieces each had a length of 55 mm and a square cross-section in which each side had a length of 10 mm. The test pieces each had, at the length-direction center thereof, a V-shaped groove having a notch angle of 45°, notch depth of 2 mm, and notch bottom radius of 0.25 mm. In order to determine absorbed energy at -80°C, vE-80°C (J), the Charpy impact test was conducted at -80°C. Three test pieces of each test material were tested, and the values of absorbed energy were arithmetically averaged. The average value was taken as the absorbed energy of the steel material.

[0062] With respect to FATT, the Charpy impact test was conducted at any temperatures to obtain a transition curve,

from which the FATT was determined.

[0063] Furthermore, samples were taken out of those test materials and examined by EBSD (OIM (orientation imaging microscopy) manufactured by TSL (TexSEM Laboratories, Inc.)). The evaluation of the samples by EBSD is as follows. An electron beam is caused to strike on one site in the surface of each sample and the resultant backscatter diffraction is examined. Thus, the orientation angles of the crystal grains in the site can be determined. The field of view having a size of $300\ \mu\text{m} \times 400\ \mu\text{m}$ is scanned while minutely shifting the position of irradiation with the electron beam (at an examination pitch of $0.3\ \mu\text{m}$). Thus, a map of the orientation angles of the crystal grains within the field can be obtained. A boundary line is drawn between the regions of any adjacent examination sites which differ in orientation angle by 15° or more, thereby obtaining a map concerning boundaries having a misorientation of 15° or larger, such as those shown in Fig. 3. The boundary lines can be regarded as crystal grain boundaries, and each region surrounded by such boundary lines can be regarded as one crystal grain. Hence, the area of each region surrounded by such boundary lines was calculated, and the diameter of a circle having the same area was calculated and taken as the diameter (EBSD grain diameter) of the crystal grain. With respect to each test material, five different fields of view of $300\ \mu\text{m} \times 400\ \mu\text{m}$ were arbitrarily selected and EBSD grain diameters were calculated for each field of view. An average value thereof was taken as average EBSD grain diameter, and the largest of those values was taken as maximum EBSD grain diameter.

[0064] The results obtained in each test are shown in Table 3.

[Table 3]

Steel No.	Steel Kind	Tensile properties		Charpy impact properties		EBSD grain diameters		Remarks
		0.2% Y.S. (MPa)	T.S. (MPa)	FATT ($^\circ\text{C}$)	vE. _{80°C} (J)	Average (μm)	Maximum (μm)	
1	C	640	729	-40	24	15	153	Comparative
2	C	604	690	-51	72	15	147	Examples
3	C	568	725	-85	184	6.3	108	Working Examples
4	C	610	728	-105	205	4.4	79	
5	A	545	645	-82	193	7.7	110	
6	A	553	648	-95	207	5.0	79	
7	A	580	662	-105	207	4.5	71	
8	B	471	746	-54	85	7.5	51	Comparative
9	B	570	680	-75	126	13	129	Examples
10	B	525	611	-83	148	-	-	Working Examples
11	B	530	664	-92	253	-	-	
12	B	557	672	-83	220	9.8	84	
13	B	567	684	-95	229	7.2	53	
14	B	553	675	-75	125	13	121	Comparative Example
15	B	564	689	-85	172	8.9	79	Working Example
16	B	597	714	-66	101	7.0	62	Comparative Example
17	B	573	688	-92	201	-	-	Working Examples
18	B	555	668	-94	228	-	-	
19	B	510	623	-110	234	-	-	Comparative Example
20	D	556	713	-87	183	4.0	80	Working Examples
21	D	610	741	-87	167	5.1	61	

(continued)

Steel No.	Steel Kind	Tensile properties		Charpy impact properties		EBSD grain diameters		Remarks
		0.2% Y.S. (MPa)	T.S. (MPa)	FATT (°C)	vE. _{80°C} (J)	Average (μm)	Maximum (μm)	
22	E	509	615	-82	151	-	-	Comparative
23	F	595	776	-43	31	-	-	Examples

