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(54) **STEEL MATERIAL, AND OIL-WELL STEEL PIPE FOR EXPANSION**

(57) There is provided a steel material having a chemical composition consisting, by mass percent, of C: 0.6-1.8%, Si: 0.05-1.00%, Mn: >25.0-45.0%, Al: 0.003-0.06%, P: ≤0.03%, S: ≤0.03%, Cu: 0.5-3.0%, N: ≤0.10%, V: 0-2.0%, Cr: 0-3.0%, Mo: 0-3.0%, Ni: 0-1.5%, Nb: 0-0.5%, Ta: 0-0.5%, Ti: 0-0.5%, Zr: 0-0.5%, Ca:

0-0.005%, Mg: 0-0.005%, REM: 0-0.01%, B: 0-0.015%, the balance: Fe and impurities, and satisfying $0.6 < C - 0.18V < 1.44$], wherein a metal micro-structure is consisting of an austenite single phase, a yield strength is 241 MPa or higher, and a uniform elongation is 40% or higher.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a steel material and expandable oil country tubular goods, and more particularly, to a steel material excellent in pipe expandability and sulfide stress cracking resistance, which is used in oil well and gas well environments and the like environments containing hydrogen sulfide (H₂S) and expandable oil country tubular goods using the same.

10 BACKGROUND ART

[0002] In drilling of oil wells and gas wells (hereinafter, collectively referred to simply as "oil wells"), a general method employed is to insert and bury casings after a drill hole reaches a predetermined depth in order to prevent a well wall from collapsing. Furthermore, the operation of inserting casings having smaller outside diameter one by one is repeated while performing the drilling. Therefore, conventionally, in the case where it is necessary to perform drilling up to a large depth, a drilling area of the oil well in a stratum-near-surface portion becomes larger in an outside-diameter direction because of the increase in the number of times a casing is inserted, which increases drilling cost and construction period, and is thus economically disadvantageous. Accordingly, in recent years, there has been proposed a method of construction in which casings inserted in an oil well are expanded in the oil well to reduce a drilling area in a stratum-near-surface portion, so that a drilling construction period can be significantly shortened (for example, refer to Patent Document 1).

[0003] In oil wells of crude oil, natural gas, and the like containing H₂S, sulfide stress cracking (hereinafter, referred to as "SSC") of steel in wet hydrogen sulfide environments poses a problem, and therefore steel pipes for casing excellent in SSC resistance are needed. In the above-described method of construction, casings are exposed to a corrosive environment after it is subjected to working for expansion without being subjected to heat treatment or the like. Therefore, a material used for casings has to be excellent in expandability and also in corrosion resistance after cold working. For example, Patent Documents 1 to 3 propose materials that are excellent in expansion capability and corrosion resistance.

LIST OF PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0004]

35 Patent Document 1: JP2008-202128A
 Patent Document 2: JP2002-266055A
 Patent Document 3: JP2006-9078A

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] In order to assure the expandability of steel pipes that is indispensable for use in the above-described process, a high uniform elongation is required. Patent Documents 1 and 2 disclose steel pipes that are excellent in SSC resistance but have room for improvement because no examination is made about uniform elongation. Also, Patent Document 3 discloses the value of uniform elongation. The value, however, indicates a result which is 21% or less. In addition, no examination has been made about SSC resistance. In order to further increase application opportunities of steel pipes that are to be expanded in an oil well, it is necessary to have a uniform elongation of, for example, 40% or more and assure an SSC resistance after expansion.

50 **[0006]** An objective of the present invention is to provide a steel material that has a high expandability, is excellent in SSC resistance after cold working and moreover has a high economic efficiency, and expandable oil country tubular goods using the same.

MEANS FOR SOLVING THE PROBLEMS

55 **[0007]** The present inventors examined the chemical composition of a steel material that satisfies the above-described conditions. As the result, the present inventors came to obtain the following findings.

(A) In order to assure a high SSC resistance and uniform elongation, it is effective to contain Mn and C, which are austenite stabilizing elements. In particular, it is effective to contain a large amount of Mn. An austenitic structure has a high resistance to SSC, and if the contents of C and Mn are properly selected, the austenitic structure is stable in cold working and difficult to cause strain induced martensitic transformation. Therefore, the occurrence of SSC, which is likely to occur in the presence of a BCC (body-centered cubic) micro-structure, can be suppressed.

(B) Mn has a problem in that it brings about the deterioration in general corrosion resistance in wet hydrogen sulfide environments. However, the deterioration of general corrosion resistance can be suppressed by containing Cu in a steel material.

(C) When a C content is properly managed, in the case where V, which is a carbide-forming element, is contained, C is consumed to form carbides. Therefore, it is necessary to adjust the C content considering the amount of C consumed as carbides.

[0008] The present invention has been accomplished on the basis of the above-described findings, and involves a steel material and expandable oil country tubular goods described below.

(1) A steel material having a chemical composition consisting, by mass percent, of

C: 0.6 to 1.8%,

Si: 0.05 to 1.00%,

Mn: more than 25.0% and 45.0% or less,

Al: 0.003 to 0.06%,

P: 0.03% or less,

S: 0.03% or less,

Cu: 0.5 to 3.0%,

N: 0.10% or less,

V: 0 to 2.0%,

Cr: 0 to 3.0%,

Mo: 0 to 3.0%,

Ni: 0 to 1.5%,

Nb: 0 to 0.5%,

Ta: 0 to 0.5%,

Ti: 0 to 0.5%,

Zr: 0 to 0.5 %,

Ca: 0 to 0.005%,

Mg: 0 to 0.005%,

REM: 0 to 0.01 %,

B: 0 to 0.015%,

the balance: Fe and impurities, and

satisfying the following formula (i),

wherein a metal micro-structure is consisting of an austenite single phase,

a yield strength is 241 MPa or higher, and a uniform elongation is 40% or higher;

$$0.6 < C - 0.18V < 1.44 \quad \dots (i)$$

where, the symbol of an element in the formula represents the content (mass%) of the element contained in the steel material, and is made zero in the case where the element is not contained.

(2) The steel material according to (1),

wherein the chemical composition contains, by mass percent,

V: 0.03 to 2.0%.

(3) The steel material according to (1) or (2),

wherein the chemical composition contains, by mass percent, one or more elements selected from

Cr: 0.1 to 3.0%,

Mo: 0.1 to 3.0% and

Ni: 0.1 to 1.5%.

(4) The steel material according to any one of (1) to (3),

wherein the chemical composition contains, by mass percent, one or more elements selected from

Nb: 0.005 to 0.5%,

Ta: 0.005 to 0.5%,

Ti: 0.005 to 0.5%,

Zr: 0.005 to 0.5%,

Ca: 0.0003 to 0.005%,

Mg: 0.0003 to 0.005%,

REM: 0.001 to 0.01 % and

B: 0.0001 to 0.015%.

(5) Expandable oil country tubular goods, which are comprised of the steel material according to any one of (1) to (4).

(6) The expandable oil country tubular goods according to (5), which are seamless oil country tubular goods.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0009] According to the present invention, a steel material having a high uniform elongation and thus a high expandability, and excellent SSC resistance after cold working can be obtained. Therefore, the steel material according to the present invention can be used suitably for expandable oil country tubular goods in wet hydrogen sulfide environments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

[Figure 1] Figure 1 is a graph showing the relationship between Mn content and uniform elongation.

[Figure 2] Figure 2 is a graph showing the relationship between Cu content and corrosion rate.

MODE FOR CARRYING OUT THE INVENTION

[0011] Components of the present invention is described below in detail.

1. Chemical composition

[0012] The reasons for restricting the elements are as described below. In the following explanation, the symbol "%" for the content of each element means "% by mass".

C: 0.6 to 1.8%

[0013] Carbon (C) has an effect of stabilizing austenite phase at a low cost even if the content of Mn or Ni is reduced, and also can improve the work hardening property and uniform elongation by means of promotion of plastic deformation by twinning, so that C is a very important element in the present invention. Therefore, 0.6% or more of C has to be contained. On the other hand, if the content of C is too high, cementite precipitates, and thereby not only the grain boundary strength is decreased and the stress corrosion cracking susceptibility is increased, but also the fusing point of material is decreased remarkably and the hot workability is deteriorated. Therefore, the C content is set to 1.8% or less. The C content is preferably more than 0.65%, further preferably 0.7% or more. Also, the C content is preferably 1.6% or less, further preferably 1.4% or less.

Si: 0.05 to 1.00%

[0014] Silicon (Si) is an element necessary for deoxidation of steel. If the content of Si is less than 0.05%, the deoxidation is insufficient and many nonmetallic inclusions remain, and therefore desired SSC resistance cannot be achieved. On the other hand, if the content of Si is more than 1.00%, the grain boundary strength is weakened, and the SSC resistance is decreased. Therefore, the content of Si is set to 0.05 to 1.00%. The Si content is preferably 0.10% or more, further preferably 0.20% or more. Also, the Si content is preferably 0.80% or less, further preferably 0.60% or less.

Mn: more than 25.0% and 45.0% or less

[0015] Manganese (Mn) is an element capable of stabilizing austenite phase at a low cost and important element to assure high uniform elongation. In order to exert the effects, more than 25.0% of Mn has to be contained. On the other hand, Mn dissolves preferentially in wet hydrogen sulfide environments, and stable corrosion products are not formed on the surface of material. As a result, the general corrosion resistance is deteriorated with the increase in the Mn content. In the present invention, if more than 45.0% of Mn is contained, even though a fixed amount or more of Cu is

contained, the corrosion rate becomes higher than the standard corrosion rate of low-alloy oil well pipe. Therefore, the Mn content has to be set to 45.0% or less. The Mn content is preferably 40.0% or less.

[0016] In the present invention, the "standard corrosion rate of low-alloy oil well pipe" means a corrosion rate converted from the corrosion loss at the time when a steel is immersed in solution A (5%NaCl + 0.5%CH₃COOH aqueous solution, 1-bar H₂S saturated) specified in NACE TM0177-2005 for 336 h, being 1.5 g/(m² ■ h).

Al: 0.003 to 0.06%

[0017] Aluminum (Al) is an element necessary for deoxidation of steel, and therefore 0.003% or more of Al has to be contained. However, if the content of Al is more than 0.06%, oxides are liable to be mixed in as inclusions, and the oxides may exert an adverse influence on the toughness and corrosion resistance. Therefore, the Al content is set to 0.003 to 0.06%. The Al content is preferably 0.008% or more, further preferably 0.012% or more. Also, the Al content is preferably 0.05% or less, further preferably 0.04% or less. In the present invention, Al means acid-soluble Al (sol.Al).

P: 0.03% or less

[0018] Phosphorus (P) is an element existing unavoidably in steel as an impurity. However, if the content of P is more than 0.03%, P segregates at grain boundaries, and deteriorates the SSC resistance. Therefore, the content of P has to be set to 0.03% or less. The P content is desirably as low as possible, being preferably 0.02% or less, further preferably 0.012% or less. However, an excessive decrease in the P content leads to a rise in production cost of steel material. Therefore, the lower limit of the P content is preferably 0.001%, further preferably 0.005%.

S: 0.03% or less

[0019] Sulfur (S) exists unavoidably in steel as an impurity like P. If the content of S is more than 0.03%, S segregates at grain boundaries and forms sulfide-based inclusions, and therefore deteriorates the SSC resistance. Therefore, the content of S has to be set to 0.03% or less. The S content is desirably as low as possible, being preferably 0.015% or less, further preferably 0.01 % or less. However, an excessive decrease in the S content leads to a rise in production cost of steel material. Therefore, the lower limit of the S content is preferably 0.001%, further preferably 0.002%.

Cu: 0.5 to 3.0%

[0020] Copper (Cu) is an element that promotes local corrosion, and is liable to form a stress concentrating zone on the surface of steel material, in the case where the Mn content of the steel material is low. However, in the case where a corrosion rate of parent phase of the steel material is high, Cu has an effect of suppressing the corrosion by forming sulfides on the surface of material in wet hydrogen sulfide environments. In the present invention, since the Mn content is high and the increase of a corrosion rate can be easily induced 0.5% or more of Cu has to be contained. On the other hand, if Cu is contained excessively, the effect is saturated, the local corrosion is promoted and stress concentrating zone on the surface of steel material can be formed. Therefore, the content of Cu is set to 3.0% or less. The Cu content is preferably 0.6% or more, further preferably 0.7% or more. Also, the Cu content is preferably 2.5% or less, more preferably 2.0% or less, further preferably 1.5% or less.

V: 0 to 2.0%

[0021] Vanadium (V) may be contained as necessary because it is an element that strengthen the steel material by performing heat treatment at an appropriate temperature and time and precipitating fine carbides (V₄C₃) in the steel. However, if V is contained excessively, the effect is saturated and a large amount of C, which stabilize an austenite phase is consumed. Therefore, the content of V is set to 2.0% or less. The V content is preferably 1.8% or less, more preferably 1.6% or less. In the present invention, remarkable increase of strength should be avoided in order to assure high uniform elongation. Also, the productivity may be reduced with the increase in the V content. Thus, the V content is further preferably less than 0.5%. In the case where it is desired to achieve the above-described effect, the V content is preferably set to 0.03% or more.