[0065] The specimens of steel No. 1 and steel No. 2 were of the steel kind C. Steels Nos. 1 and 2 are Comparative Examples for which a QT process, which is a common production process, was used. Steel No. 1 failed to have reduced EBSD grain diameters by the mere QT process and had low low-temperature toughness. In the case where the same QT process as for steel No. 1 was performed using a higher tempering temperature to lower the strength in order to improve the toughness, as in steel No. 2, satisfactory low-temperature toughness was not obtained. It is hence clear that satisfactory low-temperature toughness is difficult to ensure by merely performing the QT process.

[0066] The specimens of steel No. 3 (Working Example) and steel No. 4 (Working Example) were of the same kind of steel as steel No. 1 and were produced by a QLT process. Each case gave satisfactory results concerning both 0.2% proof stress and low-temperature toughness.

[0067] The microstructures of steel No. 1 (QT process) and steel No. 2 (QLT process) are shown in Fig. 2, and high-angle boundary maps concerning boundaries having a misorientation of 15° or larger, obtained from the results of the EBSD examination, are shown in Fig. 3. The results of an examination of the microstructures and the high-angle boundary maps showed that the L treatment had brought about a complicated microstructure in which the meandering of high-angle boundaries was observed. In steel No. 3, fine crystal grains were observed in grains. The meandering of high-angle boundaries and the dispersed inclusion of fine grains contribute to an improvement in low-temperature toughness.

[0068] It has hence become apparent that a balance between strength and low-temperature toughness, which has not been obtained with the conventional QT process, is obtained by applying the QLT process according to the present invention.

[0069] The specimens of steels Nos. 5 to 7 (Working Example) were of the steel kind A and had excellent strength and toughness due to the use of the heat treatment process according to the invention. The specimens of steel Nos. 8 to 19 were of the steel kind B. Steel No. 8 (Comparative Example) underwent an L treatment but did not undergo T treatment. In this Comparative Example, the aging effect of a Cu precipitate was insufficient and, hence, a decrease in 0.2% proof stress was observed. In steel No. 9, (Comparative Example), transformation to the γ phase had occurred in an insufficient amount because the L temperature had been lower than ($A_{C3}-80^{\circ}\text{C}$), and reduced EBSD grain diameters were not obtained. As a result, steel No. 9 had insufficient low-temperature toughness.

[0070] Steel No. 14 (Comparative Example) had undergone a treatment under the conditions of an L temperature exceeding ($A_{C3}-10^{\circ}\text{C}$). In this Comparative Example, the areal proportion of the γ phase during the L heating had been large, and the steel No. 14 had coarse crystal grains. As a result, a decrease in low-temperature toughness was observed.

[0071] Steel No. 16 (Comparative Example) had undergone a T treatment at 550°C . In this Comparative Example, the aging effect due to the reduced T temperature had enhanced the 0.2% proof stress. As a result, steel No. 16 had reduced low-temperature toughness.

[0072] Meanwhile, in steel No. 19 (Comparative Example), overaging had occurred due to the too high T temperature, and a decrease in 0.2% proof stress was observed.

[0073] Steel No. 22 (Comparative Example) was of the steel kind E, which was a comparative material. The results showed that use of the steel kind E had resulted in a 0.2% proof stress of 525 MPa or less, although the QLT process, which is recommended in the present invention, had been applied. Since this kind of steel is intended to ensure strength by the aging effect of a Cu precipitate, the effect cannot be sufficiently obtained in the case where the Cu content is low.

[0074] Steel No. 23 (Comparative Example) was of the steel kind F, which was a comparative material. Use of the steel kind F also failed to obtain sufficient low-temperature toughness even when the QLT process, which is recommended in the present invention, had been applied. The reasons for this include that since the steel kind F had too high a C content, C concentrated in the γ phase during the L heating to cause precipitation of a hard phase. Steels Nos. 10, 11, 17 to 19, 22, and 23 shown in Table 32 were not examined for EBSD grain diameter.

[0075] It can be seen from the results given above that an excellent 0.2% proof stress and excellent low-temperature toughness can be obtained by using a proper composition and a proper production process, making it possible to produce a Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness.

[0076] While the present invention has been explained on the basis of the embodiments and Examples, the embod-

iments and the Examples can be suitably modified within the scope of the invention.

[0077] This application is based on a Japanese patent application filed on February 25, 2016 (Application No. 2016-034390), the contents thereof being incorporated herein by reference.

5 INDUSTRIAL APPLICABILITY

[0078] The present invention is suitable for use as a steel for marine structures such as mooring equipment, risers, and flowlines. However, uses of the invention are not limited to these.

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Claims

1. A Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness, having a chemical composition comprising, in terms of % by mass, 0.01-0.08% C, 0.10-0.40% Si, 0.80-1.80% Mn, 0.80-2.50% Ni, 0.50-1.00% Cr, 0.80-1.50% Cu, 0.20-0.60% Mo, 0.010-0.050% Al, 0.030-0.080% Nb, and 0.005-0.020% N, with the balance being Fe and unavoidable impurities, wherein a 0.2% proof stress is 525 MPa or higher and a ductile/brittle fracture appearance transition temperature (FATT), as measured through a 2-mm V-notched Charpy impact test, is -70°C or lower.
2. The Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness according to claim 1, wherein the chemical composition further comprises up to 0.010% by mass Ca.
3. The Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness according to claim 1 or 2, wherein the Cu-containing low-alloy steel has an absorbed energy of 130 J or higher in a 2-mm V-notched Charpy impact test at -80°C.
4. The Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness according to any one of claims 1 to 3, wherein, after thermal refining, an average EBSD grain diameter is 10 μm or less and a maximum EBSD grain diameter is 120 μm or less in cases when boundaries having a misorientation of 15° or larger are taken as grain boundaries.
5. A process for producing the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness according to any one of claims 1 to 4, comprising thermal refining which comprises heating a steel to a temperature in a range of 850-950°C to conduct quenching, thereafter heating the steel to a temperature in a range of $[(A_{C3} \text{ transformation point})-80^\circ\text{C}]$ to $[(A_{C3} \text{ transformation point})-10^\circ\text{C}]$ to conduct intercritical quenching, and further conducting tempering at 560-660°C.
6. The process for producing the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness according to claim 5, wherein the thermal refining is applied to a steel for a large structure, the steel having a thick portion with a thickness of 150-500 mm.
7. The process for producing the Cu-containing low-alloy steel having an excellent balance between strength and low-temperature toughness according to claim 5 or 6, wherein the steel is produced by hot forging and then subjected to the thermal refining.