N: 0.10% or less

[0022] Nitrogen (N) is usually handled as an impurity element in iron and steel materials, and is decreased by denitrification. Since N is an element for stabilizing austenite phase, a large amount of N may be contained to stabilize austenite. However, since the present invention intends to stabilize austenite by means of C and Mn, N need not be

contained positively. Also, if N is contained excessively, the high-temperature strength is raised, the work stress at high temperatures is increased, and the hot workability is deteriorated. Therefore, the content of N has to be set to 0.10% or less. From the viewpoint of refining cost, denitrification need not be accomplished unnecessarily, so that the lower limit of the N content is preferably 0.0015%.

Cr: 0 to 3.0%

[0023] Chromium (Cr) may be contained as necessary because it is an element for improving the general corrosion resistance. However, if the content of Cr is more than 3.0%, Cr segregates at grain boundaries, and thereby the SSC resistance is deteriorated. Therefore, the content of Cr, if being contained, is set to 3.0% or less. As described above, in the present invention, a corrosion is promoted by the increase in the Mn content and the corrosion is suppressed by forming Cu sulfides. Therefore, Cr need not be contained positively, and the Cr content is preferably less than 1.0%. In the case where it is desired to achieve the above-described effect, the Cr content is preferably set to 0.1% or more, further preferably set to 0.2% or more, and still further preferably set to 0.5% or more.

Mo: 0 to 3.0%

[0024] Molybdenum (Mo) may be contained as necessary because it is an element having an effect of suppressing the corrosion by forming sulfides on the surface of material in wet hydrogen sulfide environments in the case where a corrosion rate of parent phase of the steel material is high as is the case with Cu. However, since the effect of Mo is small compared to that of Cu and also Mo is very expensive element, Mo should not be contained excessively. If the content of Mo is more than 3.0%, the effect is saturated and economic efficiency is deteriorated. Therefore, the content of Mo, if being contained, is set to 3.0% or less. In the case where it is desired to achieve the above-described effect, the Mo content is preferably set to 0.1 % or more, further preferably set to 0.2% or more, and still further preferably set to 0.5% or more.

Ni: 0 to 1.5%

[0025] Nickel (Ni) may be contained as necessary because it is an element capable of stabilizing austenite phase as is the case with Cu and having an effect of suppressing cracks during hot rolling that sometimes occur in Cu containing steel. However, Ni is an element that promotes local corrosion, and is liable to form a stress concentrating zone on the surface of steel material. Therefore, if Ni is contained excessively, the SSC resistance may be deteriorated. For this reason, the content of Ni, if being contained, is set to 1.5% or less. The effect of suppressing the cracks can be obtained even by a small amount, and the Ni content is preferably set to 0.1% or more, further preferably set to 0.2% or more.

[0026]

Nb: 0 to 0.5%

Ta: 0 to 0.5%

Ti: 0 to 0.5%

Zr: 0 to 0.5%

[0027] Niobium (Nb), tantalum (Ta), titanium (Ti) and zirconium (Zr) may be contained as necessary because these are elements that contribute to the strength of the steel by combining with C or N to form micro carbides or carbonitrides. In addition the steel material can be strengthened by precipitation strengthening during aging heat treatment when the elements having abilities to form carbides and carbonitrides are contained. However, if these elements are contained excessively, the effect is saturated and deterioration of toughness and destabilization of austenite may be caused. Therefore, the content of each element is 0.5% or less and preferably 0.35% or less. In order to obtain the effect, the content of one or more elements selected from these elements is preferably 0.005% or more, further preferably 0.1% or more.

[0028]

Ca: 0 to 0.005%

Mg: 0 to 0.005%

[0029] Calcium (Ca) and magnesium (Mg) may be contained as necessary because these are elements that have effects to improve toughness and corrosion resistance by controlling the form of inclusions, and further enhance casting properties by suppressing nozzle clogging during casting. However, if these elements are contained excessively, the effects are saturated and the inclusions are liable to be clustered to deteriorate toughness and corrosion resistance.

Therefore, the content of each element is 0.005% or less. The content of each element is preferably 0.003% or less. In order to obtain the effect, the content of one or two elements from these elements is preferably 0.0003% or more, further preferably 0.0005% or more.

5 REM: 0 to 0.01 %

[0030] Rare earth metal (REM) may be contained as necessary because these are elements that have effects to improve toughness and corrosion resistance by controlling the form of inclusions as is the case with Ca and Mg. However, if REM is contained excessively, the effect is saturated and the inclusions are liable to be clustered to deteriorate toughness and corrosion resistance. Therefore, the content of REM is 0.01 % or less. The REM content is preferably 0.005% or less. In order to obtain the effect, the REM content is preferably 0.001 % or more, further preferably 0.002% or more.

[0031] REM is the general term of a total of 17 elements consisting of Sc (scandium), Y (yttrium), and lanthanoids, and the REM content means the total content of one or more elements from the 17 elements.

15 [0032] When two or more elements selected from Ca, Mg and REM are contained complexly the total content of these elements is preferable 0.008% or less.

B: 0 to 0.015%

20 [0033] Boron (B) may be contained as necessary because this is an element that has effects to refine the precipitates and the austenite grain size. However, if B is contained excessively, low-melting-point compounds may be formed to deteriorate hot workability. Especially, if the B content is more than 0.015%, the hot workability may be deteriorated remarkably. Therefore, the B content is 0.015% or less. In order to obtain the effect, the B content is preferably 0.0001% or more.

25 [0034] The steel material of the present invention has the chemical composition consisting of the above-described elements ranging from C to B, the balance being Fe and impurities.

[0035] The term "impurities" means components that are mixed in on account of various factors in the production process including raw materials such as ore and scrap when the steel is produced on an industrial basis, which components are allowed in the range in which the components does not exert an adverse influence on the present invention.

30

$$0.6 < C - 0.18V < 1.44 \quad (i)$$

35 where the symbols of elements in the formula each represent the content of each element (mass%) contained in the steel material and is each made zero in the case where the element is not contained.

[0036] In the present invention, although the C content is regulated within the above-described range in order to stabilize an austenite phase, in the case where a steel material is strengthened by precipitating V carbides, there is a risk that part of C is consumed, austenite stability is decreased, and thereby uniform elongation is decreased. Assuming that V carbides are all V_4C_3 , an effective amount of C that contributes to the stabilization of austenite is expressed by C-0.18V as shown in the formula (i), and it is necessary to adjust the contents of C and V such that the effective amount of C exceeds 0.6. On the other hand, an effective amount of C of 1.44 or more poses problems of the inhomogeneity of a micro-structure and the deterioration in hot workability with the formation of cementite, and it is necessary to adjust the contents of C and V such that the effective amount of C is less than 1.44. The effective amount of C is preferably 0.65 or more, more preferably, 0.7 or more. Also, the effective amount of C is preferably 1.4 or less, more preferably, 1.3 or less.