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Fig. 1

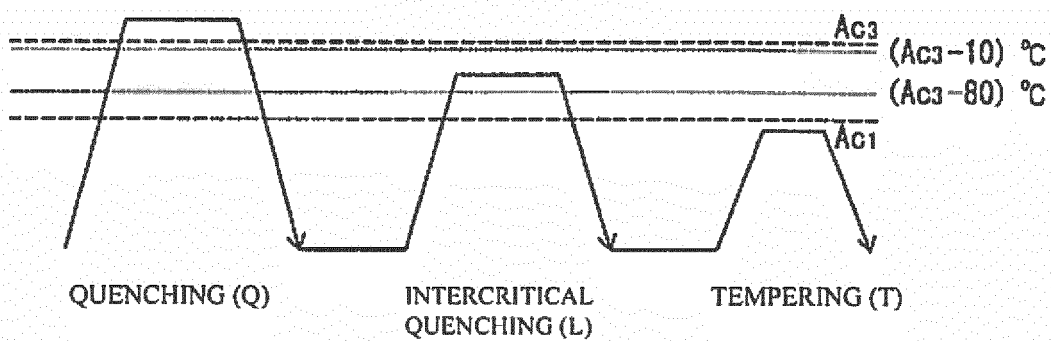
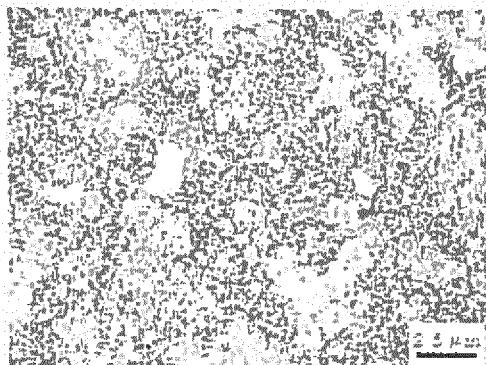
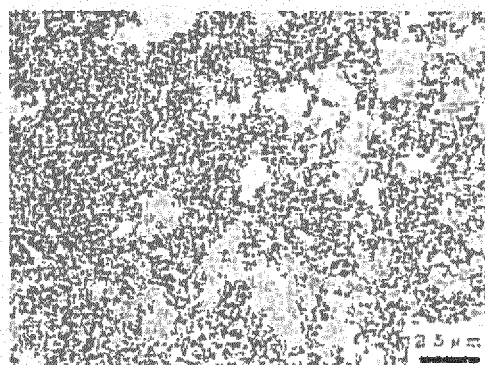


Fig. 2

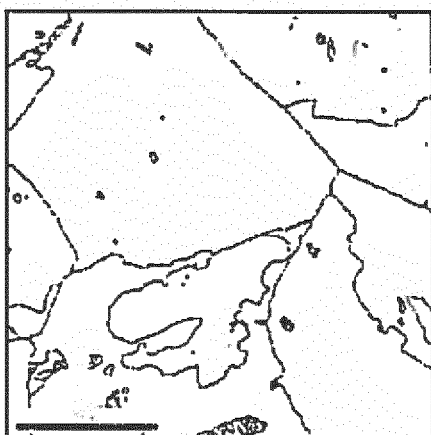


COMPARATIVE EXAMPLE (STEEL No. 1)

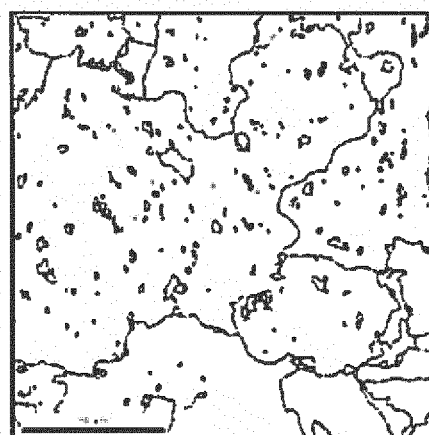


WORKING EXAMPLE (STEEL No. 3)

Fig.3



COMPARATIVE EXAMPLE (STEEL No. 1)



WORKING EXAMPLE (STEEL No. 3)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/004617

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D6/00(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-C22C38/60, C21D6/00, C21D8/00-C21D8/10

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 1996-2017

Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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.
A	JP 1-219121 A (Nippon Steel Corp.), 01 September 1989 (01.09.1989), (Family: none)	1-7
A	JP 62-177120 A (Japan Casting & Farging Corp.), 04 August 1987 (04.08.1987), (Family: none)	1-7
A	JP 6-220577 A (Kawasaki Steel Corp.), 09 August 1994 (09.08.1994), (Family: none)	1-7
A	JP 7-233438 A (NKK Corp.), 05 September 1995 (05.09.1995), (Family: none)	1-7

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

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Date of the actual completion of the international search
01 May 2017 (01.05.17)Date of mailing of the international search report
16 May 2017 (16.05.17)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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- JP 61149430 A [0011]
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- JP 2016034390 A [0077]