45

2. Metal micro-structure

50 [0037] As described above, if an α' martensite and a ferrite, which have BCC structures, are intermixed in a metal micro-structure, there is a risk of not only decreasing a uniform elongation but also causing the decrease in an SSC resistance. Therefore, in the present invention, the metal micro-structure is made an austenite single phase, which has an FCC (face-centered cubic) structure.

[0038] Even if the mixing amounts an α' martensite and a ferrite having BCC structures are such small that they cannot be detected by X-ray diffraction (XRD), there is a risk of the deterioration in a uniform elongation and an SSC resistance. Therefore, in the present invention, the volume amounts of the ferrite and the α' martensite having BCC structures are measured and evaluated using a ferrite meter made by Helmut Fischer (model number: FE8e3).

55

3. Mechanical properties

[0039] The steel material according to the present invention has a yield strength of 241 MPa or higher. On the other hand, in order to assure expandability, it is desirable that the yield strength of a steel material is lower than 862 MPa. In particular, in the case of using the steel material according to the present invention as expandable oil country tubular goods, it is desirable that the yield strength of the steel material is lower than 758 MPa, and more desirably, lower than 654 MPa.

[0040] Also, the steel material according to the present invention has to have a high uniform elongation in order to assure a good expandability. In an expanding method for normal oil wells, a pipe expansion rate is about 25%, but it is practically desirable that the material shows a sufficient elongation after being subjected to cold working of 25%. Therefore, the steel material of the present invention has a uniform elongation of 40% or higher.

[0041] The uniform elongation of a steel material generally tends to be in inverse proportion to the yield strength thereof. Therefore, for a steel material having a low yield strength, it is desirable to have a higher uniform elongation corresponding to the yield strength. Therefore, the steel material according to the present invention desirably satisfies the following formula (ii).

$$uEl (\%) > 70 - 0.06 \times YS \text{ (MPa)} \quad (ii)$$

where, in the formula, uEl means the uniform elongation (%) of the steel material, and YS means the yield strength (MPa) thereof.

[0042] In particular, if the yield strength is less than 500 MPa, it is also supposed that steel pipes having been subjected to solid solution heat treatment are strengthened by cold working in advance before shipment, and it is therefore desirable to satisfy the formula (ii).

4. Application

[0043] As described above, the steel material according to the present invention is excellent in expandability and, in addition, has a feature that the corrosion resistance thereof does not deteriorate after expansion even without being subjected to heat treatment. Therefore, the steel material according to the present invention is suitable to be used as expandable oil country tubular goods. The kind of the tubular goods is not specifically limited, and a seamless steel pipe, an electric resistance welded steel tube, an arc welded steel pipe, or the like can be used.

[0044] Typically, in expansion, it is desirable to use steel pipes that are produced by processing steel strips or steel plates having uniform thicknesses into tubular shapes and thereafter joining them, rather than seamless steel pipes that have some variations in thickness. However, the steel material according to the present invention has characteristics of being considerably hardened by working. Therefore, in the case of expanding a steel pipe having variations in thickness, a thin portion is first expanded to be hardened, and the further elongation thereof is restricted. A thick portion is then expanded, and the steel pipe is uniformly expanded as a consequence. Therefore, the steel material according to the present invention can be suitably used for seamless steel pipes. In addition, it is more desirable that seamless steel pipes include no weld zone to stably exhibit a good SSC resistance.

4. Production method

[0045] The steel material according to the present invention can be manufactured, for example, by the method described below, but the method is not subject to any special restriction.

<Melting and casting>

[0046] Concerning melting and casting, a method carried out in the method for producing general austenitic steel materials can be employed, and either ingot casting or continuous casting can be used. In the case where seamless steel pipes are produced, a steel may be cast into a round billet form for pipe making by round continuous casting.

<Hot working (forging, piercing, rolling)>

[0047] After casting, hot working such as forging, piercing, and rolling is performed. In the production of seamless steel pipes, in the case where a circular billet is cast by the round continuous casting, processes of forging, blooming, and the like for forming the circular billet are unnecessary. In the case where the steel material is a seamless steel pipe,

after the piercing process, rolling is performed by using a mandrel mill or a plug mill. Also, in the case where the steel material is a plate material, the process is such that, after a slab has been rough-rolled, finish rolling is performed. The desirable conditions of hot working such as piercing and rolling are as described below.

[0048] The heating of billet may be performed to a degree such that hot piercing can be performed on a piercing-rolling mill; however, the desirable temperature range is 1000 to 1250°C. The piercing-rolling and the rolling using a mill such as a mandrel mill or a plug mill are also not subject to any special restriction. However, from the viewpoint of hot workability, specifically, to prevent surface defects, it is desirable to set the finishing temperature at 900°C or higher. The upper limit of finishing temperature is also not subject to any special restriction; however, the finishing temperature is preferably lower than 1100°C.

[0049] In the case where a steel plate is produced, the heating temperature of a slab or the like is enough to be in a temperature range in which hot rolling can be performed, for example, in the temperature range of 1000 to 1250°C. The pass schedule of hot rolling is optional. However, considering the hot workability for reducing the occurrence of surface defects, edge cracks, and the like of the product, it is desirable to set the finishing temperature at 900°C or higher. The finishing temperature is preferably lower than 1100°C as in the case of seamless steel pipe.

<Solid solution heat treatment>

[0050] The steel material having been hot-worked is heated to a temperature enough for carbides and the like to be dissolved completely, and thereafter is rapidly cooled. In this case, it is preferable that the steel material be rapidly cooled after being held in the temperature range of 1000 to 1200°C for 10 min or longer. That is, if the heating temperature is lower than 1000°C, carbides, especially Cr-Mo based carbides in the case where Cr and Mo are contained, cannot be dissolved completely. Therefore, a Cr and Mo deficient layer is formed around the Cr-Mo based carbide, and stress corrosion cracking caused by the occurrence of pitting occurs, so that in some cases, desired SSC resistance cannot be achieved. On the other hand, if the heating temperature is higher than 1200°C, a heterogeneous phase of ferrite and the like is precipitated, so that in some cases, desired SSC resistance cannot be achieved. Also, if the holding time is shorter than 10 min, the effect of solutionizing is insufficient, and thereby carbides cannot be dissolved completely. Therefore, in some cases, desired SSC resistance cannot be achieved for the same reason as that in the case where the heating temperature is lower than 1000°C.

[0051] The upper limit of the holding time depends on the size and shape of steel material, and cannot be determined unconditionally. Anyway, the time for soaking the whole of steel material is necessary. From the viewpoint of reducing the production cost, too long time is undesirable, and it is proper to usually set the time within 1 h. Also, concerning cooling, to prevent carbides (cementite or Cr-Mo based carbides) during cooling, other intermetallic compounds, and the like from precipitating, the steel material is desirably cooled at a cooling rate higher than the oil cooling rate.

[0052] The above-described lower limit value of the holding time is holding time in the case where the steel material is reheated to the temperature range of 1000 to 1200°C after the steel material having been hot-worked has been cooled once to a temperature lower than 1000°C. However, in the case where the finish temperature of hot working (finishing temperature) is made in the range of 1000 to 1200°C, if supplemental heating is performed at that temperature for 5 min or longer, the same effect as that of solid solution heat treatment performed under the above-described conditions can be achieved, so that rapid cooling can be performed as it is without reheating. Therefore, the lower limit value of the holding time in the present invention includes the case where the finish temperature of hot working (finishing temperature) is made in the range of 1000 to 1200°C, and supplemental heating is performed at that temperature for 5 min or longer.

<Aging heat treatment>

[0053] For the present steel material, aging heat treatment can be performed with the purpose of precipitation strengthening by mainly precipitating carbides and carbonitrides. In particular, it is effective in the case where one or more elements selected from V, Nb, Ta, Ti and Zr is contained. However, exceeding aging heat treatment induces formation of excess carbides and reduce C concentration in parent phase to lead destabilization of austenite. As a heating condition, it is preferable to heat the steel material about several ten min to several h at the temperature range of 600 to 800°C.

<Cold working>

[0054] Cold working may be performed as necessary for the steel material having been subjected to solid solution heat treatment or further aging heat treatment. A working ratio (reduction of area) is not subject to any special restriction but, in particular, in order to obtain a yield strength of 400 MPa or higher and lower than 862 MPa, it is preferable to make the working ratio about 10%. In the case where the steel material of the present invention is used as expandable oil country tubular goods, it is not preferable to perform cold working excessively and a working ratio is preferably set to 25% or less, in order to assure high expandability. Excessively high working ratio makes it difficult to expand the

tubular goods uniformly in the oil wells because a uniform elongation is reduced and a strength is enhanced.

[0055] The cold working method is not subject to any special restriction as far as the steel material can be worked evenly by the method. However, in the case where the steel material is a steel pipe, it is advantageous on an industrial basis to use a so-called cold draw bench using a holed die and a plug, a cold rolling mill called a cold Pilger rolling mill, or the like. Also, in the case where the steel material is a plate material, it is advantageous on an industrial basis to use a rolling mill that has been used to produce the ordinary cold rolled plate.

<Annealing>

[0056] After the cold working, annealing can be performed. In particular, annealing can be applied with a view to reducing a strength when the excess strength is obtained by the cold working, and recovering an elongation. As an annealing condition, it is preferable to heat the steel material about several min to 1 h at the temperature range of 300 to 500°C.

[0057] Hereunder, the present invention is explained more specifically with reference to examples; however, the present invention is not limited to these examples.

EXAMPLE 1

[0058] Twenty-three kinds of steels of A to P and AA to AG having the chemical compositions given in Table 1 were melted in a 50kg vacuum furnace to produce ingots. Each of the ingots was heated at 1180°C for 3 h, and thereafter was forged and cut by electrical discharge cutting-off. Thereafter, the cut ingots were further soaked at 1150°C for 1 h, and were hot-rolled into plate materials having a thickness of 20 mm. Subsequently, the plate materials were subjected to solid solution heat treatment at 1100°C for 1 h to obtain test materials (test Nos. 1 to 23). Additionally, test materials produced in the same manner as test Nos. 1 to 23 are further cold-rolled at a working ratio of 10% to obtain strengthened test materials (test Nos. 24 to 46).

[Table 1]

Table 1

Steel	Chemical composition (in mass%, balance: Fe and impurities)														
	C	Si	Mn	Al	P	S	Cu	N	V	Cr	Mo	Ni	Nb	Ta	Ti
A	1.21	0.29	26.12	0.033	0.012	0.006	1.48	0.013	-	-	-	-	-	-	-
B	1.19	0.30	36.00	0.036	0.010	0.006	1.51	0.012	-	-	-	-	-	-	-
C	1.16	0.27	25.95	0.028	0.014	0.004	0.91	0.013	-	-	-	-	-	-	-
D	1.21	0.28	26.13	0.031	0.013	0.004	2.13	0.012	-	-	-	-	-	-	-
E	0.68	0.19	32.11	0.032	0.012	0.006	0.82	0.016	-	0.78	-	-	-	-	-
F	0.69	0.23	31.82	0.020	0.012	0.006	0.81	0.011	-	-	0.81	-	-	-	-
G	0.69	0.22	32.31	0.033	0.010	0.004	0.81	0.011	-	-	-	0.80	-	-	-
H	0.99	0.31	36.12	0.021	0.013	0.006	1.19	0.013	-	-	-	-	0.18	-	-
I	1.03	0.33	36.38	0.026	0.011	0.006	1.17	0.011	-	-	-	-	-	0.11	-
J	0.62	0.31	35.87	0.019	0.013	0.005	1.21	0.012	-	-	-	-	-	-	-
K	0.90	0.20	29.69	0.028	0.011	0.005	1.02	0.011	1.49	0.31	0.30	-	-	-	-
L	0.88	0.19	30.08	0.020	0.012	0.005	0.62	0.015	0.77	-	-	-	-	-	-
M	1.02	0.20	27.82	0.029	0.011	0.005	0.60	0.013	-	-	-	0.57	-	-	-
N	0.99	0.22	27.91	0.034	0.013	0.007	0.61	0.011	-	-	-	1.22	-	-	-
O	1.22	0.15	26.02	0.025	0.012	0.006	0.78	0.011	0.29	-	-	-	-	-	-
P	0.90	0.25	25.48	0.041	0.011	0.006	0.55	0.012	-	-	-	-	-	-	-
AA	0.41 *	0.31	30.24	0.028	0.010	0.005	0.68	0.013	-	-	-	-	-	-	-
AB	1.18	0.28	8.12 *	0.019	0.012	0.006	1.45	0.013	-	-	-	-	-	-	-
AC	1.18	0.28	26.28	0.021	0.012	0.005	0.29 *	0.011	-	-	-	-	-	-	-
AD	0.91	0.20	28.12	0.026	0.013	0.006	1.02	0.011	-	3.94 *	-	-	-	-	-
AE	0.87	0.18	28.22	0.029	0.012	0.005	0.95	0.011	-	-	-	1.52 *	-	-	-
AF	0.70	0.32	31.94	0.031	0.012	0.007	0.71	0.012	1.03	-	-	-	-	-	-
AG	0.64	0.21	15.88 *	0.018	0.011	0.008	0.58	0.011	-	-	-	-	-	-	-

* indicates that conditions do not satisfy those defined by the present invention.

[0059] With use of the above-described test materials, mechanical properties and a metal micro-structure were ex-

aminated. Thereafter, the test materials were subjected to cold working at working ratio of 25% simulating the expansion. And, mechanical properties, a metal micro-structure, SSC resistance and a corrosion rate were examined with use of the cold-worked test materials. Concerning the mechanical properties, yield strength and uniform elongation were measured. From each of the steels, a round-bar tensile test specimen having a parallel part measuring 6 mm in outside diameter and 40 mm in length was sampled. A tension test was conducted at normal temperature (25°C), whereby the yield strength YS (0.2% yield stress) (MPa) and the elongation (%) were determined.

[0060] In the present example, the test material that had a uniform elongation being 40% or higher and satisfying the following formula (ii) in relation to a yield strength was evaluated so that the uniform elongation property is good. In the following Table 2 is indicated required elongation (%) which is higher value of 40% and $70 - 0.06 \times \text{YS}$.

$$\text{uEl (\%)} > 70 - 0.06 \times \text{YS (MPa)} \quad (\text{ii})$$

where, in the formula, uEl means the uniform elongation (%) of the steel material, and YS means the yield strength (MPa) thereof.

[0061] The SSC resistance was evaluated as described below. A plate-shaped smooth test specimen was sampled, and a stress corresponding to 90% of yield stress was applied to one surface of the test specimen by four-point bending method. Thereafter, the test specimen was immersed in a test solution, that is, solution A (5%NaCl + 0.5%CH₃COOH aqueous solution, 1-bar H₂S saturated) specified in NACE TM0177-2005, and was held at 24°C for 336 h. Subsequently, it was judged whether or not rupture occurred. As the result, a not-ruptured steel material was evaluated so that the SSC resistance is good (referred to as "o" in Table 2), and a ruptured steel material was evaluated so that the SSC resistance is poor (referred to as "x" in Table 2).

[0062] Also, to evaluate the general corrosion resistance, the corrosion rate was determined by the method described below. The above-described test material was immersed in the solution A at normal temperature for 336 h, the corrosion loss was determined, and the corrosion loss was converted into the average corrosion rate. In the present invention, the test material that showed the corrosion rate of lower than 1.5 g/(m² ■ h) was evaluated so that the general corrosion resistance is good.

[0063] On the obtained test materials of test Nos. 1 to 46 before and after the cold working at the working ratio of 25%, the total volume amounts of ferrite and α' martensite having BCC structures were measured by using the ferrite meter. For all of the test materials before the cold working, the phases having BCC structures could not be detected and the metal micro-structures were austenite single phases. Therefore, the volume amounts of the phases having BCC structures for the test materials only after the cold working are shown as a BCC ratio by volume % in tables. The results are given in Tables 2 and 3.

[Table 2]

Table 2

Test No.	Steel	After solid solution heat treatment				After stimulated expansion (25% cold working)			
		Yield strength (MPa)	Required elongation (%)	Uniform elongation (%)	Yield strength (MPa)	BCC ratio (%)	SSC resistance	Corrosion rate (g/m ² /h)	Inventive example
1	A	391	47	76	942	- #	○	0.9	
2	B	378	47	69	921	- #	○	1.0	
3	C	385	47	78	945	- #	○	0.8	
4	D	391	47	80	956	- #	○	0.9	
5	E	298	52	72	838	- #	○	1.0	
6	F	307	52	74	842	- #	○	0.9	
7	G	301	52	70	830	- #	○	0.7	
8	H	358	49	69	901	- #	○	0.8	
9	I	362	48	65	915	- #	○	1.0	
10	J	295	52	67	863	- #	○	0.9	
11	K	342	49	62	899	- #	○	0.8	
12	L	340	50	60	905	- #	○	1.2	
13	M	352	49	71	910	- #	○	1.1	
14	N	363	48	66	932	- #	○	1.3	
15	O	380	47	70	921	- #	○	1.2	
16	P	344	49	69	889	- #	○	1.0	

(continued)

Test No.	Steel	After solid solution heat treatment			After stimulated expansion (25% cold working)				
		Yield strength (MPa)	Required elongation (%)	Uniform elongation (%)	Yield strength (MPa)	BCC ratio (%)	SSC resistance	Corrosion rate (g/m ² /h)	
17	AA *	267	54	38 *	618	0.04 *	○	1.1	Comparative example
18	AB *	325	51	28 *	813	- #	○	0.8	
19	AC *	386	49	68	928	- #	○	1.5	
20	AD *	343	49	76	903	- #	○	1.6	
21	AE *	321	51	77	862	- #	×	0.9	
22	AF *	308	52	42	782	0.03 *	○	1.1	
23	AG *	313	51	49	811	- #	○	1.1	
* indicates that conditions do not satisfy those defined by the present invention. # indicates that measured value is below the detection limit (0.01%).									

[Table 3]

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Table 3

Test No.	Steel	After 10% cold working				After simulated expansion (25% cold working)			
		Yield strength (MPa)	Required elongation (%)	Uniform elongation (%)		Yield strength (MPa)	BCC ratio (%)	SSC resistance	Corrosion rate (g/m ² /h)
24	A	622	40	67		1154	- #	○	0.9
25	B	604	40	58		1142	- #	○	1.1
26	C	609	40	68		1148	- #	○	0.9
27	D	601	40	66		1170	- #	○	1.0
28	E	520	40	62		1080	- #	○	0.9
29	F	531	40	60		1083	- #	○	0.8
30	G	524	40	64		1071	- #	○	0.8
31	H	578	40	58		1120	- #	○	0.8
32	I	582	40	56		1135	- #	○	1.0
33	J	519	40	59		1070	- #	○	0.9
34	K	552	40	50		1120	- #	○	0.9
35	L	546	40	47		1083	- #	○	1.1
36	M	564	40	60		1100	- #	○	1.2
37	N	598	40	56		1146	- #	○	1.3
38	O	601	40	58		1124	- #	○	1.2
39	P	588	40	61		1089	- #	○	0.9

Inventive example

(continued)

Test No.	Steel	After 10% cold working			After simulated expansion (25% cold working)				
		Yield strength (MPa)	Required elongation (%)	Uniform elongation (%)	Yield strength (MPa)	BCC ratio (%)	SSC resistance	Corrosion rate (g/m ² /h)	
40	AA *	480	40	26 *	930	0.21 *	○	1.0	Comparative example
41	AB *	542	40	19 *	1042	- #	○	0.8	
42	AC *	607	40	64	1193	- #	○	1.6	
43	AD *	562	40	59	1104	- #	○	1.8	
44	AE *	545	40	61	1095	- #	×	0.9	
45	AF *	528	40	29 *	978	0.14 *	○	1.0	
46	AG *	514	40	36 *	958	- #	○	1.1	
* indicates that conditions do not satisfy those defined by the present invention. # indicates that measured value is below the detection limit (0.01%).									

[0064] Table 2 shows that for Test Nos. 1 to 16, which are example embodiments of the present invention, a uniform elongation of 60% or higher can be provided and even in the case where the cold working is performed at the working ratio of 25% simulating the expansion, the SSC resistance is excellent, and also the corrosion rate can be kept at lower than $1.5 \text{ g}/(\text{m}^2 \cdot \text{h})$. Also, Table 3 shows that for Test Nos. 24 to 39, which are example embodiments of the present invention, a uniform elongation of 47% or higher can be provided in spite of the yield strength of 519 MPa or higher by performing the cold working at the working ratio of 10%, demonstrating that the present steel materials have excellent balance of strength and expandability. Even in the case where the cold working is performed at the working ratio of 25% simulating the expansion, the SSC resistance is excellent, and also the corrosion rate can be kept at lower than $1.5 \text{ g}/(\text{m}^2 \cdot \text{h})$.

[0065] On the other hand, for Test Nos. 17, 18, 22, 23, 40, 41, 45 and 46 in which the C content, the Mn content or the effective amount of C were less than the lower limits defined in the present invention, the test result was such that the uniform elongation was low and the expandability was poor. It is to be noted that for Test Nos. 22 and 23, although the uniform elongation were 42% and 49%, respectively and tentatively satisfied the claimed definition, formula (ii) was not satisfied and the expandability was not enough considering the yield strength were as low as 308 MPa and 313 MPa.

[0066] For Test Nos. 17, 22, 40 and 45 it is thought that small amount of micro-structure having BCC structure was detected because the effective amount of C was out of the defined range and austenite stability was deteriorated, and consequently the uniform elongation was decreased. On the other hand, since mixed amount of micro-structure having BCC structure was small and strength was not so high, in the present example, deterioration of the SSC resistance was not observed.

[0067] For Test Nos. 21 and 44 in which the Ni content was more than the upper limit defined in the present invention, the test result was such that the SSC resistance was poor. Also, for Test Nos. 19 and 42 in which the Cu content was less than the claimed lower limit and Test Nos. 20 and 43 in which the Cr content was more than the claimed upper limit, the test result was such that, although the SSC resistance was good, the corrosion rate was high, and the general corrosion resistance was poor.

[0068] Figure 1 is a graph showing the relationships between Mn content and uniform elongation of steels after solid solution heat treatment and after cold working at working ratio of 10%, respectively, for steels A and B satisfying the definition of the present invention and steels AB and AG out of the defined range. These steels have similar chemical composition except for the Mn content. As is apparent from Figure 1, the steel material according to the present invention in which the Mn content is more than 25% has high uniform elongation and excellent expandability.

[0069] Figure 2 is a graph showing the relationships between Cu content and corrosion rate of steels after solid solution heat treatment and after cold working at working ratio of 10%, respectively, for steels A, C and D satisfying the definition of the present invention and steel AC out of the defined range. These steels have similar chemical composition except for the Cu content. As is apparent from Figure 2, for the steel material according to the present invention in which the Cu content is 0.5% or more, the corrosion rate is decreased and the general corrosion resistance is improved.

EXAMPLE 2

[0070] Effects of aging heat treatment after solid solution treatment were investigated using steels K, L, O and AF which were prepared in EXAMPLE 1. The condition of solid solution heat treatment is same as EXAMPLE 1. Additionally the aging heat treatment is performed under the condition of 800°C and 1 hour. The method for evaluation test was same as EXAMPLE 1.

[0071] Metal micro-structures of the aging heat treated test materials before and after the cold working at the working ratio of 25% were investigated by using the ferrite meter as is the case with EXAMPLE 1. For all of the test materials before the cold working, the phases having BCC structures could not be detected and the metal micro-structures were austenite single phases. Therefore, the volume amounts of the phases having BCC structures for the test materials only after the cold working are shown as a BCC ratio by volume % in tables. The results are given in Table 4.

[Table 4]

Table 4

Test No.	Steel	After aging heat treatment			After simulated expansion (25% cold working)				
		Yield strength (MPa)	Required elongation (%)	Uniform elongation (%)	Yield strength (MPa)	BCC ratio (%)	SSC resistance	Corrosion rate (g/m ² /h)	
47	K	544	40	42	1092	- #	○	0.9	Inventive example
48	L	508	40	49	1053	- #	○	1.1	
49	O	510	40	46	1014	- #	○	1.3	
50	AF *	503	40	34 *	998	0.12 *	○	1.1	Comp. ex
* indicates that conditions do not satisfy those defined by the present mention. # indicates that measured value is below the detection limit (0.01%).									

[0072] Table 4 demonstrates that for Test Nos. 47 to 49, which are example embodiments of the present invention, a uniform elongation of 40% or higher can be assured while strengthening the steels such that the yield strength is 500 MPa or higher by performing the aging heat treatment for steels that contain V. On the other hand, for Test No. 50, which is comparative example, small amount of micro-structure having BCC structure was detected because the effective amount of C was out of the defined range, although the yield strength was 500 MPa or higher due to the aging heat treatment. Consequently the uniform elongation was 34% and the result was such that expandability was poor.

INDUSTRIAL APPLICABILITY

[0073] According to the present invention, a steel material having a high uniform elongation and thus a high expandability, and excellent SSC resistance after cold working can be obtained. Therefore, the steel material according to the present invention can be used suitably for expandable oil country tubular goods in wet hydrogen sulfide environments.

Claims

1. A steel material having a chemical composition consisting, by mass percent, of
C: 0.6 to 1.8%,
Si: 0.05 to 1.00%,
Mn: more than 25.0% and 45.0% or less, Al: 0.003 to 0.06%,
P: 0.03% or less,
S: 0.03% or less,
Cu: 0.5 to 3.0%,
N: 0.10% or less,
V: 0 to 2.0%,
Cr: 0 to 3.0%,
Mo: 0 to 3.0%,
Ni: 0 to 1.5%,
Nb: 0 to 0.5%,
Ta: 0 to 0.5%,
Ti: 0 to 0.5%,
Zr: 0 to 0.5 %,
Ca: 0 to 0.005%,
Mg: 0 to 0.005%, REM: 0 to 0.01 %,
B: 0 to 0.015%,
the balance: Fe and impurities, and
satisfying the following formula (i),
wherein a metal micro-structure is consisting of an austenite single phase,
a yield strength is 241 MPa or higher, and a uniform elongation is 40% or higher;

$$0.6 < C - 0.18V < 1.44 \quad \dots (i)$$

where, the symbol of an element in the formula represents the content (mass%) of the element contained in the steel material, and is made zero in the case where the element is not contained.

2. The steel material according to claim 1,
wherein the chemical composition contains, by mass percent,
V: 0.03 to 2.0%.
3. The steel material according to claim 1 or 2,
wherein the chemical composition contains, by mass percent,
one or more elements selected from
Cr: 0.1 to 3.0%,
Mo: 0.1 to 3.0% and
Ni: 0.1 to 1.5%.

4. The steel material according to any one of claims 1 to 3,
wherein the chemical composition contains, by mass percent,
one or more elements selected from

Nb: 0.005 to 0.5%,

Ta: 0.005 to 0.5%,

Ti: 0.005 to 0.5%,

Zr: 0.005 to 0.5%,

Ca: 0.0003 to 0.005%,

Mg: 0.0003 to 0.005%,

REM: 0.001 to 0.01 % and

B: 0.0001 to 0.015%.

5. Expandable oil country tubular goods, which are comprised of the steel material according to any one of claims 1 to 4.

6. The expandable oil country tubular goods according to claim 5, which are seamless oil country tubular goods.

FIGURE 1

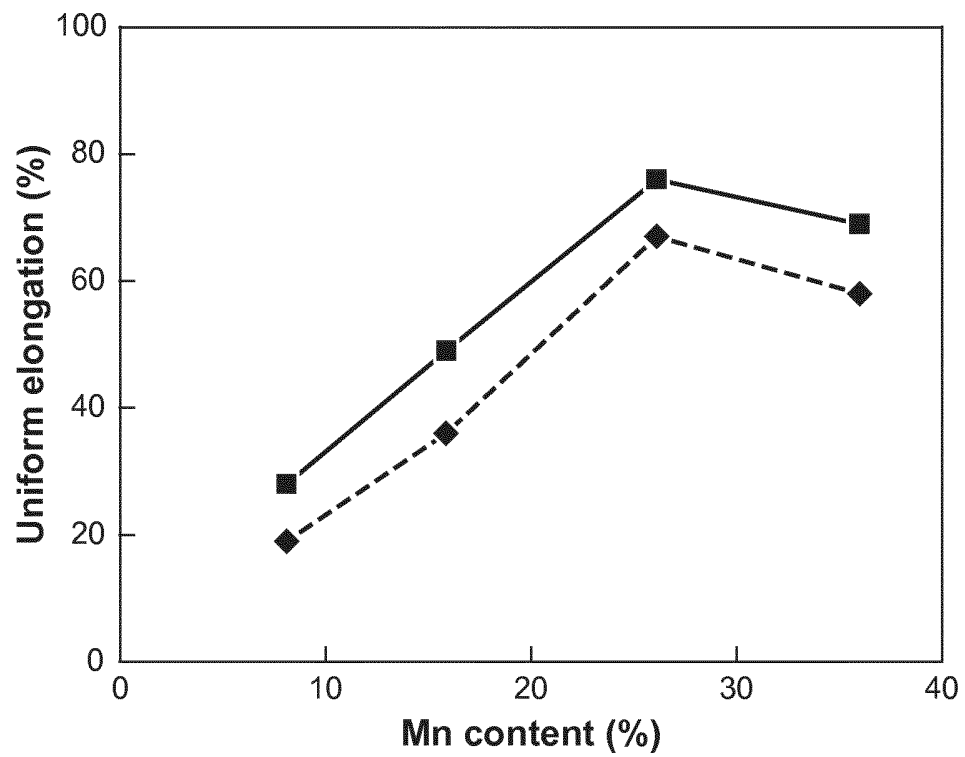
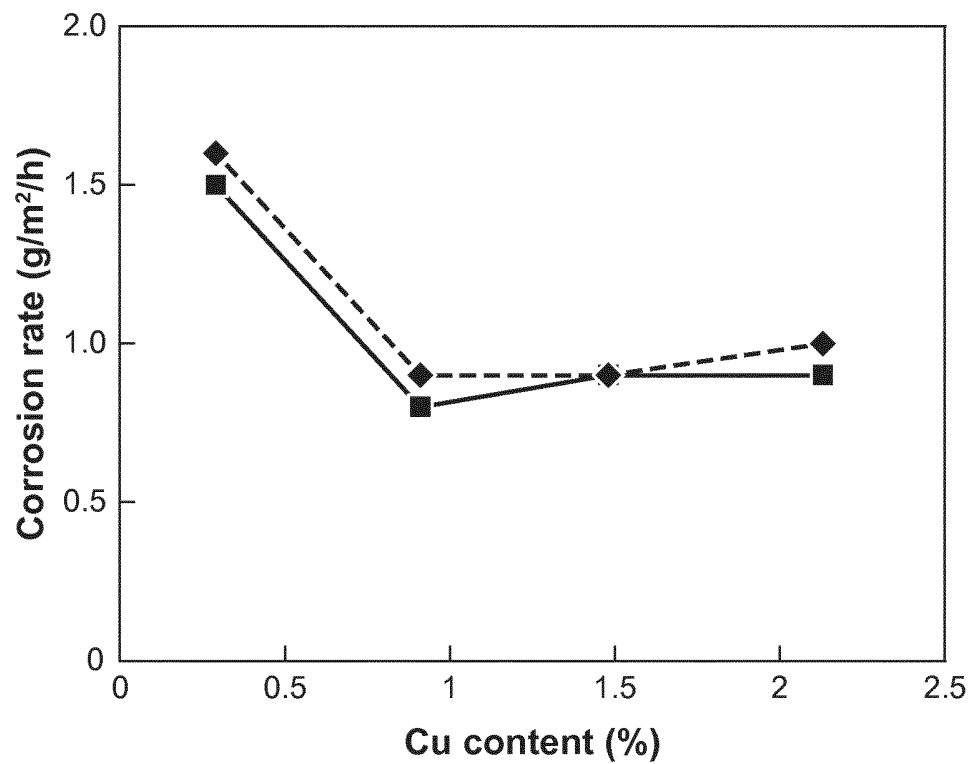


FIGURE 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/076739

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i, C21D8/02(2006.01)i, C22C38/58(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C38/00, C21D8/02, C22C38/58

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2015
Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

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 60-39150 A (Nippon Steel Corp.), 28 February 1985 (28.02.1985), claims; table 2 (Family: none)	1-6
A	JP 2001-240942 A (Kawasaki Steel Corp.), 04 September 2001 (04.09.2001), claims (Family: none)	1-6
A	JP 60-36647 A (Kawasaki Steel Corp.), 25 February 1985 (25.02.1985), claims; table 2 (Family: none)	1-6

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search
16 November 2015 (16.11.15)Date of mailing of the international search report
15 December 2015 (15.12.15)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/076739

5

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 58-197256 A (Kawasaki Steel Corp.), 16 November 1983 (16.11.1983), claims; table 1 (Family: none)	1-6

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REFERENCES CITED IN THE DESCRIPTION

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